ABSTRACT

WEI, WEI. Structure-Process-Properties of Nonwoven and Fibers Containing Inorganic Particulate Fillers-Calcium Carbonate. (Under the direction of Dr. Eunkyoung Shim and Dr. Behnam Pourdeyhimi.)

Inorganic particulate fillers are known as functional fillers for plastics, papers, paint as low cost replacement of polymer, and also change certain properties of the filled polymer products. However, the application of inorganic fillers, especially calcium carbonate fillers in spunbond nonwovens is still left with a blank area. Fiber melt spinning comprising ground calcium carbonate (GCC) filler in varying levels of weight percentage ranges from 5%, 10%, 15%, 20%, 30% to 40%, accompany with adjustment in spinning speed, draw ratio and throughput at 20~40% of loading. Calcium carbonate fillers are surface coated with stearic acid, which help to be wetted with polypropylene during melt extrusion. Precipitated calcium carbonate (PCC) which containing fillers with narrow particle size distribution have much different spinning performance, 2.5%, 10% and 25% of loading are controlled for two PCC in mono-component and bicomponent melt spinning process. Compare with GCC filled fibers, the PCC-EMforce which has large aspect ratio, perform a supreme reinforcing ability at 2.5% to 10%. Fiber are characterized using optical microscopy, SEM, DSC, TGA, X-ray and capillary rheometer for the structure-properties relationship of CaCO₃ on fiber structure uniformity, surface roughness, crystallinity and crystallization behavior, and influence of fillers on rheological and thermal properties of polypropylene.

Spunbond nonwovens comprise spun fibers and we mainly consolidate the web by thermal calendar bonding. Varying of bonding temperature apply to bonding fabrics containing with varying concentration of fillers. Fabric tensile strength and tear strength reveal the bonding
mechanism of fabrics under different bonding temperature, that increasing loading fraction of fillers expand the heat impact regions. Fabric can be filled with GCC and PCC-EMforce fillers up to 30%, to achieve optimum bonding temperature decreasing by 10°C, as the inorganic fillers are with lower specific heat that allow heat to transfer fast to melt fibers. Next bicomponent spunbond structure provide more flexible filler loading configuration in sheath/core fiber structure. We characterize the melting and recrystallized polymer semi-crystalline structure, with a comparison discussion based on skin-core structure influenced by heat transfer in sheath/core filler loading configuration. Bicomponent spunbond fabrics have its preferred light reflectance based on filler loading configuration as well, in this way, fabric optical properties are changed with the lightness and whiteness index, attributed to the loading of different amount of filler particles. It elucidates that using roughened fiber surface with filler particles will improve surface scattering and thus reduce the transparency of fabrics.
Structure-Process-Properties of Nonwoven and Fibers Containing Inorganic Particulate Fillers- Calcium Carbonate

by
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DEDICATION

To my dear father and mother.
BIOGRAPHY

Wei Wei is born on April 24th, 1988 in Xi’an, China, grown up in Luoyang, Henan Province. After graduated from Luoyang No.1 High School, Wei Wei started her undergraduate study in Donghua University, College of Textile, obtained a Bachelor of Engineering Degree majoring in Nonwovens Materials and Textile Engineering. Same year, she started graduate school at Donghua University, later transferred to Philadelphia University to continue her Master Degree and Master Thesis under adviser of Dr. Govindaraj. After finish graduate school in Philadelphia, PA., Wei started her Ph.D. program in North Carolina State University, majoring in Fiber and Polymer Science. She is a graduate research assistant from 2012 to 2015, working with Dr. Eunkyoung Shim and Dr. Behnam Poudeyhimi in the Nonwovens Institute. She defended the Ph.D. Degree in November 9th, 2015.

Wei got married with Yu Sun in 2014. Wei is an amateur piano player. She likes running, she used to participate in track and field competitions at in high school and in the college.
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CHAPTER 1  INTRODUCTION

The particles like mineral particles, carbon black particles, and polymeric fibers have been used as fillers to reinforce polymeric composites and modify their properties to achieve the desired performance in many applications. Global market of fillers for plastic is estimated to reach 15 million tons \(^{[1]}\). At present, cost reduction was the one of the main reasons to use mineral fillers. Due to the increasing resin prices and fluctuating of international petroleum price, adding inorganic fillers can reduce the costs of polymeric materials. Common mineral fillers used in polymer industry are calcium carbonate, talc, kaolin, mica, titanium dioxide, aluminum trihydrate, wollastonite. Among those fillers, the production of calcium carbonate (CaCO\(_3\)) fillers was 4 million tons in North America in 2006, which is 60\% of total fillers production \(^{[1]}\). Cost of ground calcium carbonate is $110-160 per ton for 5-7\,\mu m particles, and $140-290 per ton for 0.5-2\,\mu m particles \(^{[1]}\).

Several patents indicated benefits of using calcium carbonate in nonwovens \(^{[3-6]}\). Firstly, adding fillers can improve the whiteness and opacity of nonwovens products like baby wipes, hygiene products, medical nonwovens \(^{[7, 8]}\). Hand and comfort of nonwoven products can be improved due to the enhancement of nonwoven softness \(^{[9]}\). Other potential value of adding filler is improving breathability of fabric \(^{[7, 10]}\). Literatures about filler contained thermoplastic composites conclude fillers particles enhance Young’s modulus, impact resistance, and it did raise their heat distortion temperature \(^{[1]}\). Although calcium carbonate is routinely used as filler for polyolefin thermoplastics, it seldom applies to spinnmelt process.
Production of PP, PE, PET, nylon webs containing particle fillers would create opportunities both in emerging mineral technology and in nonwoven technology. Different types of particle size and filler surface should be considered about in the future nonwoven innovations as processing of regular calcium carbonate fillers in spunbond, meltblown, wet-laid, and dry-laid are challenges in polymer extrusion spinning and relevant web bonding mechanism.

In this research, we propose to investigate the structure-process-properties of nonwoven and fibers containing inorganic filler. We study the effect of CaCO$_3$ filler loading concentration and filler types on fiber spinning and spinline structure formation. At the same time, several key particle features are determined based on filler dispersion in the fibers. On the next spunbond process, thermal web bonding mechanism is investigated based on the amount of fillers in fibers, and the filler loading configuration in either mono-component or sheath/core bicomponent fibers. Based on that, further benefits of filler adding in fabric are focusing on how filler loading position influence fabric appearance and softness.


CHAPTER 2 LITERATURE REVIEW

2.1. Inorganic Particulate Fillers

Reinforcing filler is also referred as an additive which is applied to polymers for better mechanical properties, and it may impart other property enhancement, for example shrinkage reduction, higher toughness, flexural modulus better heat stability, and flame resistance \([1, 2, 3]\). Cost saving reason drives replacing part of plastic resin with inorganic fillers and using an organic/inorganic blend to manufacture products. Filler contained polyvinyl chloride (PVC), polypropylene (PP), polyethylene (PE) can be made into goods like window profiles, pipes, film, garden furniture, etc. \([1, 3, 4]\). Filler loading is capable with a variety of plastic processing equipment, injection molding, film blowing, extrusion coating, compression molding, laminating etc. \([1, 3]\).

Titanium dioxide is applied as pigment in polymer and paper processing as it can improve surface whiteness and reduce the transparency \([5]\). Due to high cost of titanium dioxide, manufacturer is seeking for other functional fillers as whitener and opacifier to replace titanium dioxide in polymer and paper slurry. Calcium carbonate is one common type of fillers to replace high cost titanium dioxide in pigments and coating, to make into films, papers and laminates or so. It has been commercialized of precipitated calcium carbonate filler to be applied in printing and writing cellulose papers \([6-8]\).
2.1.1. Calcium Carbonate Fillers

Calcium carbonate is the most common deposit formed in sedimentary rocks of geosphere. This abundant natural resource comes in several forms of limestone, chalk and marble. In addition to those, shells of marine organisms are also consisted of CaCO$_3$. CaCO$_3$ exists in several different crystal forms: calcite, aragonite and vaterite. Among them, calcite crystal is most frequently found in mineral filler formulations $^9$.

Based on manufacturing processing methods, calcium carbonate fillers are commonly categorized into two different types; Ground Calcium Carbonate (GCC) and Precipitated Calcium Carbonate (PCC). Major differences of these two types of calcium carbonate fillers are particle size distribution. The PCC has high purity with a fine particle size ranging from 0.7 to 2 μm. The GCC has larger particles size ranges: a fine grade with size of 3-7 μm and an ultra-fine grade with size of 1-2 μm.

The process of beneficiation of GCC starts from crushing, grinding of limestone, followed by washing and purification of particles from silicate, mica, quartz, feldspar, etc. These impurities float away from slurry during a treatment called floatation. After being dried, the fine and clean calcium carbonate particles are filtered into different grades $^{10}$.

Precipitated calcium carbonate fillers are produced via chemical reactions. There are three reaction types with different reactants: carbon dioxide gas, sodium carbonate, sodium chloride and ammonia together with calcium hydroxide $^{11}$. 

5
Lime/CO₂:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$$

Lime/Soda:

$$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaOH$$

Solvay process:

$$NH_3 + H_2O + CO_2 + NaCl \rightarrow NaHCO_3 + NH_4Cl$$

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_4OH$$

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl$$

Particle size fineness and purity of PCC can be controlled by reaction conditions. To obtain fine and high purity PCC, it is necessary to have a sufficient time of particle separation from the solution, while avoid impurities formation during the chemical reactions \(^1\). Cost of PCC is comparably higher than GCC \(^2\).

### 2.1.2. Filler Particle Size

Different processing methods of calcium carbonate functional fillers results into wide ranges of particle size from \(10^{-2}\) μm to \(10^2\) μm. Dry grinding GCC has relative coarse powder with the finest ground material in a median diameter of \(\sim 12\)μm and a broad distribution. Wet grinding GCC usually remove coarse particle by centrifuging. GCC through beneficiation and grinding shows a median particle size between about 1μm and 10μm and products by this method are commonly used in plastics. While for PCC, due to a sophisticated processing, the median particle size is 0.7-2.0μm, with the primary particle size as small as 20-70 nm \(^1\). 
Requirement for particle size range depends on what product property is designed for. Particle size selected for thermoplastic molding can have a wider distribution range than PCC particle size ranges used for papermaking and surface coating \(^1, 12\). Large particle size around 10\(\mu\)m enhances notch resistance properties and improves the thermal stability of thermoplastic molding products; while small size less than 1\(\mu\)m is a good damping key that can dissipate impact energy therefore improve the material toughness. The fine precipitated calcium carbonate selected for pulp slurry should be comparable with the pore size of cellulose fibers interlacing in paper slurry \(^6, 7\). Subramanian et al. introduced an in-situ precipitated of calcium carbonate with fine pulp fibers slurry to improving bonding internal strength and printing fastness \(^{13}\).

![Figure 2-1: Particle Size Distribution \(^{14}\).](image)

To correctly interpret the particle size, we need to understand distribution curve as it is showed in Figure 2-1. Particle size distribution represents the percent of particles (Y-axis) is equal or finer than the size (X-axis). It also determines the amount of coarse particles and the
proportion of fines \[4\]. Top cut, is the finest screen that all the material would pass through, or speak of a “95 percent finer than” or “99 percent finer than” size. D50 is the screen size that 50 percent of total particle would pass through. Similarly, D30 and D10 means that the screen size for only 30 percent and 10 percent of total particle pass through respectively, and this value would approach the finest particle size of the whole.

In polymer processing of fillers, the finest portion of fillers in total range is critical to the polymer viscosity \[15,16-17\]. The lower 10% of particle size also have to be strictly controlled because of agglomeration tendency of those fillers due to large surface area \[15\]. McAmish claimed that particle size distribution of the filler less than 5% of total particles should be less than about 0.5μm to avoid agglomeration \[18,19\]. Any agglomeration of fillers down the fiber spinning will weaken the fibers, but also cause spinneret capillary clogging issue \[9,20-21\].

The particle size distribution affects the maximum packing fraction \[22\]. The mixture of particle with different size will be packing more densely than monodispersed particle system. This is because smaller particle size can fill in the interstice between those formed by the stacking of larger particle size. Genovese investigated the effect of particle size distribution on melt viscosity, showing that bimodal distribution can effectively decrease the melt viscosity at higher filler volume fraction \[23\].

Larger particle in size distribution, top cut, may impact fiber processing and its mechanical property. The fine fiber structure will contain fatal defects when adding into polymer
material particle fillers in top cut. McAmish claimed that for spunbond processing particles with size above 10 μm may tend to weaken the nonwoven fibers structure \[^{24}\]. But this viewpoint can be only set up based on the specific processing conditions. Large particles in polymer melt may interrupt with screen filter which may cause clogging in spinpack. Clogging of screen filter may cause long term running issue. Patents referred here indicate there is a limit for filler top cut in fiber spinning \[^{15,18}\].

Particle size in range of 0.1-5 micron is suitable for making breathable microporous film \[^{25}\]. By biaxial drawing of PE film microvoids were formed which enclosing each CaCO\(_3\) particulate filler, resulting in a porosity of at least 10 percent \[^{25}\]. Microporous film is usually applied in product such as surgical gown fabrics which require a standard blood resistance and good moisture vapor transfer rate. Haffner et al. claimed several laminated structures using microporous film containing calcium carbonate fillers, attach to nonwoven spunbond web, or spunbond-meltblown-spunbond to improve the barrier property \[^{26,114-115}\]. However, they did not producing nonwoven web containing calcium carbonate fillers.

Edwards et al. claimed another blow molding method of introducing inorganic fillers less than 2μm into polyethylene terephthalate resin to stretch into plastic bottle. Dispersed particles, in amount of 60-100 ppm (parts per million), are conveyed by polyol as a liquid carrier. During blowing, the stretch force deforms the discontinuous phase of polymers into small voids around fillers. Resulting plastic bottles with quality of low haze and high clarity,
is mainly caused by difference in refractive index between microvoid phase and polyethylene terephthalate matrix\textsuperscript{[27]}.

### 2.1.3. Particle Shapes and Aspect Ratio

Shape characteristics including particle shape and aspect ratio play very important roles in filler reinforced polymer composites\textsuperscript{[28]}. Aspect ratio describes the ratio of a particle’s length to its thickness. Both shape and aspect ratio will affect a particle surface area which further influences the particle-polymer interfacial interactions. Depending on the process conditions in precipitating calcium carbonate, various particle morphologies can be formed and they are defined based on its geometric characteristics: spherical, discrete or clustered acicular, prismatic, rhombohedral, scalenohedral, orthorhombic, shown in Figure 2-2.

![Figure 2-2: Calcium Carbonate Filler Shapes\textsuperscript{[1]}](image)

Spheres, cubes or cuboids usually do not improve mechanical properties of plastics. If there are very strong adhesive forces between the filler surface and polymer chains, an additive of small aspect ratio (spheres or cubes) can have a reinforcing effect, such as increasing tensile strength\textsuperscript{[4]}. In plastic reinforcement, using flake-shape fillers works better than using cubic-shape fillers in toughening composite structure\textsuperscript{[29, 30]}. This is due to the different aspect ratio of filler particles that will result into different energy dissipation of material. Reinforced with
talc, plastics show an improvement in mechanical properties, such as rigidity, creep resistance and sometimes impact resistance \cite{1, 29, 31}. Recently in papermaking industry, people seek for opportunities of applying needle-shape aragonite fillers into wet-laid technology \cite{32}. This type of acicular shape particles with large aspect ratio have proved to improve paper sheets in tensile strength, high folding endurance and stiffness on the machine direction \cite{33}.

2.2. Polymer-Filler Interaction

Filler particles tend to form agglomerations by cohesion. In fibers, even small portion of agglomeration influence fiber structure continuity and uniformity. Weakness of fibers is caused by poor dispersion of fillers in polymer during polymer extruding, mixing and spinning. To avoid agglomeration in fiber spinning requires understanding the filler-polymer interaction from surface energy to interface compatibility.

2.2.1. Interfacial Energy

Generally, any phase transformation is towards to lowering down the free energy of a system. Specifically, in filler/polymer two-phase melt blending, inter-particle force competes with free energy of particles. Specific surface area decreases by aggregating singular particle into a bigger cluster, resulting in lower free energy of solid phase. Liquid form of polymer tends to spread onto solid which has higher surface tension, this is defined as wetting. Inorganic filler particles have higher surface tension, but its polar surface still resist polymer wetting
which has non-polar characteristic. By coating filler surface with polar acid coating, like fatty acid, polymer melt will be able to wet particles.

When liquid spread into the aggregated cluster, interstice between particles will be connected with liquid bridge. The liquid bridge between two spherical particles bears capillary pressure in the particle cluster. Adhesion force of liquid bridge calculated in equation (1).

\[ F^* = F_H \cdot \gamma \cdot x \]  

(1)

where \( F^* \) is the mean adhesion force transmitted at a contact point of particle, \( \gamma \) is the surface tension of the liquid, \( x \) is the mean particle size, \( F_H \) is the dimensionless adhesion number which can be calculated for axially symmetrical liquid bridge demonstrated by Schubert \([34]\).

![Figure 2-3: The liquid bridge model of two particles with spherical shape \([34]\).](image)

Polymer is adsorbed onto filler particles by adhesion force. Adhesion force represents the interaction potential energy between surfaces. Hasen introduced the theory of solubility parameters useful in predicting affinities to surface to improve dispersion and adhesion. Affinity between two dissimilar surfaces comes from relatively close solubility parameters \([35, 116]\). To reduce the difference between inorganic filler and polymers in their solubility parameters, for example, it helps to incorporate binders which have chemical groups like acid, alcohol and amine etc. in polymer resin because they increase local cohesion parameter of
polymer\textsuperscript{[35]}. The consequence of changing cohesion parameter is to form intensive coating layer surrounding particle surface which has rather high cohesion parameter. Binder should be adsorbed by fillers due to the close Hansen solubility parameters\textsuperscript{[35]}.

The exposure of pure calcium carbonate powder to the humid air for certain time will cause absorption of water molecules onto particle surface which lower the surface energy of the filler. The higher relative humidity level, the lower the equilibrium surface tension will be\textsuperscript{[35]}. Schubert brought up that moist agglomeration of powder has its stress-strain behavior, and built a strain model to characterize the deformation of agglomerations\textsuperscript{[34, 36]}. This model solves the breaking down mechanism of particle agglomeration under tensile and shear strain, which aims for a general powder processing but not targeted on polymer material.

2.2.2. Kinetics of Aggregation

Aggregation starts from molecule or small crystals in the solution, in which intermolecular forces such as Brownian motion, London dispersion force, electrostatic force drive particle aggregating into clusters. Two types of growth kinetics describe the aggregation of particles in the solution. Particle-Cluster Aggregation (PCA) is defined as one particle stick onto another particle at a time to the growing cluster, while Cluster-Cluster Aggregation (CCA) is defined as fractal growth is dominated by combination of cluster to cluster\textsuperscript{[37]}. Based on the kinetics of aggregation, there is a time-dependent cluster size distribution in the aggregation phenomenon. The rate of aggregation is equal to the diffusion rate $D$ divided by the deposition flux $F$. 
Witten and Sander first came up with the diffusion-limited aggregation theory based on Eden’s lattice model \[^{[38]}\]. This simple model described how particle aggregates in a lattice with a target particle and its adjacent unoccupied sites. They used the theory of the random walk in a lattice and computed exponential relationship between path length of the self-assembly of fractals with step distance.

\[
l \sim r^D
\]

Where \( l \) is the minimum path length of the fractal; \( r \) is Pythagorean distance. \( D \) is a value related with the thermal and electrical conductivity, mechanical property as well as the diffusion of fragment on the fractal.

Discrete Element Method (DEM) is a numerical method to compute the motion and effect of a large number of small particles. In the method, forces between particles attraction in the system include friction, elastic force, attractive potential forces and molecular level forces. Attractive potential forces involve cohesion, adhesion, electrostatic attraction and liquid bridging. DEM method is a good way to visualize force network in powder flow system, and to characterize the micro-dynamics of flow with continuum motion \[^{[39]}\].
2.2.3. Wetting and De-agglomeration

According to Schubert, the amount of wetting in the agglomeration influence flow ability to disperse particles\textsuperscript{[36]}. As shown in Figure 2-4, a little amount of liquid can form liquid bridge at small interstice (a) or filling into some medium sized pores sparsely (b). Due to particle cohesiveness, liquid is not able to separate individual particle interstice into an open pore (c). Up to the stage (c) the agglomerate has not been disintegrated but tends to loosen the gaps and reduce capillary pressure. A loose packing of particles reflects a large pore volume fraction (porosity) inside a particle cluster. This causes normal stress decrease in packing from solid interface due to less elastic deformation, so that liquid tend to be absorbed into the pores\textsuperscript{[36]}.

Cohesive force in the packing agglomerates can be related to several factors. Takenaka et al. proclaimed cohesive force is related to liquid saturation. When liquid saturation is less than 20\%, cohesive force in agglomerates of powder increases with the liquid saturation\textsuperscript{[40]}. But as liquid saturation continuous increase, the particle interaction can be reduced. According to Kristensen et al., moisturized agglomerate is constrained by particle interaction as well as by mobile liquid bonding\textsuperscript{[41]}. The liquid bridge forming in the porous structure is regarded as such mobile liquid bonding which may increase the adhesion at particle interface.

As liquid saturate the particle cluster, Figure 2-4 (d), the total wetting particles no longer stay in a cluster but carried by the liquid carrier in a dispersed condition. It is dominant by the
hydrodynamic force that breaks up particle agglomerations. As polymer is absorbed onto particle surface forming dense layers, repulsion between particles will be prominent \cite{116}.

Figure 2-4: Distribution of liquid in particle agglomerations \cite{36}.

Tensile strength $\sigma_t$ of moist agglomeration is related to property of particle packing. Filler constructing into a porous agglomerate geometry is highly dependent on particle characteristics (size and shape). By screw extruder kneading force, such as shearing, agitating, and compressing, local tightly packed particles are deformed into open porous structure by transferring of liquid into the pores. At the spinpack, die extrusion imposes intense shear stress onto loosely packed agglomeration which uses hydrodynamic shear force to overcome the cohesiveness between fillers and disperse in the polymer melt. In both ways, the tensile strength of agglomerates represents the maximum forces to overcome. Tensile properties of aggregates becomes quite brittle at low wetting of particles according to Kistensen et al. and the agglomerates tends to fracture after rearrangement of particles. As
wetting liquid spreads onto particle surface, the agglomerate strength $\sigma_t$ is closely related with mobility of liquid.

$$\sigma_t = kg \frac{d\bar{v}}{4\bar{v}} \frac{1-\epsilon}{\epsilon} \frac{\alpha}{t^m}$$

Where $\alpha$ is a material characteristic constant describing the intrinsic pairwise interaction of two particles; $m$, $k$ and $g$ are universal constants, $t$ is the distance between two particles, $\epsilon$ is the porosity of particle packs. $\bar{v}$, $\bar{s}$ are the mean effective volume and surface area $^{[41]}$. This model is not specified to certain stages during agglomerates disintegration as shown in Figure 4. But it reveals that the energy consumption during separation of agglomerates is inversely proportional to surface area and to porosity. So deagglomeration processes would be relatively easy for the particle agglomerates with larger surface area and large porosity.

2.2.4. Surface Treatment

As discussed in the last section, particle fillers have high cohesion energy that causes dispersion difficulty in polymer solution without specific surface treatment. During particle filler processing, the moisture adsorbed on filler surface make it more difficult to achieve uniform mixing of particles and polymer. Surface coating can change surface polarity of filler from polar to non-polar and enhance the affinity between particle and polymer. Surface coating also protects powder from forming into moist agglomeration during storage, thus reduce the energy consumption in drying, blending, and compounding with polymer $^{[1,42]}$. Surface treatment on powder particles is contributing to build a stabilized dispersion system in polymer. In powder processing technology, stearic acid surface modification has been
applied for agglomeration control. Papirer et al. measured the surface energy of stearic acid coated calcium carbonate fillers in different degree of coverage \[^{43}\]. They further gave explanations on changing CaCO\(_3\) surface polarity to non-polar surface by calculating surface energy. The surface energy decreases by covering the particle polar surface with C\(_{18}\) alkyl chains which are fixed perpendicularly to the CaCO\(_3\) surface \[^{43}\]. Steric acid enhance the repulsion between particles by adsorbing polymer around particles. Polymer chains cover the surfaces prevent particles get close to each therefore hinder the agglomeration formation \[^{44, 45}\].

This method enhances the wettability of polymers onto particles. Their affinity comes from close solubility parameters after surface treatment \[^{35}\]. Effective dispersion comes from the lowered particle surface energy or the increased polymer surface tension that tend to cover liquid around solid particles which enhance the repulsion between fillers. Electrostatic charging onto fillers would stabilize filler dispersion in polymer furthermore.

Filler surface treated with coupling agent can enhance the affinity between filler to thermoplastic matrix. Coupling agents have the general formula \((R\prime - O\cdots)\_a - M - (R - X)\_a\), where M implies metal and usually select from silicon, titanium, or zirconium. X is a functional group bonds with polymer. R is an organic group. \((R\prime - O\cdots)\) forms a leaving group, which can react with \(-\text{OH}\) presents on the filler surface, or react with moisture at filler surface \[^{46, 47}\].
Reactive coupling agent has been widely used to improve the mechanical properties of composites \[51, 128\]. Surface coated aluminum hydroxide with dicumyl dioxide and silane coupling agent can improve the tensile properties of polyethylene composite because of good interfacial interaction between particles and polyethylene matrix \[^{48}\]. Viscosity of the compound with silane-treated silica becomes lower because silane bonded silica acts as lubricant. After being treated with silane, the silica aggregation tends to be less polarized so that the agglomeration is easy to be split off under lower shear rate \[^{49}\].

Filler surface coating is a practical method to enhance the compatibility of polymer/filler composite, and stabilize the processing condition of spunmelt nonwovens and fibers. Fillers with coating treatment can not only reduce agglomeration of the calcium carbonate particles, but also improve the surface texture of the fibers \[^{18, 19}\]. Surface coating substances include fatty acid treatment \[^{50}\]; coupling agent treatment such as silanes, titanates and zirconate \[^{1, 52}\]; and lubricants such as esters and waxes for carbonates and silicates \[^{4}\].

2.3. Polymer Processing in Melt-spinning and Spunbond

Extrusion for spunbond processing starts from feeding polymer raw material into hopper. Blending filler compounded masterbatch with pure polymer resin is much easier to process than directly mixing powder into polymer \[^{127}\]. The pre-compounded filler masterbatch can be mixed in certain blend ratio with polymer resin uniformly and efficiently. Compare with single screw extruder, using twin screw extruder is believed to improve the mixing efficiency \[^{53-54, 127}\]. However, this process is very sensitive to humidity, and at high humidity the
compounding process becomes difficult because the cohesive force gathers particulate fillers and causes agglomeration. Gorna et al. applied their technique in compounding precipitated calcium carbonate with different polymers PP, PS, HDPE, LLDPE and PLA [55]. Erwin discussed melt mixing technologies in screw extruder with step-by-step description on polymer stock melting, blending and mixing [53]. There are a series of screw extruder interior parameters, including the optimization of flight clearance, flight flank geometry and spacing of the slots, which can influence filler dispersion and agglomeration. From partial melting to fully melting in the screw extruders, filler particles are subject to the intensive strain of laminar flow that cause uniform dispersion of particles in the melt, as well as the local compression that cause clogging. It has been found by Bigio et al. that reorienting the mixture (rubber + pigment) during single screw extrusion will enhance mixing effectiveness by shear flow [56, 117]. Some special screw interior structure fits well for the fillers convey and mixing, such as Maddox mixing section and Hankers mixer.

2.3.1. Melt Viscosity

Due to polymeric chain viscoelasticity, macromolecules undergo conformation transformation during fiber spinning. Polymer melt contained filler particles was claimed to have higher melt viscosity and low melt elasticity [15, 57]. Shear viscosity increases with filler volume fraction [58, 59]. While at high shear rate, fillers overcome the jamming effect from thick viscous flow as shear thinning provide a relative free flow path for particles [31]. Melt viscosity is sensitive to the portion of smaller particle size 0.1 to 1μm [23, 17]. Although small
particle size increases the apparent viscosity, using stearic acid surface treatment will induce a decrease in complex viscosity\[^{60}\].

Mooney equation (5) explains viscosity as a function of volume fraction, shape factor, aspect ratio, packing characteristics and interaction parameters. This equation is valid across the entire concentration range:

$$\ln\left(\frac{\mu_c}{\mu_m}\right) = K_e V_f \left[1 - K_e (V_f / \phi_{max})\right]^{-1}$$

(5)

Where $\mu_c/\mu_m$ is the ratio of the viscosity of the composite to that of unfilled matrix, $\phi_{max}$ is the maximum packing factor, defined as true volume of filler/apparent volume occupied by filler, $V_f$ is the volume fraction of fillers. $K_e$ is a geometric parameter known as the Einstein coefficient, which is dependent on aspect ratio and degree of agglomeration\[^{1}\].

This equation indicates viscosity ratio $\mu_c/\mu_m$ is basically proportional to filler volume fraction $V_f$, which means higher the filler loading fraction, the more viscous filled polymer flow would be. Particle size and size distribution are critical factors influencing viscosity of filled polymer, due to the packing of filler particle determine the maximum packing factor $\phi_{max}$. A dense packing means true filler volume occupied in an equal apparent volume goes higher, as shown in Figure 2-5. Apparent volume occupied by fillers defined as the denominator for $\phi_{max}$, is assumed level off at an equilibrium state in polymer melt, as two circles illustrated in Figure 2-5. Varying particle size distribution influences the true volume of fillers packing inside, therefore resulting in different $\phi_{max}$. With a mono particle size, or
very narrow particle size distribution, packing volume is restricted in the volume because there are relatively large gap in between each particle. While for a wider particle size distribution, filler with smaller size would be filling into the interstice and increase up the filler true volume inside of the apparent volume.

![Particle packing in an equal apparent volume](image)

**Figure 2-5**: Particle packing in an equal apparent volume, maximum packing fraction dependent on particle size distribution, (a) polydisperse, (b) monodisperse.

In a polydisperse system melt viscosity is also dependent on the portion of small particle size. Zaschke et al. claim when fraction of particle size in 0.1~0.7 μm exceeded 40 wt. % in total particles, the melt viscosity shoot up greatly \[^{17}\]. This bimodal size distribution contained larger particle in 2~4 μm and smaller particle in 0.2~0.6 μm \[^{17}\]. In another study by Kim et al. proclaim 20 vol.% of small size (0.2 μm) in a bimodal distribution achieve the highest maximum packing fraction and lowest viscosity \[^{61}\]. This is because small particles act as lubricant for large particles to slide and flow with polymer. However, continuously adding up
the concentration of small size portion will result into agglomeration due to high cohesion energy. Genovese compared three types of particle size distributions and find that the poly-dispersing system tends to keep melt viscosity at relatively lower level comparing to mono-dispersing system [23].

Fillers existence in polymer decreases melt elasticity with increasing filler loading. Die swell outside spinneret reflects the chain relaxation after release from the die capillary. Die swell ratio is defined as the dimension of die swell to the capillary dimension. It was found that filler particles CaCO₃ and talc existing in die extrusion may hinder the die swell [62], showed in the reduced die swell ratio on polymer extrusion. Die swell increases with the shear rate because high pressure in the spinneret induces dilatancy. Ariffin et al. also found that particle shape impact chain relaxation: CaCO₃ has more dilatancy than talc loaded in same melt extrusion condition [62]. Fillers with larger aspect ratio yield to shear force from polymer flow at spinneret which can assist particle alignment under torsion, more importantly enhance filler-polymer interaction in larger specific surface area.
During the fiber process, polymer melt experiences high elongational deformation after it extruded from the spinnerets. Trouton’s Law allows us to calculate elongation viscosity from shear viscosity.

\[ \eta_e = 3\eta_s \]  

(6)

Based on the study of Zoukrami et al., the elongational viscosity of calcium carbonate filled low density polyethylene did not correlate with filler loading concentration \textsuperscript{60}. Other filler characteristics mentioned in the article are surface treatment and filler particle size. Without surface coating elongational viscosity increases, and explanation was given as with restricted in chain mobility result in strain hardening and higher viscosity. Filler particle size was also correlated with elongation viscosity, that reduction in average size can affect viscosity at lower rate, but less significant on strain hardening of LDPE polymer at higher rate \textsuperscript{39}. 
2.3.1.1. Melt Fracture

In polymer flowing through spinneret, the contraction force above a critical shear rate could result into melt fracture of polymer outside of spinneret \(^{[63]}\). Muliawan found that loading particular filler baron nitride into polyethylene increase the critical shear rate for on-set of melt fracture from 850 s\(^{-1}\) to 1500s\(^{-1}\). This fact indicates using boron nitride fillers can enhance shear rate flexibility in polymer processing that will overcome melt fracture issue at high flow rate \(^{[42]}\).

Elongational stress thrown onto polymer jet is the main cause of defects such as tear, rupture and crack \(^{[64]}\). Since the elongational stress is higher in surface of polymer jet than the core, then tearing initialize at the exterior surface of extrudate outside of spinneret \(^{[64]}\). By aiding of adhesion promoters and slip promoters, the extrudate appearance can be improved to avoid sharkskin on its surface \(^{[65]}\). There are several studies using capillary rheometer to study the rheology and extrudate properties including die swell and distortion or melt fracture \(^{[42, 44, 66]}\).

2.3.1.2. Orientation of Filler Particles

High shear rate tends to orient fillers to certain degree along the polymer melt flow direction. Kim, et al. regarded calcium carbonate as isotropic particle which does not align with high shear rate in rheometer, while talc is anisotropic that two silicate layers make it a platelet shape particles which will be rotate with shear flow \(^{[67]}\). But as shear rate increases, the contact area of talc particle with polymer reduces due to the orientation of talc in shear stress direction, resulting into lower shear viscosity at high shear rate than calcium carbonate filled case \(^{[117]}\).
Three processes of orientation occur along with polymer extrusion under shear stress, and we assume they are occurring at the same time in fiber spinning because of time of fiber running is very fast. These are polymer crystalline orientation, polymer amorphous orientation as well as the filler particle orientation in coexistence with the former two types [12]. For CaCO₃ added polypropylene in different levels of loading, maximum orientation of crystallites is obtained when the concentration of calcium carbonate is in the range of 15-20% [25].

Mykhaylyk et. al claim shear rate in spinline is related with two critical threshold of conformation transformations, orientation of polymers is associated with $\tau_d$ the reptation time and drawing fibers is associated with Rouse time $\tau_R$ of the longest chain [68,126].

$$\dot{\gamma} > \frac{1}{\tau_R} > \frac{1}{\tau_d} \quad (7)$$

In fiber formation, elongational shear stress drag polymer from spinneret into very fast speed and filaments cross-section from large area as measured in free fall filaments attenuated into very fine fiber diameter. Drawing of fibers is the main contribution to orientation formed in fibers, so that the deformation of fiber is closely related to the spinning speed of each drawing godet. According to Younes et al. fiber draw ratio is calculated from the velocity ratio $R_D$ between the second draw roll to the first draw roll, or calculated from solid state draw ratio $R$ [69].

$$R = \frac{L_2}{L_1} \ (actual) \Leftrightarrow R_D = \frac{V_2}{V_1} \ (adjusted) \quad (8)$$
Where L is the length, denote 1 and 2 refers to before drawing and after drawing. V means the velocity of draw roll. As mentioned previously, particulate fillers do not have viscoelasticity as polymer melt. The distribution of filler particles on one side influence by streamline of liquid, and particle spontaneous movement on another side should be regarded as an independent phase. When a spherical particle falls down under gravity in a viscous flow, buoyancy force, gravity force and friction force will reach a balance when the falling velocity of the sphere reach to the terminal settling velocity (Navier-Stoke’s Law).

\[
U_t = \frac{x^2 g(\rho_s - \rho)}{18 \mu}
\]  

(9)

Where x is particle diameter, g is gravitational constant, \( \rho_s \) is particle density, \( \rho \) is liquid density, \( \mu \) is the zero shear viscosity. This law is based on the assumption of no turbulence around the sphere.

Particle Reynolds number Re give a ratio of inertia of particle in a liquid to viscous.

\[
Re = \frac{xu\rho}{\mu}
\]  

(10)

If Reynolds number is larger than 0.2, then turbulence flow is existing in the streamline surrounding spheres. The extra in fiber spinning is hydrodynamic force imposed on particle fillers. Spinline dynamics becomes more complex because viscosity keeps increasing as polymer cools down. But not until crystalline orientation form in fibers, will filler be anchored in polymer material permanently.
2.3.2. Fiber Spinning Process

The spinning tension is following the force balance equation before the spinline solidify at frostline:

\[ F_{\text{air drag}} + F_{\text{gravity}} + F_{\text{extension}} = F_{\text{viscous}} + F_{\text{surface tension}} + F_{\text{inertial}} \]  (11)

Where \( F_{\text{air drag}} \) is drag force from the relative movement from high pressure air to the running filaments. \( F_{\text{extension}} \) is from roller guiding equipment that is stretching filaments by high speed spinning. \( F_{\text{air drag}} \) and \( F_{\text{extension}} \) is downwards in gravitational direction in balance with \( F_{\text{viscous}} \), \( F_{\text{surface tension}} \) and \( F_{\text{inertial}} \) three components towards to the opposite direction. With fiber taking up by high velocity roller, \( F_{\text{extension}} \) is regarded as a major contributor. High pressure air has equivalent function in stretching fibers as mechanical equipment, for example, aspirator in spunbond using high pressure air to stretch filaments downwards. The less dominant force in this spinline direction is gravitational force which is relatively small. In the opposite direction towards spinneret, \( F_{\text{viscous}} \) is a major source in balance with dragging. The inertial force \( F_{\text{inertial}} \) and \( F_{\text{surface tension}} \) are smaller than viscous force as polymer jet approach to the solidification defined as frostline. Fedorova brought up with the numerical method of interpreting each spinline force component, involving the acceleration of fibers, the air friction by aspirator from quenching, and the gravitational force. The author neglected viscoelastic effects by assuming Newtonian flow \[70\]. Based on the theory of Ziabicki, when estimating the rheological force at the spinneret \((z=0)\), Newtonian fluid is a reasonable assumption for non-Newtonian fluid \[71\].
\[ P_{xx} = \lambda \left( \frac{dv}{dx} \right) \]  
\[ \vec{F} = 3A_f \eta_f \frac{dv}{dz} \]  

Where \( P_{xx} \) is tensile stress distribution, \( \lambda \) is elongational viscosity, \( A_f \) is fiber cross-section area, \( \eta_f = \eta_0 \) is zero shear viscosity, \( V \) is moving velocity at position \( z \) of spinline from position zero at spinneret.

\[ \dot{\eta}_E(\dot{\varepsilon}) = \frac{\sigma_{11} - \sigma_{22}}{\dot{\varepsilon}} \]  

Where \( \sigma_{11} - \sigma_{22} \) is normal stress difference, \( \dot{\varepsilon} \) is the strain rate. While in non-Newtonian fluid, the Trouton’s ratio of \( \eta_E = 3\eta \) would be applied when regard the zero shear viscosity \( \eta_0 \):

\[ \lim_{\dot{\varepsilon} \to 0} \left[ \eta_E(\dot{\varepsilon}) \right] = 3\eta_0 \]  

Polymer jet is viscous fluid and it exposes to elongational stress which is promptly increasing with strain rate during the spinning process. Non-Newtonian behavior of polymer at certain temperature shows a decrease shear viscosity with shear rate, \( \eta_f \), t. Actually \( \lambda \) decrease with elongational strain accelerates from zero spinneret to a rate at frost line. It indicates rheological force is also associated with strain rate \( \frac{dv}{dx} \) and stretch ratio \( \frac{\text{take-up velocity}}{\text{initial velocity}} \), resulting in cross-section area of fiber shrink down in millisecond.

After filaments solidify, they are drawn onto several spinning godet. Fibers reduce its diameter and improve the anisotropic property. A uniform spinline tension is the key to the
stability in fiber drawing. In another word, if spinline stability is influenced by adding particulate fillers, it may be because of spinline tension changes. A lot of reasons may cause filler particles change the tension. Difference in crystallization kinetics in quenching may result into a different crystalline phase at different position. Crystallinity developed by quenching and those formed by drawing may change the spinline tension. Ambient air temperature and air velocity greatly determines the filament internal stress even more than mass flow rate and take-up speed \(^{[72]}\). Higher tension caused by too much crystallinity developed in quenching may move up the frost line and bring brittleness to fibers. Other possible cause of spinline tension changes are from defects in molecular structure, and stress concentration on the agglomeration of filler particles, etc. It is a complex physical problem to reveal the relationship between fiber crystalline structure formation with fillers loading and spinning parameters (spin speed, stretch ratio and ambient temperature around fibers).

2.3.2.1. Shear Induced Crystallization

Formation of different crystals at take-up speeds are shown in Figure 2-7. A row nucleation formed in low speed rate will eventually transform into highly stretched non-twisted lamellae structures, and in some cases such velocity dependent crystal structures may have a sheath-core effect in fiber crystallization \(^{[73]}\). Due to high spinline stress at fiber sheath, untwisting of row nucleates start from sheath as indicated in reversed triangle shape in Figure 2-7 (dash line). A transition from sheath to core of fibers is also influenced by increasing the spinline speed.
Crystallization kinetics under shear stress was studied by many researchers including Eder, Janeschitz-Kriegl, Zibabki, just name a few of them \cite{71, 74-75, 121, 124-125}. About inorganic filler and nucleation agent effect on the melt spinning of iPP was mentioned in study of Yu and White, but their experimental analysis did not show mineral fillers can enhance the crystallization rate in the spinline as it does in the quiescence condition. Polymer melt consist of sites with ability of nucleation as temperature cooled in either rapid pace or slow cooling. Janeschitz-Kriegl well explained this nucleation mechanism from beginning with initial dormant nuclei into an elongated shish-kebab style under shear induced crystallization. A high draw ratio melt spinning process applied organoclay platelet fillers into PA6 and PA66, as mentioned in work of Onder et al., the induced strain directly enhance the development of more stable $\alpha$ form crystals in PA6, but less induce the formation of less stabilized $\gamma$ form \cite{109}.
2.3.2.2. Heat Transfer in Multifilament Quenching

A fast heat and cooling circle can be achieved when inorganic fillers being added into injection molding production line, this is because inorganic fillers has larger thermal conductivity and low heat capacity than polyolefin as shown in Table 1. Filled polymers will cool down faster due to low specific heat and large thermal conductivity \(^{[20, 123]}\). Table 2-1 includes polyolefin thermal conductivity, specific heat and specific gravity compared to three types of inorganic fillers. Lower specific heat of inorganic fillers means less energy is required to increase temperature of unit mass of inorganic fillers by unit degree of temperature (kelvin). Thermal conductivity of calcium carbonate is five times larger than polyolefin, and will conduct energy more efficiently throughout of the polymer material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity W/(m*K)</th>
<th>Specific Heat KJ/(Kg*K)</th>
<th>Specific Gravity g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyolefin</td>
<td>0.5</td>
<td>1.8~2.4</td>
<td>0.9~0.96</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>2.7</td>
<td>0.9</td>
<td>2.7</td>
</tr>
<tr>
<td>Aluminum Oxide</td>
<td>20~36</td>
<td>0.75</td>
<td>3.98</td>
</tr>
<tr>
<td>Titanium Dioxide</td>
<td>2.5-5.0</td>
<td>0.68~0.69</td>
<td>4.05</td>
</tr>
</tbody>
</table>

Kase and Matsuo proposed their method in calculate the temperature profile in fiber radius in the take-up process \(^{[74, 117]}\). Fedorova used computational modeling to build the heat transfer on spunbond influenced by air drag coefficient and heat transfer coefficient \(^{[70]}\). Spruiell and White did not correlate heat transfer to the fiber morphology development because of the fact
that heat transfer throughout the small diameter of filaments can be neglected \cite{75}. As we know, quenching and drawing of polymeric fibers is a fast and continuous process, so that the rate of polymer solidify in the quenching chamber will impact the extensional forces for fibers encountered in the aspirator suction regions \cite{118}. So fiber formation into different structure included orientation of polymeric chains and the chain alignment under impact of filler particles must be considered for a better understanding of fiber tensile properties.

![Spunbond schematic graph showing quenching chamber, attenuation and web formation on a moving belt.](image)

**Figure 2-8**: Spunbond schematic graph show quenching chamber, attenuation and web formation on a moving belt.

### 2.3.3. Spunbond

In the last section 2.3.1 and 2.3.2, spinning process was reviewed from polymer flow containing filler to fiber crystallization under the spinline tension. In this section 2.3., some
literatures on spunbond web processing are going to be reviewed, included the impact of bicomponent fibers on web consolidation.

A spunbond web is composed of long continuous fibers that randomly collect on the moving belt. Similar as melt spinning, filaments from spinneret are draw with high speed air into fine diameter. As illustrated in Figure 2-8, the difference in fiber forming between spunbond and melt spinning is at how the stretching force imposed onto filaments. While during spunbond process filaments is under high strain from air dragging from aspirator that fiber structure form into highly oriented molecular chains in the aspirator. Spinning velocity of spunbond can vary from 1000 m/min to 8000 m/min. From experience, nylon fiber is spun at 4000 m/min and PET at 6000 m/min. Fibers in spunbond nonwovens are highly oriented by stress-induced crystallization or into amorphous region alternating semi-crystalline phase, both of which achieve the outstanding mechanical properties of fiber used for different applications. Due to strong crystallization kinetics of polypropylene, increase spin speed does not influence its crystallization very much. Spin speed for polypropylene is set at around 2000 m/min.

Available spunbond grade polymer materials are polypropylene, polyethylene, polyesters (PET, PBT and PLA), nylon and elastomers. The spunbond grade raw material is usually formulated with processing agent such as anti-oxidant, antistatic agent, plasticizer. While for the inorganic particulate fillers, calcium carbonate, is prefer to be pre-compounded with same polymer and make into a masterbatch.
2.3.3.1. Web Formation

In web processing, fibers fall onto a moving belt in oriented fashion mostly in machine direction (MD). But the distribution of fibers in each direction on the belt is also influenced by filament relative velocity to belt velocity, as well as air suction under the moving collector belt [70,113]. Temperature of fibers is cooled upon this point so the free entanglement of fibers below air slot is mainly by a randomization from aerodynamic force. Because fibers escape from constrain of high velocity air, so there are some relaxation of polymer molecular chains according to the viscoelasticity characteristic of polymer. However, few papers have talked about the impact of added particulate fillers on web formation and fiber distribution in the web. Michielsen stated that randomization of fibers in web formation will influence the efficiency of thermal bonding effect because the number of fiber-fiber bonding increase with randomness [76].

2.3.3.2 Bicomponent Spunbond

About loading particulate fillers in multi-component fibers was mentioned by Bornemann and Haberer [77]. They produced fibers mixed with different concentration of fillers in one of core/shell component and wind them up for producing nonwoven sample. A form of non-inherent component which act as additive spun into Nylon fibers by Monsanto Company. Such additive brings antistatic properties to nylon fibers. This build-in nature is similar to the calcium carbonate fillers wrapped in the sheath fibers [78].
In another patent by Peng et al., they brought up the methodology of calculating particle spacing L on a two-phase composite and use a ratio between the spacing to particle largest dimension \((L/D)\) to characterize the packing of filler in bicomponent fiber \([79]\). Because of different types of geometric dimension of filler particles, fillers can be either wrapped inside of fibers or stick out of fiber surface. According Peng’s model, the filler only added in fiber sheath structure can stick out of fibers if filler dimension is larger than sheath thickness, as shown in Figure 2-9.

![Diagram](image.png)

Figure 2-9: Bicomponent fiber structure have filler particle loaded in sheath component showing a stick-out effect on fiber texture \([79]\).

In this model particle spacing for sphere and cubic shape of calcium carbonate is calculated based on equation:

\[
L = \left(\frac{k}{\alpha_{av}}\right)^{1/2}d
\]

(16)
Where $L$ is particle spacing, $\alpha_{av}$ is the ratio of particle volume fraction to the polymer matrix volume fraction, $d$ is particle size which is uniform to $D_{50}$. $k$ is the geometrical value which characterize the equivalent size of particle to a square, a cubic or to a triangle, as claimed in the patent. Their calculation is based on experimental $k$ value can be used to estimate the relationship between average filler particle size, volume fraction of fillers, and spacing between filler stick-out $^{[32]}$. Although bicomponent fibers are produced in the experiment with different sheath/core ratio, they did not use microscopy image to confirmation the particle spacing calculated from this model. It also lack evidence that if dispersion is uniform or not.

DeLucia and Hudson and McAmish claimed improvement of softness by use of CaCO$_3$ $^{[18], 80}$. Incorporating fillers in fibers result into surface roughness and improve hand of nonwoven fabrics. In bicomponent nonwovens using two polymers which has a higher and a lower melt point, such as PP/PE, PET/Co-PET, can also be used to improve fabric soft hand during web bonding $^{[70]}$. Hisakatsu et al. reported production and properties of bicomponent spunbond nonwoven containing fillers. This bicomponent fiber contains fillers in polymer blend of low melt point LDPE added and a copolymer of ethylene-vinyl acetate. The resin blend ratio is 95/5 to 60/40, and filler particles concentration varying from 1000~35000 ppm. Combined with high melt point polypropylene located either in core or side by side, such structure will enhance adhesiveness in spunbond web bonding $^{[21]}$. During thermal bonding, the Ethylene-vinyl acetate copolymer blended LDPE which has lower softening point and lower melting point will become tacky before core component is disturbed. Inorganic filler
powders appear on fiber surface, forming an uneven topography which resistant adhesion between filaments formation. Hisakasu also claimed it is necessary to use spin finish to assist drawing smoothness on godet by covering uneven surface \[21\].

On the aspect of improving the spinline stability in bicomponent melt spinning, Hisakatsu pointed out adding a hydrocarbon lubricant into filler loaded component (LDPE + copolymer) can improve the spinline stability by provide a thin film between bumpy surface with rotating roll \[21\].

2.3.3.3. Thermal Calendar Bonding

Thermal bonding can be accomplished by flat belt through-air bonding, drum through-air bonding and calendar bonding. The through-air bonding blow hot air into nonwoven webs and cause fiber become sticky and adhere to fiber-fiber crossing. Differently, calendar bonding is melting fibers by direct contacting of hot calendar rolls. Under compression from calendar rolls, fibers in nonwovens are melted to form a bonding. Usually calendar roll has embossed pattern which will form point bonding in different shapes (round, ellipse, tri-angle, rectangular, etc.). The percent of coverage of engraved patterns influence the area of web being melted and recrystallized \[70,81\]. These raised points conduct heat to fibers, and melts fiber-fiber interface, therefore generates bonding patterns.
As heat transfer to fibers is dependent on whether fibers are under bonding area or not. Contacting between nip pattern and fibers results into heat transfer by conduction. In between two nips is valley that cannot directly conducting energy to fibers so that heat is transferred by convection and radiation only [122]. Fibers not under nip pressure are referred as bridge fibers which are usually not melted. By experiment analysis of Nanjudappa and Bhat, crystal size and crystallinity of bridge fibers is smaller than bonded fibers [82]. Impact of calendar roll temperature (120-150°C) on varying crystal size is more significant on bridge fibers than bonded area [82]. Crystal size of polypropylene bridge fibers increases with temperature up to 140°C, and then decreases with higher temperature [82, 121-122]. Michielsen mentioned there is little morphology changes in bridge fibers and explained it as time is insufficient in heating of bridge fibers so that molecular chains cannot undergo deformation and relaxation [76].

Fabric bonding strength is also related with fiber tensile strength. Polymer amorphous orientation undergoes chain relaxation when exposing to heat. Melting and recrystallization at bonding behave polymer conformation transformation that may impact the periphery area around the bonding. At periphery, some bridge fibers can be softened and flatten when calendar roll temperature is sufficiently high [70, 76, 82]. Thus fused fibers expand outside
bonding area give a larger bonding effective region, and improve the friction between bridge fibers and with bonded area under engraved rolls. While on the contrary, stress tends to concentrate on these periphery areas at over-bonding temperature due to the discontinuity strength between bonds and bridge fibers [83, 84]. Polymer reptation is yielded by molecule chain flexibility in the bonding periphery region, as stated by Wei et al. that there is improved strength at low oriented amorphous region [85]. This is because amorphous in polymer macromolecular structures respond fast with increasing entropy during thermal bonding, thus polymer chains reach out to adjacent fibers at soften state. Based on polymer melt elasticity theory, fillers may hinder elasticity of polymer chains in molten state. Previous works cover any research on the impact of inorganic filler contained fibers on polymer chain orientation and its influence on bonding semi-crystalline conformation.

Relevant literatures on thermal bonding fabrics were mainly focused on fiber bonding process under varying of calendar emboss coverage, calendar roll temperature, line speed in regard of different fiber polymeric structure [76, 81]. These account for the thermal conduction under different calendaring parameters and how does heat diffuses from one side of fabric into mid-plane of the web. Otherwise from material wise, very few people guide us to an insight into heat conducting mechanism of inorganic filler particles in spunbond fibers and webs.

Thermal conductance through the path of particle filler in polymer composite has been discussed in work of Park et al. It has been proposed that aspect ratio of particle fillers play
an important role in improving heat conductivity $^{[111]}$. Because large aspect ratio (length to width ratio) of filler tend to form bridge between them which conducting heat throughout the network. This phenomenon has not been studied in nonwoven filled with inorganic fillers in different particle size and aspect ratio.

2.4. Structure-properties Relationship in Nonwovens Containing Fillers

There is few number of research or patents are related to spunbond nonwovens containing particle fillers. In the perspective of polymer morphology influenced by fillers, a lot of research papers cover plastics, film and fibers filled with inorganic particles guide us to a better understanding of properties of filler added nonwovens.

2.4.1. Nucleation Effect of Fillers on Crystalline Structure

Dispersed filler particles in polymer can trigger crystallization growth because particles add more nucleation sites in the melt. Firstly, nucleation effect of calcium carbonate filler in polypropylene is influenced by CaCO$_3$ crystal form. Theory of nucleation can be referred to the publication of Cobbs which includes the bulk free energy changes for a formation of new nucleation sites and embryonic nucleus $^{[112]}$. Adding particle fillers enhance heterogeneous nucleation in the system by the crystallization from surface of impurities and form nuclei at the interface between particle fillers with polymer. Calcite and aragonite, due to the difference in their crystal hardness, result into different nucleation rate as demonstrated by Kowaleski, and Avella el al $^{[86, 87]}$. They also use epitaxial crystalline phase to describe the polypropylene crystallize at cleavage of calcite fillers that grow parallel to the flat crystalline...
phase, as shown in Figure 2-11. Several researchers studied crystallinity of polymers containing particle fillers \cite{91}.

Secondly, filler particle size is an important factor that influences nucleating effect of polymer. Compression molded s-PP composite shows a double crystallization peaks but this only occur at more than 10 wt.% of 1.9μm CaCO$_3$ particle size, either larger size (2.8 μm or 10.5 μm) or low filler loading level did not have similar effect. This is explained as a self-nucleating effect that is due to a high surface-area-to volume ratio \cite{92}. Such effect of particle filler in polymer will entrap the residual of s-PP around the rough particle surface which is uncoated surface, in this way during melting and cooling experiment, those crystallites may survives and behave like nucleate sites in the crystallization process \cite{88}. Nucleation by trapping polymers at uncoated particulate filler surface seems pronounced because fatty acid coating may shield CaCO$_3$ fillers from being contacted with polymer or elastomer chains to function as active nucleating sites \cite{60}.

Other than crystal form and particle size of CaCO$_3$, nucleating of polymer is also related with surface treatment, such as fatty acid. Avella M. et al. explained fatty acid coated nano-CaCO$_3$ slow down crystallization rate of polypropylene and it is because coating softened at polypropylene crystallization temperature, while polypropylene-g-maleic anhydride copolymer still has nucleation that increase nucleis numbers while decreasing spherulite size \cite{86}. 
There were some other arguments about calcium carbonate fillers hardly induce nucleation, especially with surface treatment. Zoukrami and co-workers investigated the nucleating effect of CaCO$_3$ on low density polyethylene (LDPE), and concluded about filler particle size on crystallization temperature was not affected by addition of CaCO$_3$ $^{[60]}$. Especially for 56-72 nm PCC in composite (10 vol.%) with high density polyethylene (HDPE), whether crystallization temperature improved or not depended on surface treatment $^{[136]}$, which indicated there was weak nucleating effect for uncoated CaCO3 on crystallization of HDPE, while after surface treatment with different concentration (mg/m$^2$) of stearic acid, the nucleation effect was gone.

2.4.2. Crystal Growth

There are two steps of crystallization, nucleation and crystal growth. The crystal growth involves growth of spherulite until they interpenetrate between each other, and also involves thickening of the crystals or growth of new lamellae within or between existing lamellae stacks from remaining amorphous regions within the spherulite, as it is showed in Figure 2-12. Hedge found in nano-clay filled polymers spherulite stops growing when the crystals growth impinge each other $^{[93]}$. The direct result of nucleation effect in polymer is that the number of spherulite increases while the size of each spherulite shrinks, illustrated in Figure 2-13 $^{[89]}$. Figure 2-14 shows how spherulite grows with time in isothermal crystallization. Polypropylene with no filler grew spherulite of a large size over a longer period of time. The addition of CaCO$_3$ can reduce the ultimate size of the spherulite and shorten the time to reach an equilibrium size $^{[12]}$. There is a filler concentration dependent on the crystalline structure.
of polymer in isothermal crystallization.

In fiber melt spinning, filaments cool down quickly and shish-kebab fiber structure formation is mainly driven by the shear stress induced crystallization [94]. So crystals formed from nucleating around fillers may not have enough time to grow as in the quiescent nucleation. However, crystal growth should not be neglected in fabric thermal point bonding. Because small crystals initializing at nuclei (filler) have sufficient time to grow at bonding area of spunbond fabrics as its temperature gradually cool down after leaving calendar rolls.

Figure 2-11: Morphology of PP crystallized in the contact calcite crystals.
Based on Avrami model, temperature dependent isothermal crystallization make us understand the filler nucleation effect in polymer melt. Kinetic constant $k$ in Avrami isothermal crystallization model, equation (15) and (16), determine both the nucleation rate and growth processes $^{[95]}$. The presence of some nuclei would result in a decrease in crystallization activation energy $^{[95, 119]}$. 

Figure 2-12: Schematic Formation of Chain-stack Lamellae from Radial Boundary of Spherulite $^{[19]}$
Figure 2-13: Polarized microscopy show the nucleation effect of 0.5% talc in polypropylene (right-hand side) and compare with the crystallization of filler-free polypropylene (left-hand side) [89]

Figure 2-14: Isothermal Crystallization of PP Containing Different Concentration of CaCO₃ [96]

\[ \frac{X(t)}{X_\infty} = 1 - e^{-kt^n} \]  \hspace{1cm} (17)
Where $X$ is the crystallinity developed by the polymer in a time $t$, at a constant temperature $T$, $X_\infty$ is the crystallinity in an infinite time. $n$ is Avrami exponent, $k$ is kinetic constant. Crystallization rate can be described by Arrhenius equation (16):

$$k^{1/n} = k_0 \exp(-\Delta E_c / RT)$$

Where $\Delta E_c$ is the crystallization activation energy; $k_0$ is a pre-exponential constant; $R$ is the gas constant; $T$ is the absolute crystallization temperature.

Nucleation effect of filler particles is indicated by an increasing of crystallization temperature ($T_c$) $^{[89,120]}$. In the comparison study of filler-free PP with 0.5 wt.% talc filled PP, the filler added polymer system show more crystallites number growing and the volume of each crystal become smaller, as shown in Figure 2-14 $^{[89]}$. From WAXD peak location, fillers adding result in two additional peaks at 29.0 and 39.4° at CaCO$_3$ loading is more than 5% $^{[92]}$. But addition of CaCO$_3$ in s-PP matrix does not alter the polymer crystalline structure as shape and position of other peaks are the same $^{[88]}$. As for isotactic PP with an $\alpha$-crystalline monoclinic characteristic, several peaks are positioned at (1 1 0), (0 4 0), (1 3 0), (1 1 1), and (0 4 1) $^{[121]}$. Nucleation effects caused by different particle surface area can result in X-ray diffraction pattern differing in their peak height $^{[97]}$.

It also pointed out that in DSC isothermal crystallization curve (125°C), $\Delta \omega$ (represents width at half-height of crystallization peak) decrease as talc concentration increase in PP $^{[98]}$, which
means that higher filler concentration correspond with relatively smaller range of exothermal peak. This indicates a reduction in the size distribution of spherulite [95, 98].

2.4.3. Effect of Fillers on Mechanical Properties of Materials

In breaking mechanism of two phase material, assuming fillers is rigid and matrix phase is relatively soft, interface crack due to weak bonding is a prevailing theory in general plastic composites with filler particles. Weak interfacial adhesion results in the formation of cavity around the fillers area. Although the stress field near a particle is independent of the particle size, the volume of polymer withstanding a stress concentration will be directly related to the particle size [22, 121]. So that increase the particle size usually result into more defects in polymer because the flaw increase with the particle size.

Debonding is most related to embedding of fillers as being processed in fibers spinning. Debonding is referred to filler separation from matrix as polymer is under tensile stretching. This separation initialize at the pole direction along the tensile force direction [100]. Dissipation in energy by a joint movement between particle fillers and polymers cause material brittleness and could result into sharp fracture at certain interface if there is strong adhesion [29-30, 100-101]. Surface tension determines the adherence between two components in the polymer [99].

Zhang et al. characterize impact resistance of polypropylene composite filled with elastomers and CaCO$_3$ by using Notched Izod Method. It was confirmed that that elastomer particle
filler added polypropylene behave higher resistance than CaCO$_3$ filler added sample $^{[102]}$. There are two reasons for this result: first, different surface tension may result into different interfacial adhesion strength; second, the energy may be absorbed by the deformation of elastomer particles so that impact resistance is higher in this case. Particle size of CaCO$_3$ influences how much extent impact resistance can be improved. 1μm particles showed 60% improvement at 12 vol.% of loading compared with pure polypropylene resin, while 50 nm particle will improve impact resistance by almost 350% $^{[102]}$.

2.4.3.1. Tensile Properties Influenced by Filler Loading

Based on B. Pukanszky, decreased interaction results in decreased tensile strength and increased deformability $^{[89]}$. A parameter $B_\sigma$ reflects the effect of the interaction between filler and matrix, included in the equation (4).

\[
\sigma_T = \sigma_{T0}\lambda^n \frac{1-\phi_f}{1+2.5\phi_f} \exp(B_\sigma\phi_f)
\]

(19)

Where, $\phi_f$ is the volume fraction of the filler. $\lambda$ is relative elongation, $\lambda = L/L_0$; $\sigma_T$ is true stress of materials; $\sigma_{T0}$ is the true tensile strength of the matrix polymer; $n$ characterizes the strain hardening tendency of the matrix.

\[
A = \frac{1-\phi_f}{1+2.5\phi_f}
\]

(20)

\[
A = 1 - \frac{3.5}{\phi_f+2.5}
\]

(21)

where $A$ is the minimum value of matrix area in the cross-section perpendicular to the load.
direction. $A$ is increased by reducing of volume fraction of the filler $\phi_f$. $B_\sigma$ and $A$ are two factors that determine the composition dependence of tensile yield stress and tensile strength [100, 103].

In a particulate filler composite, the Poisson ratio follows equation:

$$\frac{1}{\nu} = \frac{\phi_f}{\nu_m} + \frac{1-\phi_f}{\nu_f}$$

(22)

Internal pressure:

$$p_i = \frac{1-2\nu}{6(1+\nu)} E_0$$

(23)

Where $\nu$ is the Poisson ratio, $\phi_f$ is volume fraction of fillers, $\nu_m$ and $\nu_f$ are the volumes of individual components of matrix and filler respectively. $p_i$ is the internal pressure of the composite. $E_0$ is initial modulus of the composite.

Mica is distinctive from other filler particles in its special particle shape – plate forms particles that can be additional value for reinforcement [1]. Compared with shape of talc, mica has higher aspect ratio which results in a higher interfacial interaction between filler and polymer matrix that can better transfer stress and increase tensile strength [28]. Not only interfacial adhesion, but also orientation of mica planar flakes has great impact on mechanical performance, such as an increase on modulus, tensile and flexural strength. For polymers embedded with talc or mica, plate-like structure gives a complicated and tortuous diffusion path of vapor and liquid and therefore lowers gas permeability [1]. The maximum interface adhesive strength is also influence by particle shape, as mentioned that spherical
particles has maximum strength at pole, while moving to the equator as for the rod-shape like particles [104, 121].

2.4.4. Fabric Whiteness and Opacity

Calcium carbonate can be regarded as color pigment to resin that balance the white and brightness of fibers and fabrics. Benefit from the whiteness of filler particles, light will tend to be scattered at plastic surface rather than reflected at a regular angle which cause an unpleasant lustering effect of the fabric. Fabrics made from polymer resin without adding any colorants possess an intrinsic whiteness. Adding fillers will combine fabric whiteness with the pigment, editing local dullness of fabrics.

Paper modified with calcium carbonate filler in fine pulp pores outstand in the surface smoothness as well as pure white color. Kumar and co-works demonstrated the importance of particle size distribution of calcium carbonate on the optical properties of coated paper [105]. PCC contains 87% of size less than 1μm while GCC only contains 38% of size less than 1μm and 60% less than 2μm in size distribution, modifying base paper with PCC coated sheet perform whiter [105]. They also pointed out that calendaring reduce the pore geometry of papers which resulted in a changed light scattering effect. However, evidence in whiteness improving by calendaring is only for the base paper with high whiteness level, but less likely associated with change of geometry of coated CaCO₃ sheet. It is still not addressing the issue in how does light reflectance happen at fiber-fiber cross bonding by calendaring if the geometry of fibers embedded with fillers will be changed.
A beam of incident light is reflected at surface, when numbers of beams transmit in a certain angle there will be mirror reflection. Since fine fibers entangled in nonwovens form a great amount of pores and air-fiber interfaces, light scattering occurs substantially at fiber surface. While in micro topography, calcium carbonate fillers may change the mirror effect of fibers as fillers particle improve light scattering coefficient. In surface coating of paper, the roughness is closely related with CaCO$_3$ particle shapes$^{[13, 106]}$. Particles with large aspect ratio, such as PCC in rhombohedral and orthorhombic, tend to align during coating consolidation$^{[106]}$. Such uniform arrangement of PCC resulted in less rough surface compare to GCC, attaining the smoothness will increase the gloss of coated papers$^{[106]}$. PCC synthetize in-situ with pulp suspension was investigated by Tiarks et al. and Subramanian et al. based on a balance between paper opacity and mechanical strength$^{[107]}$. This method directly precipitated CaCO$_3$ filler onto pulp suspensions, settling at the voids in the cellulose fine fiber network$^{[107]}$. Agglomerations of PCC due to high specific surface area were discussed as one reason to modify the light scattering efficiency of surface of paper and paint$^{[14, 105, 108]}$. However, there was few research revealing calcium carbonate fillers on opacity of spunbond structure by spinning filler particles into fiber. Not mention that long filaments in spinning are much longer than the cellulose fiber in paper sheet, therefore the optical properties of fabrics should have some different effect even applying CaCO$_3$ fillers with similar characteristics.
REFERENCES


CHAPTER 3 Systematic Study of Structure and Properties of Melt Spun Polypropylene Fiber Loaded with Inorganic Fillers – Ground Calcium Carbonate

ABSTRACT

This article brings up a spinning process of adding inorganic particulate fillers with polypropylene by extruding thermoplastic polymer into fiber form materials. Composites structure of melt-spinning polypropylene fibers contains increasing concentration levels of calcium carbonate (CaCO\(_3\)) fillers – Ground Calcium Carbonate (GCC). From the mono-component fiber structure the dispersion of filler particles and surface roughness of fibers reveal the spinning formation of fibers at different parameters, include throughput, spin speed and drawing determine the compatibility of inorganic phase in polypropylene flow jet. Produced fiber samples are characterized by DSC and Wide angle X-ray to inspect the crystallinity of fiber forming structure under spin-draw formation. Spinning speed is challenging as higher strength usually cause fiber spin-line breakage. Addition of GCC with average size of 2.2\(\mu\)m accompany with weak interfacial bonding especially after fibers being drawn at higher spinning speed. Based on weak-link theory, the strength of fibers is negatively correlated with gauge length since probability of fatal defects increase with gauge length. We also find that filler loading concentration may related to the probability of defects included in the spinning, especially caused from agglomerations due to less dispersion. By observation using optical microscopy and scanning electron microscopy (SEM), image analysis elucidate particle dispersion state in polymer material. We mainly study tensile
behavior, including fiber tenacity, toughness, secant modulus and elongation at breaking to validate the structure weakening effect in fiber spinning. The fiber tensile gauge length effect is offset with a prominent breaking mechanism from weak interfacial linking than minor defects existing in crystalline region, as high filling concentration causes micro void surround fillers. It has been found crystallinity keep decreasing from 5 wt. % to 10wt. % then rise up at higher loading concentration, with crystal size in polypropylene fibers increases.

**Key Words:** Ground Calcium Carbonate, Melt Spinning, Single Fiber Tensile Property, Crystallinity, Shear Viscosity
3.1. INTRODUCTION

Calcium carbonate fillers are abundantly applied in food, plastics and cosmetic products that originate from limestone and chalk, after processes and treatment in milling or precipitating the inorganic material is transformed into particulate form minerals \[^{[1]}\]. A large proportion of manufacturing require to use calcium carbonate minerals to lower cost in raw material, such as plastics and papers, it also thicken latex and painting to impose white and opaque over coated background. The average particle size \(d_{50}\) between 3\(\mu\)m to 10\(\mu\)m are commonly used in injection molding, filler particles change composite density, thermal conductivity, impact resistance, flexural rigidity and notch resistance \[^{[2, 24]}\]. The previous investigations on thermoplastic polymers, such as polypropylene (PP) \[^{[6, 7, 20, 27]}\], nylon \[^{[29]}\], HDPE \[^{[3, 34]}\], and polyester \[^{[14]}\], has born tremendous phenomena and explanations on plastics extruded structure \[^{[2, 3, 6-8]}\] containing with calcium carbonate fillers, but only a few tried to step into melt spinning structure and nonwoven fiber structure \[^{[4, 5, 31-33, 35]}\]. Relevant research focus on solving such a problem in how to improve compatibility of polymer/inorganic of comingled system, from filler particle size, surface treatment and melt compounding condition \[^{[13, 29]}\], try to enhance wetting of hydrophobic polymer onto calcium salt surface for an uniform blending. As to the fiber spinning, compatibility of polymer in addition with particulate fillers is not well addressed in the elongation deformation of polymer melt flow.

Fiber and nonwoven products are applied in hygiene, wipes, baby diapers, medical gown and masks for their good absorption, skin contact comfortability, penetration repellency, filtration efficiency, and mechanical properties. Polypropylene is with vast market share due to its
lower price and flexible grades to meet with different processing conditions, especially in combining with spunbond technique. So at this point, melt extrusion PP added with inorganic filler – calcium carbonate become an extraordinary selection of new material into product development, ultimately achieving replacement of petroleum derivative thermoplastic with renewable, whiteness, non-hazardous, green resources with lower production cost.

Fibers are spinning from extruding, in this process polymer melt start oriented under high elongation deformation, meanwhile by quenching semi-crystalline phase form with particle fillers. Concentration of inorganic particles affects polymer crystalline structure and mechanical properties. Nucleating effect from CaCO₃ in isothermal crystallization dramatically changes the number of heterogeneous nucleus and reduces the volume of crystallites [3]. Whether inorganic filler improve crystallization rate or not, is changed with drawing force onto polymer flow [20]. Under high shear stress, polymer is extruder to highly oriented morphology, when filler particle may also align with the flow pattern [10]. Shear viscosity is also found to increase with filler volume fraction [11]. Because of shearing thinning behavior, elongation viscosity may be reduced by adjusting larger higher elongation rate, either by lower down the throughput or induce larger flow tension. Meanwhile using high shear rate, filler does not apparently affect shear viscosity, [3, 10, 11], also the alignment of particles with shear flow will lower the bulk free energy of polymer system and assist the epitaxial growth of polymer [15, 37]. However, since the filler particle may have weak interfacial bonding with polymer, so larger extension rate when exceed the maximum tensile strength fiber may encounter breaking in the spin-line [27]. Fiber tensile strength and
toughness is associated with the spinning mechanism at varying of filler loading concentration in fiber. According to Pierce weak-link, fiber strength is equal to the segment within fiber material when its breaking stress is lower than other segments \[^{[19]}\]. Fiber structural weakness can be reflected from testing gauge length, that reduce gauge length to zero gauge length in theory achieve the infinite strength as probability of fatal structural defect is completely avoided. However, higher loading concentration of inorganic fillers increases the change of agglomeration due to insufficient mixing. Stearic acid coated particles have lower surface tension to reduce the cohesiveness among particles and improve the affinity with polymer \[^{[13,37]}\].

This paper intends to construct fibers structural-physical properties relationship using melt spinning to develop multi-filaments containing calcium carbonate filler. By investigating filler particle embedded fibers formation, we will know better of the impact of fillers on spinnability and fiber tensile properties. Based on fiber properties, the functional of particulate fillers can be imposed to spunbond nonwoven by embedding into mono-component fibers. The objective is to find key parameters of calcium carbonate fillers that influence melt extrusion and fiber spinning formation under a systematic structure-properties relationship.
3.2. EXPERIMENTAL

3.2.1. Materials

PP polymer resin was compounded with calcium carbonate fillers into masterbatch. PP are isotactic Polypropylene (iPP) with \( M_w \) of 180,000g/mol (PI= 3.3) is identified as CH36OH supplied from Sunoco Chemicals (PA). This type of polypropylene is of spunbond grade that has melt flow index (MFI) at 36gram/10mins. Masterbatch is compounded calcium carbonate fillers with stearic acid coating (1~1.5%) in 70:30 with PP, which is supplied from Imerys (Roswell, GA). Particle size distribution is in range of 0.5μm~10μm, with an average particle size at 2.24μm, and BET surface area of 4.8 m\(^2\)/g. Filler concentration level at 5%, 10%, 15%, 20% at 500 meter per minute (mpm), 1250 mpm and 2000 mpm. Spinning parameters set at constant throughput and spin-draw ratio, as included in Table 3-1. With further level up from 20 wt.% (6.4 vol.%), 30 wt.% (10.5 vol.%) to 40 wt.% (18.8 vol.%), throughput is set at 0.6 ghm compare to 0.9 ghm, and godet drawing ratio changed accordingly, included in Table 3-1.

3.2.2. Melt-spinning Processing

Fiber melt-spinning process is conducting on Hills multifilament melt-spinning units. What illustrated in Figure 3-1 is a schematic graph of the multifilament melt-spinning equipment. This unit contains a single-screw extruder with Maddox mixing section. There are four zones in 24”/1” (L/D) Screw Extruder: feed zone, melting zone, mixing zone and metering zone, with heating temperature of each zone is from 190°C, 210°C, 215°C to 230°C. A constant polymer flow is metered at three pump speed levels. Melt pump feed filled polyer material to
the spinneret at constant volumetric throughput. Screen filter, with 325 mesh size is filtering out impurities and big chunk of inorganic fillers outside of spinpack. 15.0 RPM, 18.1 RPM and 27.3 RPM which are corresponding to certain volumetric throughput levels. Throughput levels are included in Table 3-1. Spinneret has 69 holes in total with each single diameter at 0.4mm. Molten polymers undergo transition from liquid to solid at frost line which is located right below quenching aspirator. Spin finish of 10% Lurol PP-912 Lubricant apply onto filaments by dipping in an oil trough. Amount of spin finish is controlled at 10%~40% of oil pump motor, to adjust with filler concentration in PP fibers as shown in Table 3-7 (APPENDIX I). Fiber spin-draw mostly occurs between feed rollers and draw roll. The velocity of each roller is set at certain level, to gradually increase up to spinning speed of 500 meters per minute (mpm), 1250mpm, 1500mpm, 1750mpm and 200mpm. Fibers are either drawn at ratio of 1:2 or 1:1 which are depending on the speed ratio between draw roll and feed roll. Finally, multi-filaments are send to relax roll and wind onto a bobbin.
Figure 3-1: Schematic graph of mono-component melt spinning extrusion unit (Hills Inc.)
Table 3-1: Spinning Parameter Settings for Melt Extruding and Spin-Draw Process:

<table>
<thead>
<tr>
<th>Extruder—Spin pack Temperature (°C)</th>
<th>Tm</th>
<th>Zone 1</th>
<th>Zone 2</th>
<th>Zone 3</th>
<th>Zone 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruder</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spin Head</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>230</td>
</tr>
<tr>
<td>Pump Block</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>240</td>
</tr>
<tr>
<td>Quench Air</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17-19</td>
</tr>
<tr>
<td>Rolls</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Spinning: 69 Holes, 0.4mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MFI of PP: 36 g/10min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exterior Pressure: 400psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Throughput</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TH5: 0.5ghm 0.635 cc/hole/min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pump Speed: 15.0 RPM</td>
</tr>
<tr>
<td>TH6: 0.6ghm 0.766 cc/hole/min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pump Speed: 18.1 RPM</td>
</tr>
<tr>
<td>TH9: 0.9ghm 1.155 cc/hole/min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pump Speed: 27.3 RPM</td>
</tr>
<tr>
<td>Draw ratio</td>
<td></td>
<td>DR=2 (B)</td>
<td>DR=1 (A)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spinning Speed (MPM)</td>
<td>1250</td>
<td>1500</td>
<td>1750</td>
<td>2000</td>
<td>500</td>
</tr>
<tr>
<td>Feed Roll</td>
<td>600</td>
<td>725</td>
<td>850</td>
<td>950</td>
<td>450</td>
</tr>
<tr>
<td>Draw Roll</td>
<td>1200</td>
<td>1450</td>
<td>1700</td>
<td>1900</td>
<td>475</td>
</tr>
<tr>
<td>Relax Roll</td>
<td>1250</td>
<td>1500</td>
<td>1750</td>
<td>2000</td>
<td>500</td>
</tr>
<tr>
<td>Quench</td>
<td>Q20 (20%), Q50 (50%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

There have been two trials successfully conducted in our Fiber Science Lab of the Nonwovens Institute (NWI). In trial plan I, the main factor in Design of Experiment is wt. % concentration of calcium carbonate in PP fibers. Therefore, 5, 10%, 15% and 20% of fillers were added into fibers, under the same spinning condition of throughput (THR) = 0.635 cc/hole/min, quenching = 20% and spin finish amount of 10%. Fibers spinning speed was gradually increase from 500 meters per minute (mpm), 1250 mpm to 2000 mpm (draw...
ratio =1:1), detailed processing information on different spin-draw ratio is included in Table 3-1. In Trial II, spinning speed, throughput and draw ratio are three main parameters that are being studied, as included in Table 3-1, with filler loading concentration keep loading up to 20%, 30% and 40%. Spin finish pump more as fiber loaded with higher concentration of CaCO$_3$ fillers.

### 3.2.3. Structure and Properties Characterization

#### Filler Particle Distribution

Fiber structure is studied using optical microscope (Zeiss). Image after captured by Nikon camera (DS-Fil) are applied for filler dispersion characterization and fiber diameter measurement. Other fiber morphology like defects inside of fibers is revealed from image.

#### Fiber Surface Morphology

Fiber surface is observed using Hitachi S-3200N Scanning Electron Microscopy (SEM) in Analytical Instrumentation Facility (AIF) in North Carolina State University. Fiber cross-section was prepared by cutting the sample in liquid nitrogen and cut in vertical direction to the fibers. Next a sputter coating using Au/Pd (60/40) chemical element, coat the sample for 10 minutes.

#### Particle Size Distribution

We analysis particle size distribution of calcium carbonate fillers using a laser diffraction particle size analyzer (Beckman Coulter) in Department of Natural Resources in North Carolina State University. This device allows measure particle size from 0.04 ~2000μm by
measuring the forward scattering (diffraction) of light over the particles suspended in liquid, such as water. Particle size distribution is determined from laser diffraction method, and the angle of diffraction is inversely proportional to particle size, and the intensity in a diffraction beam reflect the number of fillers with a specific surface area suspended in certain area of the medium \[30\]. But as surface of calcium carbonate is coated with stearic acid, we use acetone as suspension medium for GCC. Calcium carbonate fillers are premixing with 100 mL acetone, after treatment by mechanical shaking for 12 hours the suspension is applied to the instrument. The plastic disposable pipette was washed using acetone and draw a slight amount of suspension (10mL) to fill into the cell.

**Differential Scanning Calorimeter**

Thermal property of polymeric material is evaluated using DSC. Differential Scanning Calorimeter (DSC), from Perkin-Elmer Pyris, it gives a circle of melting and cooling of material under heating rate of 20ºC/min from 25 ºC to 190 ºC, then cooling from 190 ºC to 25 at 10 ºC/min. Endothermic and exothermic peaks are analyzed using software Pyris V 3.0. Fiber crystallinity is calculated based on equation:

\[
\chi_c(\% \text{ crystallinity}) = \frac{\Delta H_m}{\Delta H^0_m} \omega \times 100\%
\]

where \(\Delta H^0_m\) is the heat of fusion (165 J/g) for 100% iPP; \(\Delta H_m\) is the heat fusion per unit gram of fiber sample; \(\omega\) is mass fraction of PP in the fiber composite. Sample used in DSC is fibers of weight around 5mg.
Wide angle X-ray (WAXD)

The scattering patterns were scanned using Omni Instrumental X-ray diffractometer (Biloxi, MS). Bragg angle $\theta$, plane distance $d$, crystal size of the sample were measured from diffraction pattern. The diffractometer was equipped with Be-filtered Cu Ka radiation with a wavelength of 1.54Å and generated at 35 KV and 25mA. The fiber samples were wound around the sample holder and locate at the same horizontal level with holder front surface. The samples were scanned in the 20 range 5°to 40°with an increment of 0.05°. Plane spacing $d$ of crystal unit was calculated using Bragg's equations:

$$\lambda = 2d \sin \theta_B$$  \hspace{1cm} (2)

where $\lambda$ is wavelength of X-ray (1.54 Å), $d$ is inter-planar spacing (Å) and $\theta_B$ is Bragg angle. The crystal size of the samples is calculated based on Scherer's equation:

$$t = \frac{0.9 \lambda}{B \cos \theta_B}$$  \hspace{1cm} (3)

where $t$ is crystal size (Å), $\lambda$ is wavelength of X-ray (1.54 Å), $B$ is full width at half maximum (radian).

Fiber Tensile Test

Fiber mechanical property is being studied using fiber tensile test, on MTS instrument Q-Test attached with a 50gram load cell. Gage length is 1 inch (2.54cm), and elongation rate is 15mm/min. At least 10 specimen of each sample were tested. Linear density of each fiber specimen is measured using Vibromat and Denier (gram/9000 meter) is used for Q-test
analysis. Fiber tenacity, toughness, secant modulus at 5% are normalized with fiber linear density in the testing. Strain at breaking is evaluated as well. The stress-strain curves are constructed using representative curve out of ten specimens, which has similar strength and elongation as the average. After each fiber sample are tested under a constant gauge length 1 inch. The gauge length is adjusted to different levels as 0.5 inch, 1.5 inch and 2.5 inch, then ten specimens for each samples was tested with constant extension rate and load cell.

**Fiber Shrinkage**

We random pick up five fiber specimens with initial length $l_0$ (around 10cm), attached one end with an U-shaped pin which impose a pre-tension to the fiber sample. Next boil a breaker of deionized water on a heater plate, containing a thermometer for consistency at 100 °C. Fibers are immersed in boiling water for 5 minutes relaxation, then the second reading is recorded as $l$. Then the shrinkage of fiber samples is calculated according to equation below (Eq. 5):

$$Fiber\ shrinkage = \frac{l-l_0}{l_0} \times 100\%$$ (4)

**Capillary Extrusion Rheometer**

Rheology property of polymer is tested using Rosand Precision Advanced Capillary Extrusion Rheometer - Rosand capillary rheometer RH7-2. The shear viscosity are measured over a range of shear rate of 20-10,000/s, was determined at three temperature levels (225°C, 230 °C, 240 °C, 245°C and 250 °C). The capillary rheometer involves a cylindrical die with cone-entry front, and the pin-hole die with a diameter of 1mm. First, the apparatus was
preheated up to the targeted testing temperature. The fiber samples of approximately 20-30g was then loaded into the cylinder and tamped down by the piston to compress the polymer melt and eliminate any air bubbles. The sample was primarily preheated in the cylinder for 4 min in order to allow the fiber samples to melt, in the interval between 1st and 2nd heating, a compression with 200 Mpa pressure impose consolidation to the molten polymer.

3.3. RESULTS AND DISCUSSION

We produce polypropylene melt spun fibers in three trials- the first one was pilot spinning starting from low 500 meters per minute (mpm) up to higher draw roll velocity, and increasing weight fraction of ground calcium carbonate (GCC) from 5% to 20%. In Trial I, we mix levels of concentration of GCC-FiberLink which is surface treated with stearic acid. The maximum spinning speed was set at 2000 mpm. Maximum loading is limited to 15% at 2000 mpm with 0.635 cc/hole/min throughput. Next in the Trial II we studied different spinline parameters related to spinline stress comparing fibers containing with 20~40 wt.% of calcium carbonate. The reason for choosing a higher loading concentration is based on previous literatures and patents, which claimed the upper limit of mineral fillers is as much as 60 wt. % in molding articles and films [24]. In the Trial II, we adjust throughput at 0.6 ghm and 0.9 ghm, as well as two draw roll speed ratio at 1:1 and 1:2. Because fiber cross-section area is significantly increasing when leveling up the throughput, meanwhile, high output rate allow sufficient amount of polymer extrude from spinneret which reduce the spinline tension apparently. By turning up throughput from lower level 0.635 (cc/hole/min) to 1.155 it is possible to produce push the highest loading concentration up to 30%. The third trial was
mainly studied the effect of particle types on fiber melt spinning structure-properties, we are going to discuss this part in the next Chapter IV.

3.3.1. Fiber Spin Forming Morphology

PP control fibers looks crystal clear without adding filler particles, which tend to scatter light through the fibers with 5~20% of CaCO₃ (Figure 3-2). Based on the graph, we are standing on a pre-assumption that fibers are continuous structure with filler uniformly distributed throughout the length. Meanwhile, internal void appears in fibers. It is suspected that such open slit formed around cubic particles by elongating the polymer jet. Previous research by Liang and Zuiderduin has explained micromechanics of rigid particulate spheres embedded polymer composite, where define this phenomenon as particle debonding [6, 7]. Another possible reason to form voids is during spin-drawing of fibers from long cylindrical filament into very fine fibers, plastic deformation of polymer cause interfacial separation of filler particles. The initial separation at each pole of filler particles along tensile direction generates separation of particles from polymer [34]. Previous results also mentioned similar finding, and associate the flatten microvoids formation with drawing ratio in melt spinning of polyester [38].
Figure 3-2: Filler disperse uniformly inside of spinning fibers.

Table 3-2: Fiber Diameter of Melt Spinning of PP/CaCO₃ Fiber Samples:

<table>
<thead>
<tr>
<th>Sample ID Conc.-%</th>
<th>Filler Content (%)</th>
<th>Fiber Size (Denier)</th>
<th>Diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average</td>
<td>CV (%)</td>
</tr>
<tr>
<td>PP -500</td>
<td>0</td>
<td>9.9</td>
<td>10.3</td>
</tr>
<tr>
<td>Ca5-500</td>
<td>5</td>
<td>10.9</td>
<td>15.0</td>
</tr>
<tr>
<td>Ca20-500</td>
<td>20</td>
<td>13.8</td>
<td>19.0</td>
</tr>
<tr>
<td>PP -1250</td>
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<td>4.9</td>
<td>8.1</td>
</tr>
<tr>
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<td>9.0</td>
</tr>
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<td>4.6</td>
<td>9.7</td>
</tr>
<tr>
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<td>4.6</td>
<td>10.0</td>
</tr>
<tr>
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<td>5.0</td>
<td>15.3</td>
</tr>
<tr>
<td>PP -2000</td>
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<td>2.6</td>
<td>8.9</td>
</tr>
<tr>
<td>Ca5-2000</td>
<td>5</td>
<td>2.8</td>
<td>9.1</td>
</tr>
<tr>
<td>Ca10-2000</td>
<td>10</td>
<td>2.6</td>
<td>10.8</td>
</tr>
</tbody>
</table>
The average diameter of fiber increases with calcium carbonate loading concentration, theoretical diameter should be consistent at same spin speed because volumetric throughput is constant at 0.635 cc/hole/minute. As loading concentration varies from 5% to 20%, the diameter first increases from 26μm up to a larger diameter at 29μm with 5~10 wt. %, then recover back at 15~20%. Initial rise in fiber diameter reveal there is an expansion in fiber cross-sectional dimension, which may be caused inner porous structure coming from fiber spin-draw (Fig. 3-2). The CV (%) of fiber size incline up with filler concentration, heterogeneous polymer/filler material also related with standard deviation. The variation comes from the instability of drawing process, that spinning tension may not be distributed uniformly. For spin speed at 2000mpm, CV of fiber increases from 8% to 15.6% after loaded with filler. At faster spinning velocity, oriented crystallization change the mesomorph of polypropylene into monoclinic phase crystallites in fiber spin orientation as shown in Figure 3-5, drawing induced higher crystallization rate and improve the amorphous orientation in polypropylene chains. Fiber breakage occurs at 2000 mpm spinning speed, meaning loading more than 5% in fibers, the amorphous structure stretch to a more oriented extent and freeze after polymer crystallized, however without sufficient molecule relaxation due to the fillers restrict polymer viscoelastic flexibility. Using higher throughput (0.9 ghm) it allows us to fill more than 10% of CaCO₃ fillers into fibers, as shown in Figure 3-4. Polymer chains are imposed with more extension ability by giving bulk energy to amorphous molecules with higher entropy but less chain rigidity after freezing by quenching.
Figure 3-3: Calcium carbonate particle size distribution

Fiber shrinkage reflect extent of amorphous orientation develop in fiber drawing which temporarily settle down in fiber structure. Drawing induced molecular orientation forming into fold lamellae crystallites in some part, while adding filler impurities contribute more amorphous orientation, which means at same spinning velocity PP fibers has apparently lower bulk energy, so the crystallization kinetic energy is significantly motivated by shear stress \(^{[11, 27]}\). With higher crystallization rate, shrinkage decrease in a fast response to spinning velocity for PP fibers (Fig. 3-7). Different results were recorded that PP keep increasing heat relaxation with melt spinning velocity from 1000-3000 mpm, which is contradict to our results on PP fibers \(^{[12]}\). The reason for this might be the drawing PP fibers improved crystalline orientation so crystalline birefringence goes up with velocity. Another possible reason may come from higher heat treated temperature at 140°C that may result this temporary orientation in mesomorph to be relaxed, while lower down to 100°C may only affect the relaxation movement of amorphous orientation by coiling back inter-lamellae tie
molecules. More shrinkage of filled fibers is attributed to the random tie chain molecules which hinder shear-induced crystallization of fiber.

Figure 3-4: Fiber morphology produced at same spinning condition with 20~40 wt.% loading of GCC-FiberLink in Polypropylene fiber (a)~(d).

Surface morphology of fiber becomes roughened with filler particle. One reason associated with bumpy topography is the particle size distribution of fillers, as shown in Figure 3-3, it has an average size at 2.2μm, \( d_{75} \) at 4μm, top cut at largest 5% in total distribution account up to 12μm. So in mono-component fibers, these fillers dispersed around fiber surface tend to
cause surface unevenness, especially as fibers are stretched along fiber axis, polymer contract in the transverse direction due to its large poisson ratio. While calcium carbonate fillers can be regarded as rigid sphere which move along with polymer stretching by rheological stress, but also can be retarded by restricted deformability. This cause particle fillers protrude out in drawing process, especially at higher loading fraction when the polymer viscosity is apparently increased (Figure 3-6). The polymer cross-section dimension contracts in the spinning will cause phase separation from rigid particles, whereas any cluster of particles that cannot deform with polymer jet will stick outside of fibers and form surface roughness.

Figure 3-5: Spinning speed effect on mesomorph transform into α-monoclinic of polymer at 500 mpm, 1250 mpm and 2000 mpm.
Figure 3-6: Shear viscosity by shear wiping from low shear rate 20 s$^{-1}$ to 10,000 s$^{-1}$ at 230°C comparing with PP control fiber sample with 30% and 40% filled fiber samples using capillary rheometer.
3.3.1.1. Crystalline Structure

Mineral fillers change the diffraction peaks of polypropylene and induce separated peak at calcium carbonate distinct crystallography. Comparing with PP fiber, there are peaks located at $2\theta = 30^\circ$ and $37^\circ$, which was also found to be associated with calcium carbonate fillers \cite{7}. Previous result showed that the calcite has the major characteristic peaks at $2\theta =29.0^\circ$ and $39.4^\circ$ when loaded more than 5\% \cite{13}. Peak at $30^\circ$ has a distinct intensity and represent the existing of calcite with large rhombohedra phase. Based on Scherer equation 3, the crystal size at $(1 0 4)$ increases with loading concentration from 20\% to 30\%, but reduces at 40\%. The calcite crystal cleaves along $(1 0 4)$ planes easily, as shown in morphology of GCC.
particles in Figure 3-9. While the crystal size at (1 1 0) enlarging concentration from 20% to 40% (Table 3-3).

Fiber develops α polypropylene after loading with CaCO₃, similar as the shear stress induced monoclinic in Figure 3-8, PP fibers mesomorph crystalline structure has transformed, appear with three sharp peaks at 2θ = 15°, 18° and 19.4°. The results observe peak intensity become less pronounced with more filler loading concentration as shown in Figure 3-8, which is in consistent with previous results by Supaphol et al. [13]. The inter lamellae d-spacing (Å) at varying loading of CaCO₃ keep decreasing at each diffraction peak (0 4 0) and (1 3 0) as shown in Table 3-3, indicated packing density of folded chains increases in shish-kebob elongated platelet crystallites. Nevertheless polypropylene is still keeping the (1 1 0) plane at the closest spacing during drawing, meaning the flow oriented molecules seeks a lower bulk energy level by excluding out any impurities in the material. This plane represents the parallel long chain molecules align along spinning stress, form by unfolding less perfect small crystallites into highly oriented crystalline structure [8, 20]. Because fibers are highly-drawn on godets, those lamellae plane keep thickening in a*-axis and b*-axis in the vertical plane relative to c*-axis direction. Large portion of inorganic particles are mainly wrapped up within amorphous molecules, or favorably inhabited at less perfect small crystallites at (0 4 0) and (1 3 0) planes, resulting in d-spacing in this two planes narrowed. Furthermore, we can use the mechanism of epitaxial growth to explain this phenomenon at intra-lamellae structure, specifically the heterogeneous calcite absorb polypropylene free tie molecules and assist its folding vertically onto the planes [15, 40].
Figure 3-8: X-ray diffraction patterns compare fibers containing different amount (20–40%).
Table 3-3: WAXD Diffraction Pattern Information Lamellae d-Spacing and Crystal Size:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Peak Position</th>
<th>2θ(º)</th>
<th>d (Å)</th>
<th>Crystal Size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-2000</td>
<td>(1 1 0)</td>
<td>15.54</td>
<td>5.70</td>
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<tr>
<td></td>
<td>(0 4 0)</td>
<td>17.55</td>
<td>5.03</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>(1 3 0)</td>
<td>19.36</td>
<td>4.58</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>(1 1 1)</td>
<td>22.04</td>
<td>4.03</td>
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</tr>
<tr>
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<td>71</td>
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<tr>
<td></td>
<td>(1 3 0)</td>
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<td>69</td>
</tr>
<tr>
<td></td>
<td>(1 0 4)</td>
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<td>379</td>
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<tr>
<td></td>
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<td>(1 1 0)</td>
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</tr>
<tr>
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<td>2.92</td>
<td>361</td>
</tr>
<tr>
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<td>(1 1 0)</td>
<td>37.16</td>
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<td>370</td>
</tr>
</tbody>
</table>

Figure 3-9: Calcite cleavage form of crystals of GCC powder SEM picture.
3.3.1.2. Melting and Cooling Behaviors

We investigate on melting behavior of fiber polymer materials (Figure 3-9). There is one endothermic peak as shown in Figure 3-9 without much variation in the peak position after loaded with calcium carbonate fillers. According to the melting temperature shown in Table 3-5, only at 500mpm increases filler fraction cause melting temperature decreases by 2-3˚C as polymer entropy $\Delta S$ is related to amount of fillers which randomize polymer. This is because at higher spinning velocity, DSC endothermic peaks of a PP fiber without filler exhibits double melting peaks while as filler loading level raises up from 20% to 40% (Figure 3-10), the melting range narrowed into single melting peak. The narrowed endothermic peak range indicated reduction in crystal size population in fiber crystalline.$^{[14]}$
From Figure 3-10 (a), higher loading concentration promoted the fast melting rate to reach up to maximum heat flow in the system. However the total heat flow reduces as polymer material is replaced by part of inorganic material, so the heat fusion $\Delta H$ decreases with loading concentration as expected.

Table 3-4: Melting Temperatures and Crystallinity of CaCO$_3$/PP Fibers:

<table>
<thead>
<tr>
<th></th>
<th>Conc. (wt.%)</th>
<th>$T_{\text{on-set}}$ (°C)</th>
<th>Peak ($T_m$)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-1250</td>
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<td>154.6</td>
<td>165.3</td>
<td>53.2</td>
</tr>
<tr>
<td>Ca5-1250</td>
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<td>154.8</td>
<td>166.6</td>
<td>49.2</td>
</tr>
<tr>
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<td>165.1</td>
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</tr>
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<td>165.1</td>
<td>52.4</td>
</tr>
<tr>
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<td>154.6</td>
<td>164.9</td>
<td>51.0</td>
</tr>
<tr>
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<td>55.8</td>
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<td>Ca5-500</td>
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<td>152.6</td>
<td>162.6</td>
<td>47.2</td>
</tr>
<tr>
<td>PP-2000</td>
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<td>156.8</td>
<td>160.3</td>
<td>49.6</td>
</tr>
<tr>
<td>Ca5-2000</td>
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<td>156.6</td>
<td>160.4</td>
<td>48.3</td>
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<td>Ca10-2000</td>
<td>10</td>
<td>156.8</td>
<td>161.5</td>
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<tr>
<td>PP-2000A*</td>
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<td>161.1</td>
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<td>Ca40-2000B*</td>
<td>40</td>
<td>154.3</td>
<td>165.0</td>
<td>55.4</td>
</tr>
</tbody>
</table>

* A denote DR=1, B represents DR=2, both are produced with 1.155 cc/hole/min throughput.

Fiber crystallinity, as listed in Table 3-4, reduces after loaded with CaCO$_3$ up to 10%, it shows that crystallinity is related to throughput, spin speed and draw ratio since under high shear stress for a longer residence time crystallization would be sufficient and crystallinity is
higher. The polymer at lower throughput (0.635cc/hole/min) can induce a high crystallization rate, but as polymer jet cross-sectional is much smaller than fibers produced at 1.155cc/hole/min, so the fast cooling will result into less time during the crystallization. However, crystallinity of melt spun fibers based on quenching of PP is barely increased by (Table 3-4).

Although filler particles add more impurities into heterogeneous nucleating polypropylene, however, from only a limited 2-3°C improvement on crystallization temperature (T_c), mean that the nucleation effect is barely existed in PP melt spinning (Table 3-4). Similar result was noticed that adding stearic acid coated calcium carbonate into iPP the non-isothermal crystallization is unaffected or at not as distinct as talc filled polypropylene[^13^]. This result on T_c of PP is much higher than the results recorded by Fujiyama and Wakino [^37^], maybe due to different molecule weight between two cases. We also find similar results shown the filler concentration dependence on T_c is risen up from 5% to 20 wt.% in Fujiyama’s results, but the increment is more prominent in their work because they are using PP in injection molding that cooling time is much longer than PP fiber spinning. Previous results showed that there was nucleating effect of 0.5 wt. % talc in polypropylene when larger amount of nucleation sites may distinctively appear in the system, but its size reduction is mainly caused by impinging as they keep growing [^15^, ^27^]. However, calcite is not as active as talc in nucleating efficiency, 10 wt.% chalk cannot compare to 0.5 wt.% of talc in their α – nucleating capability, which refers to the ability to transform β – polypropylene into polymorphic crystalline [^16^-^18^]. Due to heterogeneous nuclei in polypropylene melt could dominate over
any nucleating ability from inorganic impurity, especially in a short residence time. It is hypothesized fillers will actually hinder polymer lamellae compaction to achieve highly crystallized phases. The crystallites populations may be hard to form densely compacted lamellae plane, resulting in small crystal growing on a closed tightly packed space where involving a large fraction of loading.

Table 3-5: Crystallization Temperature of CaCO₃ Fibers with Different Filler Loading Levels. Spinning Speed was 1250m/min:

<table>
<thead>
<tr>
<th>CaCO₃ Conc. (%)</th>
<th>Onset T&lt;sub&gt;c&lt;/sub&gt; (°C)</th>
<th>Peak T&lt;sub&gt;c&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>122.0</td>
<td>118.1</td>
</tr>
<tr>
<td>5</td>
<td>124.0</td>
<td>120.5</td>
</tr>
<tr>
<td>10</td>
<td>124.4</td>
<td>121.1</td>
</tr>
<tr>
<td>15</td>
<td>124.7</td>
<td>121.3</td>
</tr>
<tr>
<td>20</td>
<td>124.3</td>
<td>121.2</td>
</tr>
</tbody>
</table>
Figure 3-11: Melting curves of 2000mpm fibers (a) and 1250mpm fibers (b) with CaCO₃ filler concentration PP, 20%, 30%, 40%.

3.3.2. Tensile Properties

Index in single fiber tensile properties include breaking stress defined as tenacity, breaking strain, secant modulus at 5% and toughness. Stress represent in a normalized strength in different fiber size (unit: denier), which is the denominator to the force (unit: gf). Toughness is calculated from amount of energy to result into fiber breakage. Modulus is the ratio of stress...
over the 5% strain, which is an important index to describe fiber material elasticity before it stretched over yielding point. Our first finding is adding 5~20% of inorganic fillers –GCC reduce the tenacity and toughness. Modulus keeps at consistent value only slightly reduced. Polymer orientation determine the modulus levels, does not matter even if polypropylene developed amorphous orientation dominant in fibers. Strain at break reflect the extent of polymer molecule oriented during spinning, higher strain means fibers are less oriented. In tensile behavior, fiber breaks when folded planes are unfolded and pulled out of crystalline phase. The involved inorganic fillers have very little impact on fiber strain at breaking. Therefore, tenacity is considered as the main attributor to lower toughness.

We can interpret fiber tensile behavior from its stress-strain curves from Figure 3-13 (a, b), firstly the main difference for PP and fibers containing with fillers is the upper section at the end of plastic deformation region, that PP chains can develop more potential in high stress and strain. Calcium carbonate fillers did not strengthen fibers, but shorten plastic deformation extent which means during unfolding those crystalline molecular chains, the dispersed filler particles assist in gliding of long polypropylene chains. Thereafter, loose structure of lamellae keep elongating to the extent where stress rupture the chain molecules and cause transverse breaking. Energy of working under the curves are decreasing as strain at breaking apparently drops above 10% (Figure 3-13 (a)), and tenacity deteriorate with higher filler amount in fibers (Figure 3-13 (b)). Another unexpected finding is for the deformation curve reshape at one of concentration –10%, specifically, a convex shape plastic deformation occurs following shorter period of reorationation. This phenomenon occurs for this sample at least for five times out of
ten specimens from Ca10-1250 as this representative curve does in Figure 3-13. Loading 10% GCC fillers in polypropylene may hinder crystal growth from embryo that initialize nucleating, however with 3 vol. % (10wt.%) of impurity (inorganic) the polymer behave like differentiating and protecting their intrinsic nucleating sites rather than starting nucleating from other impurities. In the competitive recognition of polymeric nuclei and inorganic nucleating sites, the time left for crystal growing may not be long enough. Therefore, amorphous volume fraction increases at 10% of loading. As a result, the amorphous orientation should dominate over fiber structure that its tensile behaves as toughening in the beginning of plastic deformation. We would expect that crystalline structure under heterogeneous nucleating result into much uniform and small crystal growing. As Figure 3-12 (b) shows 20% to 30% of filler loading to polypropylene can effectively increase the heterogeneous of polymer system, so that during following quenching, fast cooling form smaller lamellae size. The fiber tensile will behave like a conjunctive chain linked by lamellae plate-let, that increasing strain will respond to a very steady increment on the stress.
Figure 3-12: Single fiber tensile properties with 2.5~20% of GCC fillers.
Next challenge is on varying concentration of calcium carbonate fillers above 20%, equal to volume fraction 6.4 vol.%, 10 vol.% and 15 vol.% to 20 wt.%, 30 wt.% and 40wt.%, respectively. It is suspected as filler concentration reach to its upper limit the structure formation in melt spinning become much more difficult for several reasons. One is fiber strength, as shown in Figure 3-13 (b), the elongation become longer than PP control fibers then follow by a sudden reduction from higher breaking strain of 270% to 170%. This means the fiber structure must undergo a dramatic deterioration at this level. Structural defects in fiber structure are related with filler agglomeration, resulting in weak adhesion at the interface between filler and polymer, as shown in Figure 3-18. Fiber breaking at defects caused by agglomeration can be explained by weak link theory. The fiber strength is equal to the weakest link strength, referring as defects in fiber semi-crystalline structure forming as crystallization of lamellae mismatch in chain folding or cavity in the amorphous region. More likely those defects after incorporated with fillers are micro voids in amorphous due to dissimilarity of chemical property of inorganic CaCO$_3$ with polymer matrix.

3.3.2.1. Weak Link Theory

We have addressed the issue of weaken fiber structure after being loaded with inorganic phases, which is somehow in our expectation, however, decline in fiber tenacity did not follow in a linear or exponential trend, as shown in Figure 3-12. Some evidence supported the function of fillers in improving elastic modulus and yield stress (Figure 3-13). Because as fiber diameter become smaller, fibers tend to form more weak link points at structural defects where CaCO$_3$ with large than 5μm of particle size which is almost quarter of fiber diameter. Based on weak link theory, the strength of one fiber or yarn is equal to the lowest strength
Figure 3-13: Fiber stress-strain curves at filler concentration from 5% to 20% as shown in (a), and for loading concentration raise up to 20~40% (b).

linking in the fiber. Such weak spots as to CaCO₃ contained fibers can be regarded as any cross-sectional linkage in fibers that form a potential craze initiator at organic/inorganic interphase. Based on particle size distribution of GCC-FiberLink shown in Figure 3-3, there is top cut that d₀₉₈ > 10μm, d₁₇₅ at 4μm and d₅₀ with 2.24μm. Stress could propagate from a pin
crack around particulate periphery region, and expand radially to adjacent semi-crystalline region\[7, 15\]. This eventually rupture fiber sample when drawing force exceed the weak link strength.

The Weibull distribution characterizes the structural defects distributed throughout fiber unit segment \(l\), and \(n_\sigma\) represent the average defect index defined as:

\[
n_\sigma = \frac{N}{l}
\]

where \(N\) is the total number of defects in a length \(l\) of fiber segment. So the survival possibility of a fiber with length \(L = n \times l\) is denoted as \(P_s\):

\[
P_s = \prod_{\xi=1}^{\xi=n}(1 - P_{f_\xi}) = \prod(1 - P_{x<\bar{x}_\xi})
\]

where \(x\) is the strength of fiber containing a number of structural defects throughout the length \(l\), where \(x_\xi\) is varied from \(\xi = 1\) to \(\xi = n\), where \(n\) is the total number of segments in a fiber with gauge length \(L\) in the testing. Then the average segment over \(n\) count is \(\bar{x}_\xi\).

When any segment has less than average \(\bar{x}_\xi\), indicating this segment must be regarded as a weak link composing the whole long fibers. Also for number of segments in a bundle, a ranking from lowest to the highest strength is a possible way to find out the cumulative probability of failure.

\[
\Delta l_\xi \to 0, \quad P_{f_\xi} \to 0
\]

\[99\]
where $l = \Delta l_1 + \Delta l_2 + \Delta l_3 + \cdots + \Delta l_n$, based on the assumption that the distribution of defects in cylindrical fiber is uniform, so the failure possibility is related with the average defect index $n_{\sigma}$. As inorganic filler particle gain its fraction in fibers, $n_{\sigma}$ will increase which means distribution in unit segment of fibers contain with higher concentration will likely to encounter with greater number of fatal failure. Gauge length at specific $l$ will result into number of defects $N = l \times n_{\sigma}$. Zero gauge length gives a polymer a perfect condition to exclude out factors that may result in material breaking. Increasing gauge length it should be corresponded with larger polymer strength theoretically. But in the real fiber tensile property, particulate fillers do not have perfect uniform dispersion, sometimes come across with aggregations and aggregation (Fig. 3-14). So fiber strength is hard to have consistently monotonic decreasing with gauge length. There is a likelihood of severe structural defects have come up at same probability in a gauge length range above 1.5 inch, as shown in the result of Figure 3-14 (CaCO$_3$ 20%). From y-axis interception with regression linear, the zero gauge length is estimated which takes off the effect of gauge length, so that mainly focus on the intrinsic property of fiber material. The $b$ value for PP fiber, and 10% and 20% CaCO$_3$ (GCC) contained within fibers are respectively calculated as 370 MPa, 327 MPa and 229 MPa, with at least 30% loss after loaded with inorganic fillers. Based on previous assumption

$$e^{-P_{f\xi}} \rightarrow 1 - P_{f\xi}$$  

$$P_s = e^{-P_{f1}} \cdot e^{-P_{f2}} \cdot e^{-P_{f3}} \cdots \cdot e^{-P_{fn}} = e^{-(\Delta l_1 \cdot n_{\sigma} + \Delta l_2 \cdot n_{\sigma} + \cdots + \Delta l_n \cdot n_{\sigma})}$$  

$$P_s = e^{-n_{\sigma} \cdot l}$$
that filler particle dispersion is uniform throughout fiber length, so volume fraction at each section linking in fibers is constant at $\phi_u$. We can denote the inter-particle spacing at $\phi_u$ is $d$, which is apparently increasing with more amount of loading. Those particles may be packed tightly in the fibers cross-sectional regions, if any loose packing, there can result in a lack of valid strength transfer linkage among the stack. At wt.% = 20%, the $b$ in linear regression plot has dropped expectedly, but unexpectedly is from its decrement rate from 10% to 20%. From the gauge length effect, we suspect that fillers start to granule into clusters accumulating at fiber cross-sectional spots randomly. That possibility of any severe agglomerations results into breakage strength lowering down.

At unit volume of fiber, loading concentration determine the number of weak interfacial conjunction that determine the segment strength. While from the gauge length effect as shown in Figure 3-15, the linear regression overlay define material properties that under a controlled length. PP fiber as well as CaCO$_3$ filled at 10% has declining rate increase from -17.29 to -21.28, which means length scale weak links distribution in filled fibers cause more severe breaking mechanism. This could be due to the micro-voids forming at 10% CaCO$_3$ loaded within fibers, that significantly reduce fiber crystalline orientation in fibers. But as keep increased to 20 wt.%, the slope deviate from the other two samples, with tendency to be constant in length range from 0.5 inch to 1.5 inch. The reason for less dependence on gauge length is that probability of weak links occurred throughout a 1.5 inch segment is equal to a larger gauge length of segment. Severe flaws distributed in length L (1.5-2.5inch) reach to equilibrium also suggest a much uniform fill/polymer dispersive interaction in the fibers.
Figure 3-14: Filler agglomeration at 40% GCC, compare spin-draw ratio A-1:1 1850/1900/2000 (a) with B-1:2 900/1800/2000 (b).

Because of structural irregularity with particles, the strength testing have a CV around 5~10% for fiber strength, and the variation comes out larger at higher gauge length scale (Figure 3-15). This is due to probability uncertainty in the distribution of defects that may occur along any segment period of fibers, especially in longer filament spinning. Weibull distribution has been modified into different formats in tensile strength analysis. If the fiber strength ($f^*$) is
defined as the peak load over the fiber cross-section area at the maximum extension, we may consider a cumulative function of tensile strength \( Pr\{x_\xi < f^*\} = G_i(f^*) \). This function should be monotonic increasing with \( f^* \), we also interpret the occurrence of fiber specimen with strength equal or lower than a specific stress ranked among \( n \geq 20 \) as the probability \( Pr\{x_\xi < f^*\} \). Naito et al. gives a definition of cumulative probability of failure, \( P_F \) as equation (12)\(^{[19]}\):

\[
P_F = \frac{i}{n+1}
\]

where \( i \) is the number of fibers that have lower than strength level \( f^* \) and \( n \) is the total number of fibers tested. Then we can apply our experimental results into a statistical distribution known as Weibull distribution as:

\[
P_F = 1 - \exp \left[ -\frac{L}{L_0} \left( \frac{\sigma_f}{\sigma_0} \right)^m \right]
\]

where \( L \) is applied gauge length, which is 1 inch for the standard Q-test in our following experiment. \( L_0 \) is a reference gauge length. We are using 1 inch continuously, if so, use \( \left( \frac{\sigma_f}{\sigma_0} \right)^m \) denote the ratio between tensile strength \( \sigma_f \) of fibers with length \( L \) to the characteristic stress. And this equation can be further written as:

\[
\ln \left( \ln \left[ \frac{1}{1-P_F} \right] \right) = m_f \ln(\sigma_f) - m_f \ln \left( \sigma_0 \left( \frac{L_0}{L} \right)^{\frac{1}{m_f}} \right)
\]

\(14\)
where $m_f$ is Weibull modulus, can be obtained by linear regression from a Weibull plot of equation (14) of $\ln \left( \frac{1}{1-P_F} \right)$ vs. $\ln(\sigma_f)$ \cite{19}. As shown in Figure 3-16, it is plotted four different calcium carbonate loading concentrations from PP with 0%, 20%, 30% and 40% with a Weibull plot function based on equation (14). Slope of each samples in its plot gives us an estimation of Weibull modulus $m_f$, which means an unit increment in x-axis results into a corresponding increase in $\ln \left( \frac{1}{1-P_F} \right)$. Apparently, this is a function of $P_F$, and the failure probability monotonically increases with $\ln \left( \frac{1}{1-P_F} \right)$. Weibull cumulative function defines that the failure probability is equal to 1 when the tensile strength is larger than any other lower strength, which testing in this case include 25 specimens of fibers. Then as decrease the $\ln(\sigma_f)$ the failure probability function $P_F$ correspondingly reduce since several specimens have exceeded this tensile strength level at $\sigma_f$. We may also regard these specimen connect one by one on head-to-tail, forming a long filament with a certain distribution of strength in each segment. The slope, or the modulus, represents the distribution density of segmental pieces that positively increases with $\ln(\sigma_f)$. When tenacity increases, those number of fibers fall below the strength level will be increasing from $n_\sigma$ to $n_{\sigma+\Delta\sigma}$, with the $\Delta\sigma$ represents the number of fibers with strength within range $(\sigma, \sigma + \Delta\sigma)$. Varying $\varphi\%$ in sample must contribute to different probability density in a Weibull distribution. Higher modulus $m_f$ indicates strength distribution is uniform through the whole samples. It reflects a close physical property from one specimen to the other, although a variation in strength comes with spinning, a relative closer distribution will increase the ratio between $\Delta n$ to $\Delta\sigma$. This means the probability of one segment encountering with structural
defects will be influenced by its adjacent segments, which has $\Delta \sigma_1, \Delta \sigma_2, \ldots$ of finite element in strength variation. After loading more than 20 wt. % of CaCO$_3$ fillers, we have found fiber tenacity show a significant smaller CV (%) at 30 wt. %. So from increasing slope of $m_f$ for varying of concentration from 20% to 30%, we would expect more stuffing with inorganic phase weaken fiber strength though, at 30% the tightly packing enhance the viscoelastic continuity in response to external tensile stress. While compare to 20% which possess a lower $(\Delta n/\Delta \sigma)$ ratio at high strength, 30% of filler in the fibers perform rather uniform and higher Weibull modulus in the whole range. Furthermore, above 30%, as indicated in Figure 3-16 crossing points, the Weibull modulus reduce sharply which means structure of fibers deteriorate severely at 40% and the distribution of breaking strength become widely distributed for responded failure function $\ln \left( \frac{1}{1-p_F} \right)$. And such weakened fiber structure is due to irregular filler particle size that increase the chance of unavoidable agglomerations, surrounded by the voids in polymer matrix, that cause a large CV(%) and low Weibull modulus in its tensile behavior (Figure 3-18 (a) and Table 3-6).
Figure 3-15: Gauge length of single fiber tensile strength from 0.5 inch to 2.5 inch of melt spun fiber samples: PP control, 10% GCC-FiberLink loaded fibers and 20% loaded fibers.

Table 3-6: Weibull Plot based in eq. 14 of Fiber Tensile Strength Filled with Varying Amount of Calcium Carbonate Fillers:

<table>
<thead>
<tr>
<th>Filler Concentration</th>
<th>$\bar{\sigma}_f$ (MPa)</th>
<th>CV (%)</th>
<th>$m_f$</th>
<th>$y=ax+b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>257.2</td>
<td>10.3</td>
<td>13.201</td>
<td>$y=13.201x-70.619$</td>
</tr>
<tr>
<td>20%</td>
<td>209.8</td>
<td>8.6</td>
<td>12.549</td>
<td>$y=12.549x-67.577$</td>
</tr>
<tr>
<td>30%</td>
<td>172.5</td>
<td>7.36</td>
<td>14.587</td>
<td>$y=14.587x-75.623$</td>
</tr>
<tr>
<td>40%</td>
<td>134.8</td>
<td>11.1</td>
<td>9.6366</td>
<td>$y=9.6366x-47.731$</td>
</tr>
</tbody>
</table>
Figure 3-16: Weibull plots for melt spun fibers PP and filled with 20~40% spun from DR=1:2 at 0.9 ghm throughput.

Fiber tensile behavior at two spin-draw conditions denoted as A (DR=1:1) and B (DR=1:2) include in a set of fiber tensile properties in Figure 3-17. With 15 mm/min extension rate, the draw ratio 1:1 (1850/1900/2000) sample could be restricted in its extension over the yield point of stress-strain curve. This could be due to less oriented polymer chains in the spinning, so during the subsequent extension, force can pull apart those random coiled polymer chains under lower stress. While when given a spinline draw ratio (DR=1:2) to fibers, those single
fiber tensile behave like a very intense drawing after fibers are solidified on several godets (950/1900/2000). It is end up with less strain at breaking; because of fibers develop more alignment in previous spinning already. But from much higher tenacity at 1:2 compared to 1:1, we understand that drawing start from 950 mpm in feed roll, will impose a longer quenching duration in the spinning, therefore, we would expect molecular orientation have enough time to transform amorphous phase into lamellae crystallites. Using a velocity ratio at godet drawing of fibers provides a stable spinning to polypropylene fibers, especially when loaded with more than 30 wt.% of calcium carbonate fillers. Since over loading hinder the viscoelasticity respond in polymer deformation, a reduction in feed roll speed to increase draw ratio to 1:2 allow for an elongated period of time in the phase transformation in fiber spinline.

Draw ratio as included in Figure 3-17 further show a relationship between filler concentration with two draw ratio levels (1:1 and 1:2). High draw ratio increases the tenacity and reduces percent of strain at breaking. Fiber modulus is associated with the chain stiffness in the initial deformation of elastic region, which is sensitive to filler loading concentration. Modulus increases after changing draw ratio from 1:1 to 1:2, meaning that fibers orient better by drawing to develop chain stiffness. Especially below 20%, 2000 mpm at 1:1 drawing impose an intense chain alignment and higher modulus. But above 20%, we see modulus is dramatically dropping down even below draw ratio 1:2 as shown in Figure 3-17. This means fiber structure is severely weakened represent in either initial elastic deformation or post yield point plastic deformation, resulting in less orientation and insufficient polymer
crystalline compaction, so strain at breaking is increasing compared to draw ratio 1:2. Loading of 30% of CaCO₃ declined fiber shrinkage from 1250 mpm to 1500 mpm (Fig. 3-6). The upgrade from 30% to 40% has caused severe deterioration in single fiber tensile as shown in Figure 3-15, with a substantial partial breaking down of polypropylene chain molecules which resulting in reduction in Weibull modulus $m_F$. While at 2000 mpm, 30% of loading persisted in crystalline orientation at same level as 1500 mpm that even higher speed cannot yield with more chain relaxation (Fig. 3-7). This again indicated 30 weight fraction of calcium carbonate fillers can still promote the crystallization orientation under shear stress in the polymer extrusion. While loading more than 30 wt. %, either by lower down spinning speed to approve for sufficient time of crystallization, or by increase up draw ratio from 1:1 to 1:2, will contribute to improving fiber orientating and forming into uniform structure.
Figure 3-17: Filler concentration vs. draw ratio impact on single fiber tensile properties for fibers spinning at 2000 mpm and throughput = 0.9 gram per hole per min.
Figure 3-18: Defects of filler particles in fiber formation: (a) weak adhesion, filler separation from polymer matrix; (b) agglomeration of small particles.

As to spinning structure form at varying of take-up speed, which is referred as relax roll speed or wind up speed, has shown from 1250 mpm to 2000 mpm the spinline tension can still withstand high loading concentration up to 30~40%. As shown in Figure 3-7, boiling water shrinkage reflected how much oriented molecular chains transform into highly compacted crystalline orientation. Stress induced crystallization form a regular spinning formation of fibers, increasing the speed for polypropylene has shown a decreased boiling water shrinkage with spinning speed. This means polymer chain structures will develop crystalline orientation in the fiber formation. Because shrinkage comes from chain relaxation in the boiling water, chain orientation form in its temporary amorphous orientation which tend to recoil upon heating. Increasing spinning speed impose larger spinline stress to polypropylene fibers, however, in existence of inorganic filler particles the shrinkage correlation to speed is apparently higher than polypropylene pure fibers. The heterogeneous
system filled with calcium carbonate hinder crystalline orientation which resulted into more boiling water shrinkage compared to polypropylene. Furthermore, shrinkage either level off for 30% of filler loading or level up for 40% of filler loading as shown in Figure 3-7. This phenomenon reveals that increasing spinning speed brings processing difficulty because of lacking sufficient time to allow the growth of crystal phase into highly oriented morphology. The addition of calcium carbonate on one side has nucleation effect to trigger the crystal growth. Talc and mica filled polymer system orientation index in crystalline and amorphous regions become much different from neat polymer at low shear rate, however, increasing shear stress would lower the difference in orientation especially with alignment of filler particles [20]. They also indicate heterogeneous nuclei of filler particles usually occur at quiescent condition, but there is less nucleation effect at high shear stress in melt spinning as homogeneous nuclei of polypropylene melt mainly dominated in the primary nucleating [21].

3.3.3. Discussion on Viscosity

Polymer melt contained filler particles have higher melt viscosity and low melt elasticity [22, 23], and inevitably retard the polymer chain coil-stretch property in polymer extrusion. Shear stress imposed on a polymer/filler blend primarily align polymer by melt extrusion from capillary. The morphology of fibers become unstable, and the reason that fiber property highly depend on filler loading is because the melt viscosity dominate over the polymer extrusion and structure solidification. Therefore, we investigate melt viscosity at different loading of calcium carbonate fillers to predict polymer and filler interaction during the melt extruding. As shown in Figure 3-6, there is shear thinning behavior of polypropylene. More
internal voids are probably related with high viscosity of polymer melt because lack of chain flexibility to wet those particles. Also lower fiber tenacity is related to internal agglomerates as shown in Fig. 3-18, the affinity between such clusters should be sheared apart by polymer flow. However, with high viscosity it hinders the polymer molecules from ease of alignment with shear direction, leaving with unaffected polymer coil that is inclusive with fillers agglomerations. Reducing the loading concentration will give polymer relative flexible chain mobility to dispersion fillers outside capillary without much irregular clusters forming on flow jet. Generally in capillary of spinneret under throughput 0.7~0.8 cc/hole/minute, the pressure will generate shear rate around 700~1000 s$^{-1}$. Therefore, the viscosity difference between pure PP melt to 40% filled polypropylene is within 30 poise range. As the rheological behavior of polymer material is defined by the spin extensional viscosity, in equation (15).

$$
\eta_{es} = \frac{\sigma_{zz} - \sigma_{rr}}{\dot{\varepsilon}}
$$

(15)

Where $\sigma_{zz} - \sigma_{rr}$ is the tensile stress within the fiber ($\sigma_{zz}$ and $\sigma_{rr}$ are the normal stress on longitudinal and radius direction). In fiber melt spinning, force balance on melt spinning follows:

$$
F_{ext} = F_r(x) = F_{rheo}(0) + F_{surface} + F_{inertial} + F_{friction} - F_{grav}
$$

(16)

$F_{rheo}(0)$ is the rheological force outside of spinneret capillary in the elongational flow. Since the elongation strain rate is increasing in fiber spinning, so strength impose on unit area of fiber is based on the equation, considering about the reduced fiber diameter $R(x)$. 

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Spinline stress increases with take up speed from 1250 mpm to 2000 mpm. Nuclei start from polypropylene embryo as polymer cool down, at the same time, those calcium carbonate mineral fillers form platform in the lamellae crystal growing. Our results showed that WAXD diffraction patterns develop a monoclinic polypropylene after being embedded with filler particles. But as filler loading increases, the inter particle spacing get closer for a less perfection crystalline diffraction peak as intensity drops from 20% to 40% (Figure 3-8). Fillers excluded outside the crystalline boundary could carry irregular voids in that amorphous region. These are closely related with spacing in a limited volume in fibers spinning outside of the spinneret. Fiber crystallinity decreases with concentration, but drawing develop a higher crystallinity (Table 3-4). Addition of CaCO$_3$ to polymer melt reduces the viscoelasticity that if spinnability is targeted for higher loading concentration, a drawing is necessary to improve the fiber strength as well as molecular orientation.

Based on the study of Zoukrami et al., the elongational viscosity of calcium carbonate filled low density polyethylene does not correlate with filler loading concentration $^{[25]}$. Based on our results in shear viscosity difference between $\Delta \eta_s$, $\dot{\varepsilon} = 10000 = \eta_s, \phi = 0 - \eta_s, \phi = 0.4 = 60$ poise (Fig. 3-6), then elongational viscosity $\Delta \eta_{es} = 3\Delta \eta_s = 180$ poise $= 18$ Pa $\cdot$ s $= 18000$ Pa of tensile stress difference ($\sigma_{zz} - \sigma_{rr}$) between PP fiber and CaCO$_3$ filled at 40% at 1000s$^{-1}$. The elongational viscosity is assumed to be temperature dependent accordingly to the Arrhenius law:

$$F_{rheo}(x) = \eta_{es} \dot{\varepsilon}(x) \pi R^2(x)$$ (17)
\[ \eta_{es}(\dot{\varepsilon}, \theta) = \eta_{es}(\dot{\varepsilon}, \theta_0) \exp[B(1/\theta - 1/\theta_0)] \]  

(17)

where B is a material constant coming from the experiment. Since quenching of fibers cause polymer solidification, so the viscosity should be related to the position leaving from the spinneret holes. While compare to 20\%, loaded with 40 wt. \% of calcium carbonate fillers also increases shear viscosity compared to PP polymer, however, at certain temperature range (220~250°C) loaded with more fillers than 20\% will not definitely bring a sharp increase in viscosity like 220, 225, and 235°C, which even reduce the viscosity level than 20\%. More interestingly, although 230°C is a transition of melt rheology of polypropylene as well as for 20 wt. \% filler contained sample, at which point will shear viscosity significant reduce compare to 225 °C. B value in Arrhenius equation (17) for PP and 20 wt. \% filled sample is 5525 and 5299, while for 40 wt. \% the material constant reduce its value down to 1233. This value may represent the retardant from more filler loading particles that hinder response of polymer chain molecules to thermal energy, specifically the conformation relaxation of polypropylene lack enough kinetic energy reaching to higher enthalpy level unless continuously increasing up system temperature.
3.4. CONCLUSION AND SUMMARY

Adding calcium carbonate fillers into polypropylene, the structure and properties of PP fibers have changed with loading of fillers. GCC FiberLink (with 1.5% stearic acid coated particles) with average size 2.2μm and top cut above 10μm was melt spun into polypropylene fibers. Although there are interfacial defects such as voids and clusters at higher loading, fiber structure still possess with rather uniform dispersion with filler particles. Meanwhile, at higher loading 20~40 wt. surface of fibers get rougher and agglomeration induced weak fiber structure causes fiber tenacity decreases. Based on our analysis, the spin-draw ratio effect on the highly filled polymer material represents in fiber molecular chain orientation, as drawing
impose crystalline orientation of fibers also avoid the structure deterioration at high loading fraction. To avoid the bumpiness on fiber surface, drawing fibers by at least 1:2 draw ratio will impose a better fiber formation as to 40% of loading concentration. Because there will be less draw force impose at the section before fiber solidify which help polymer row nuclei respond to the extensional force.

At same spinning condition, lower fiber tensile properties represent increasing amount probability of severe defects in unit length of fibers. The zero gauge length strength is following the concentration dependence, as material intrinsic structure is weakened. However, at 20% of loading (Fig. 3-14) the gauge length is less dominant in lowering the fiber strength due to the fact that weak band already control the weakest link in a finite volume of fibers. Fiber crystalline structure for fibers develops mono-clinic from mesomorph with crystal size enlarged. Melting behavior of filler contained polymers also respond to a narrow endothermic peak from DSC. Without much nucleating from inorganic CaCO₃ particles, nevertheless, narrow the crystal size population in polypropylene fibers attribute to densely particle packing affect the secondary crystallization of polymer in time scale. However, from constant on-set melting temperature at lower loading concentration, in together with same 2θ in diffraction patter, we conclude that fillers did not induce primary nucleation to polypropylene. Most likely, these fillers stay in the amorphous, hinder the development of crystalline orientation in fiber formation. In the end, further increase up to 40%, polymer jet may encounter with higher elongational viscosity, especially at lower shear rate range.
REFERENCES


32. McCormack AL. Film formed of blend of polyolefin and filler and fibrous polyolefin nonwoven web bonded directly to film to form a laminate. 1997.


CHAPTER 4 Particulate Fillers Toughening Micromechanics using Calcium Carbonate Fillers on High Strength Melt Spun Polypropylene Applied for Spunbond Microporous Materials

ABSTRACT

Particulate fillers such as calcium carbonate is widely applied in polymer material for lower the cost in processing, changing mechanical properties, opacity, surface smoothness which improve the product economic value. Nonwoven by spunbond continuously produce polymeric resin blended with calcium carbonate fillers into random laid fiber webs, where filler particles forming with polymer from melt extrusion to solidify into filaments, to impose featured fiber attenuated structure. In this chapter, 2.5 wt. %, 10 wt. % and 25 wt. % of ground calcium carbonate (GCC) and two types of precipitated calcium carbonate (PCC) spun into melt spun polypropylene fibers. Afterwards, 100 gsm nonwovens containing with 10 wt. % of each type are primarily characterized from its geometrical structure of fiber diameter, fabric thickness, and solid volume fraction. Scanning Electron Microscopy (SEM) and optical microscopy are applied for characterizing fiber surface morphology and particle dispersion include internal microvoid structure of fibers. Our results on characterization of structure give filler particle type dependence on fiber diameter, that needle-shape EMforce results fiber obtaining smaller diameter, and spunbond thickness is reduced. Comparing to PCC-EMforce, GCC-FiberLink tend to crack along two poles of particles forming groove around them, which may be because of its larger average particle size at 2.24 μm and top cut above 10μm. Fiber modulus and toughness is also associated with particle specific surface
area and the high aspect ratio of aragonite PCC fillers, that improve on tensile mechanical performance of fabric as in a two dimensional fibrous nonwoven structure. The enhanced polymer thermal degradation property by using fillers is characterized to perform particle size dependence on degradation rate based on the study using Thermal Gravimetric Analysis (TGA), the finer and smooth PCC particles can enhance interfacial heat transfer in degrading polypropylene. Overall, we explain the fiber internal structure from melt extrusion with shear viscosity at varying of shear rate, and explain the effect of particle shape on the filler alignment in polymer melt extrusion.

Key Words: Structure-Property Relationship, Ground CaCO₃, Fiber Melt Spinning, Particle Size Distribution, Precipitated CaCO₃

4.1. INTRODUCTION

Inorganic fillers are fine particles mixed with polymeric raw material in melting, extruding and shape forming into a commercial product, containing with such particular fillers is supposed to lower cost of polymer resin. Meantime, functional fillers are tailored for specific applications in plastics, films, papers and paints since these small particles change the flow density in plastic processing and impact the subsequent cooling and demolding [1], [2], [3]. More important, filler particles possess with specific surface area interact with long chain molecular in different viscous behavior, can either thickening or reorienting under the shear deformation in the capillary slits. This is important as to spinning with long filaments, staple fibers and yarns as an implication of delicate cross-section area and longitudinal dimensions
must cope with filler particles movement with polymer flow and elongational deformation. Calcium carbonate fillers, as the most popular inorganic fillers have been applied to melt spinning to form a varying loading in polypropylene fibers \[4\]. However, relevant inventions in spinning and spunbond lack various selections in CaCO\(_3\) particle types, even if has preference to certain particle size range for spinning \[5\]. Challenge in spinning stability confine filler particle loading concentration and particle size distribution to a very limited range, it still ask for a flexibility of choices in other types of fillers to know the key parameters of particulate fillers.

The reason why we care about variation of calcium carbonate filler types can be associated with two particle characteristics- particle size and particle shape. Particle size plays a key role in fiber extrusion since cross-sectional shrink with extensional motion of polymer jet may form great amount of structural defects at polymer-filler interface that resulted fiber breakage. In choosing mineral filler, not only particle size should be taken into consideration, but also to keep certain particle size distribution. The portion of small size within certain range is critical to melt viscosity, without sufficient wetting fine particles tend to agglomerate under cohesion. Therefore, to avoid cracking at weak interfacial bonds must solve the issue of affinity to polymer by using stearic acid coating \[6\]. On another side, fiber strength is also sensitive to the larger particle size as stress concentration may expand craze at surrounding small crystallites debond from polymer matrix. Karakas and Celik has discussed the ratio between D\(_{97}\) to D\(_{50}\) which define the large size portion to the medium size portion, and this ratio D\(_{97}\)/D\(_{50}\) is influencing melt viscosity, opacity and gloss of the calcium carbonate filled
paint. In another work by Gorna and co-worker, amorphous calcium carbonate precipitated into different size distribution that must reply on pre-compounding with plastic resins.

Two types of calcium carbonate are ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC). Due to the different mineral processing, GCC are usually in cubic shape in crystallography form of calcite; PCC from chemical precipitation usually involve a variety of particle types such as scalenohedral, spherical, needle or cluster aragonite. Particle size and shape defines the effective phase at filler-polymer relative movement, without a conductive stress transfer network, the breakage could occur at any weak interfacial bonding. In aspect of particle shape, long rod-like and plate-like fillers are functioning as reinforcing agent for polymer composite. Relative larger specific surface increases the interfacial friction and extend the pull out time in the relative movements to plastic deformation of polymer strand. Toughening of polymer matrix by adding functional fillers, talc, mica, rubber and carbon black has been studied during the last two decades.

Spunbond meet with a great number of raw material species, making it accessible to mixing polymer resin with particulate filler, processing agent, additives, pigment, during polymer resin preparation into spunbond grade pallets. Spunbond nonwoven is mainly applied in hygiene products, baby diapers, cosmetic masks and medical textile, all requiring adding values in fast speed, aesthetic, softness as well as low energy cost in webbing, bonding and
finishing to meet with the competition in the market. Therefore, the whole processes from polymer to fiber web control the movement of filler particles within the polymer matrix. Multi-filaments spun from spinpack of polymer extruder are collected on a moving belt with random distribution in Machine Direction (MD) and Cross Direction (CD). Polymer crystallization accompany the alignment of fillers into the specific site, such anchor of fillers inside of filaments is going to be drawn by aspirator high velocity air. Polymers mainly develop shear-induced crystalline structure during attenuation. Therefore, it becomes important to investigate the impact of calcium carbonate parameters on spunbond fabric properties started from mechanism of fillers interaction with polymer spinning.

This chapter is targeted to explore characteristics in calcium carbonate size distribution and particular shape on spunbond forming structure, especially evaluate the impact on melt viscosity, mechanical property and thermal property. Objective is using the technique of melt spinning and spunbond, to reveal structure-property relationship related with processing issue such as fiber breakage, which can be explained more thoroughly by synthesizin parameters of \( \text{CaCO}_3 \).

4.2. METHODOLOGY

4.2.1. Materials

Pure polypropylene resin carries with three different types of calcium carbonate. These additives come from mineral suppliers such as Specialty Minerals Inc. who sells a bunch of
species of calcium carbonate tailored for different applications. Polymer is isotactic-Polypropylene (PP) CH360H (Braskem, Brazil). Melt flow index = 35. Molecular weight = 180,000 and the polydispersity = 3.3. Calcium carbonate is pre-compounded with PP in certain weight fraction with surface treatment of stearic acid. Information is included in Table 4-1.

Table 4-1: Technical Specification of Three Types of Calcium Carbonate Fillers:

<table>
<thead>
<tr>
<th>Technical Index</th>
<th>FiberLinkᵀᴹ 201S</th>
<th>EMforce®</th>
<th>Superpflex®</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite Type</td>
<td>GCC</td>
<td>PCC</td>
<td>PCC</td>
</tr>
<tr>
<td>Top cut (μm)</td>
<td>12</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Mean size (μm)</td>
<td>2.24</td>
<td>Major axis: 1.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Minor axis: 0.25 (aspect ratio:5.4)</td>
<td></td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>4.8</td>
<td>10.3</td>
<td>5.2</td>
</tr>
<tr>
<td>Filler Surface</td>
<td>1~1.5% Stearic acid</td>
<td>3-4% stearic acid</td>
<td>2% stearic acid</td>
</tr>
<tr>
<td>Dry Brightness</td>
<td>-</td>
<td>&gt;94</td>
<td>97</td>
</tr>
</tbody>
</table>

4.2.2. Melt-spinning Process

Spinning of fibers containing compounded calcium carbonate masterbatch from three types of fillers begin with mono-component fiber processing to bring out the following series of material processing. Mono-component spinning was studied using the Hills Multi-filament Melt Spinning Unit in our Fiber Science Lab. Experiment study filler type and concentration two parameters. Processing conditions are organized in Table 4-2, include spinpack
temperature, throughput, as well as the draw roll speed combination for fiber spinning. Filler concentration is accurately controlled from 2.5%, 10% and 25%. Comparing with FiberLink which keeps pump pressure at constant level, EMforce fillers cause pressure rise at 20%, and Superpflex result into severe pressure shooting up at 20%. Precisely pressure at each filler concentration level could be consulted to Appendix F.

Table 4-2: Setting for Mono-component Melt Spinning Process:

<table>
<thead>
<tr>
<th>Extruder—Spin pack Temperature (°C)</th>
<th>Extruder</th>
<th>155-160</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1</td>
<td>Tm</td>
<td>Zone 1</td>
</tr>
<tr>
<td>Zone 2</td>
<td></td>
<td>Zone 2</td>
</tr>
<tr>
<td>Zone 3</td>
<td></td>
<td>Zone 3</td>
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<tr>
<td>Zone 4</td>
<td></td>
<td>Zone 4</td>
</tr>
<tr>
<td>Spin Head</td>
<td></td>
<td>230</td>
</tr>
<tr>
<td>Quench Air</td>
<td></td>
<td>18</td>
</tr>
</tbody>
</table>

Spinneret: 69 Holes, 0.4mm
MFI of PP: 36 g/10min
Constant Mass Throughput: ~0.6 ghm(grams per hole per minute)

<table>
<thead>
<tr>
<th>Draw Rolls</th>
<th>Speed (m/m)</th>
<th>Feed roll</th>
<th>Draw roll</th>
<th>Relax roll</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>2000</td>
<td>1980</td>
</tr>
</tbody>
</table>
4.2.3. Spunbond

Web forming is produced by 0.5 Meter Bicomponent Spunbond Line (Hills - Nordson) in the pilot plant of the Nonwovens Institute. Two extruders convey polymer material into spinneret. Spinneret has 1162 holes, polymer melting was filtered by 250 mesh size screen filter, and then pump out of the spinneret capillary at constant mass throughput at 0.6 ghm. Calendar bonding compress the fiber web by a 18% of point bonding coverage, vary from 130°C to 150°C for FiberLink filled webs; 135°C to 150°C for PCC filled webs. All three types of fillers are compared at point bonding temperature of 135°C.

Different parameters produce in the spunbond nonwovens are filler types: FiberLink, EMforce and Superpflex. Filler concentration is controlled by blending to weight fraction at 5% and 10%. For mono-component fibers, throughput level is maintained at 0.6 ghm, but as we increase up the loading concentration from 5% to 20%, volumetric throughput must be adjusted according to melt density to keep constantly at 0.6 ghm. The melt density at varying of loading concentration is included in Appendix A Table 3-8, which correspondingly lower the volumetric throughput as loading concentration is above 10%.
Table 4-3: Temperature and Speed Profiles of Spunbond and Calendar Bonding:

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>Extruder Zone 1-Zone 6 400-425-440-455-465-465</th>
<th>Extruder Zone 1-Zone 5 400-425-440-455-465</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary core</td>
<td>Spinhead</td>
<td>Quench air</td>
</tr>
<tr>
<td>Speed</td>
<td>Thoughput 0.3 ghm</td>
<td>0.3 ghm</td>
</tr>
<tr>
<td>Speed</td>
<td>Quench air 25%, 1055 RPM</td>
<td>45%, 1619 RPM</td>
</tr>
<tr>
<td>Speed</td>
<td>Aspirator Fan</td>
<td>Calendar pressure 750 psi</td>
</tr>
<tr>
<td>Temperature (°F)</td>
<td>Spinhead 465</td>
<td>Quench air 40%</td>
</tr>
</tbody>
</table>

4.2.4. Characterizations

Particle Size Distribution Analyzer

Tests were conducted using light scattered particle size analyzer (Beckman Coulter) in Department of Natural Resources of North Carolina State University. The GCC (FiberLink) is immersed using acetone as non-polar suspension, but washing the whole set of instrument should be with 1L of acetone. Regular testing on the analyzer is using water as dispersion medium. To prepare hydrophilic calcium carbonate suspension, all three types of fillers burn and ash at 800°F furnace for 10 hours, in order to remove the stearic acid coating. Afterwards, take a scope of calcium carbonate powders and immerse with deionized water. Blend the mixture delicately until the visible clusters are uniformly dispersed into the medium. Let it stand still for 3 minutes. Then draw a 0.5mL liquid, from the middle layer of liquid in depth from the beaker. Send 2 drops of quiescent suspended liquid into the machine and start analyzing by the software.
Optical Microscopy

All fiber samples from the melt spinning are observed to reveal particle distribution in fibers. A Zeiss optical microscope with an objective of 40× was used and images were captured with a Nikon high-definition color camera DS-Fi1. Fiber diameters are measured from the images from 10 fibers, average over 30 readings.

Scanning Electronic Microscope (SEM)

Fiber surface and fiber cross-section are observed using Hitachi S-3200N SEM at the Analytical Instrumentation Facility of NCSU. Fiber samples coat with gold for 15 minutes. For preparing fiber cross-section, cutting comes right after immersing in liquid nitrogen for a few seconds.

Single Fiber Tensile Property

The single-fiber tensile properties of the PP/CaCO3 fibers were evaluated according to ASTM 3822-10 with an Instron MTS instrument with 50-g load cell (Canton, MA). The gauge length was 2.54 cm, and the rate of extension was 15mm/min. The tenacity, toughness, and strain at break were calculated from the tensile stress-strain curve. Secant Modulus was the slope of stress-strain curve at 5% of strain. The average of 10 samples is reported.

Differential Scanning Calorimeter (DSC)

The melting and crystallization behavior of the filaments samples were analyzed by Discovery TA Instrument Differential Scanning Calorimetry (DSC). All samples were first
heated at 20°C/min from 25°C to 195°C, followed by cooling at 10 °C/min rate. Thermograms were obtained from DSC analyzed with the Trios software. Crystallinity is calculated from endothermic heat flux change $\Delta H$. Crystallinity is calculated based on equation:

$$\chi_C(\%\text{ crystallinity}) = \frac{\Delta H_m}{\Delta H_m^0 \omega} \times 100\%$$  \hspace{1cm} (1)

Where $\Delta H_m^0$ is the heat of fusion (165 J/g) for 100% iPP; $\Delta H_m$ is the heat fusion per unit gram of fiber sample; $\omega$ is mass fraction of PP in the fiber composite.

**Fabric Thickness**

Thickness gage is applied for this testing in the Physical Testing Lab in the Nonwovens Institute. 10 different readings are recorded. Basis weight is measured as well for an estimation of solid volume fraction of fabrics.

**Nonwoven Grab Tensile Test**

Five MD samples and five CD samples were tested using the United Grab Tensile Tester based on standard ASTM D5034. Testing used the type of CRE operating at speed of 300mm/min and tester records the breaking strength as well elongation at breaking for each sample.

**Thermal Gravimetric Analysis (TGA)**

Fiber thermal degradation property was tested using Perkin Elmer Pyris 1 TGA. A fiber sample, around 5~10mg, was put into a platinum plate which is attached to a micro balance.
Samples were heated up from 25°C to 600°C in a rate of 20°C/min under air. Then sample weight in percent is plotted with increasing temperature, which illustrates the sample degradation behavior.

4.3. RESULTS

All three types of calcium carbonate particles were melt spinning to produce fibers filaments gathered as parallel bundle and drawn by three godet rollers. During 10 minutes of spin processing, adding up concentration of PCC fillers above 10% cause severe instability, which involve EMforce has specific surface area of 10.3 m²/g, that at 25 wt.% this type of particles cause breakage below the spinneret. The other Superpflex (SF) fillers also encounter fiber breaking and the drawing instability on godet. Specific spinning performance include in Appendix D Table 4-11. This spherical filler particle is in 5.2 m²/g specific surface area compared to GCC which has 4.8 m²/g, but more significantly is from its finer smooth particle size as shown in Figure 4-1, narrower than FiberLink particles.
Figure 4-1: Calcium carbonate particle morphology (a) GCC-FiberLink; (b) PCC-Superpflex; and (c) PCC-EMforce. SEM with magnification: 25 000x.

4.3.1. Particle Size Distribution of CaCO₃

Morphology of ground calcium carbonate (GCC) FiberLink™ 201S is shown in SEM pictures of Figure 4-1 (a), particle size range from large flakes to small particles comprise the wide range of mineral geometry shapes. Patterns on particle surface clearly indicate crystallography structure of calcite formed in nature. Some small pieces of GCC particles are generated during grinding of limestone in attached to the relative larger flake surface. Based on Weiner and Addadi, calcite form of calcium carbonate possess with cleavage rhombohedra plane with is (1 0 4) in its X-ray diffraction pattern [33]. The form of cleavage plane determines the in-plane stability with closely packed calcium arranged with carbon ions near around. But the high layer energy is compensated with lower attachment energy of
those layer stacks, as show in Figure 4-1 (a) so that crack may happen at weak inter-plane attachment region \(^\text{[11]}\).

The specific character PCC filler is in the high specific surface. This type of precipitated calcium carbonate minerals is targeted for plastic reinforcement in flexural rigidity and high toughness, which is contributed to its high aspect ratio and large specific surface area. The anisotropic of such filler reflects in its main axis and minor axis is with 1μm and 0.25μm, respectively. EMforce differ in crystallography from FiberLink as indicated from X-ray diffraction peak, this crystal forms as aragonite which is different from calcite form of FiberLink as well as the Superpflex mainly showed in Figure 4-3. Crystal growth of aragonite is preferable along c-axis relative to other crystallographic, therefore, under specific temperature and pressure aragonite will form into thin needles or termed as acicular crystals \(^\text{[11]}\). EMforce develops polymorph crystalline phase with more imperfections in crystalline existed in the particular minerals. But Superpflex is with a uniform polygonal crystal shapes, indicating that the relative rate in growing of crystal is approximately equal in all direction \(^\text{[11]}\). However, from the lower X-ray diffraction peak, we can see that Superpflex fillers possess with less perfect crystalline structure as GCC does especially in (1 0 4) plane.
Figure 4-2: Particle Size Distribution of Precipitated Calcium Carbonate (Superpflex), comparing to Ground Calcium Carbonate (FiberLink).

From its particle size as shown in Figure 4-2, 75% falls in size range of 1μm to 10μm, there are 20% less than 1μm, with the finest portion falls at 0.1μm~0.2μm. Top cut of coated FiberLink fillers range from 9μm to 15μm which takes less than 1% of total particles. From percent of particles pass the mesh size, this particle size distribution curve demonstrated with $d_{90}=5.4\mu m$, $d_{50}=2.28\mu m$ and $d_{10}=0.42\mu m$. Comparatively, Superpflex with a narrower size distribution, obtain a smaller size fraction in the distribution, specifically $d_{90}=3.22\mu m$, $d_{50}=1.38\mu m$ and $d_{10}=0.22\mu m$. PCC increases the amount of particles in 0.1 to 1 micron and the percent of particle smaller than 1 micron reach to 40%.
Figure 4-3: X-ray diffraction peaks showing the calcium carbonate fillers crystallography character comparing GCC and two PCCs.

4.3.2. Filler Dispersion in Fibers
Figure 4-4: Dispersion with 10% of CaCO₃ (a) FiberLink; (c) EMforce; (d) Superpflex in PP fiber (b). (e-f) is fibers containing 25% with 40x optical microscopy.

The added calcium carbonate fillers can be found from the scattered light shown in microscopy image. Multiple scattering at particle surface is look like dark spots, as shown in Figure 4-4 (a-g), where higher concentration (25%) becomes denser in the polypropylene fiber. The fibers include some long flat shape internal voids around GCC particles. Such internal structure is expected due to the incompatibility of inorganic fillers with polymer, which is corresponding with previous work by Ookawa that micro-voids formed at different draw ratio in melt spinning of polyethylene fiber [32]. The long axis of rhombus aligns with
fiber z-direction which is in the same direction with shear stress. The dimension of long axis is with 1~20μm, compare to short axis no more than 5μm for GCC. Such internal cracking should be regarded as one reason to cause fiber diameter enlargement.

4.3.3. Structure of Melt Spinning Fibers

Fiber diameter illustrated in Figure 4-5 indicate the changing with different types of calcium carbonate fillers loaded at 10% and 25%. Fiber diameter D and radius R (μm) based on density (g/cm$^3$) of spun fibers, by using mass throughput outside each spinneret hole with spinning speed at take-up winder, is estimated according to equation (3):

$$D = \sqrt{\frac{4W \times 10^6}{\pi \nu \rho}}$$  \hspace{1cm} (3)

Where $W$ is mass throughput (g/hole/min) of spinning, $\nu$ is spinning speed (meters per minute: mpm). $\rho$ is fiber density, which is varied with CaCO$_3$ filler particle with a specific gravity of 2.7 g/cm$^3$ apparently larger than PP at 0.9 g/cc. So the mixed fiber density is estimated from equation (4):

$$\rho_c = \phi_f \cdot \rho_f + \phi_m \cdot \rho_m = 2.7\phi_f + 0.936(1 - \phi_f)$$  \hspace{1cm} (4)

Where $\rho_c$, $\rho_f$ and $\rho_m$ are density of composite, fiber and polymer matrix respectively; $\phi_f$ is volume fraction of fillers. As fiber diameter is a parameter specified to the spinning conditions so that it is assumed that spinning speed is equal to the draw godet velocity at 2000 mpm. First it has been found average fiber diameter follow the sequence as EMforce < FiberLink < Superpflex. Filler size influence the standard deviation of fiber diameter, Superpflex loaded with 10% has relative smaller CV = 3.2 indicating spinning was stable.
with a very uniform fiber morphology by drawing. While FiberLink induce larger diameter CV =7.3 (%) at 10%, with linear density slightly increase compare to other two PCC fillers (Table 4-4). The fibers filled with EMforce obtain relatively same diameter level as PP control fibers.

![Graph showing CaCO3 Types on Fiber Diameter](image)

**Figure 4-5:** Filler particle shape influence on fiber diameter

**Table 4-4:** Fiber Structures Specification of Three Types of Fillers:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Fiber Diameter D (micron)</th>
<th>Fiber Linear Density (denier)</th>
<th>Theoretical Density $\rho_c$</th>
<th>Theoretical Radius R</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>22.3 (5.8%)</td>
<td>3.4</td>
<td>0.90</td>
<td>20.6</td>
</tr>
<tr>
<td>FL-10%</td>
<td>25.1 (7.3%)</td>
<td>3.6</td>
<td>0.96</td>
<td>20.6</td>
</tr>
<tr>
<td>EM-10%</td>
<td>23.7 (6.6%)</td>
<td>3.5</td>
<td>0.96</td>
<td>20.6</td>
</tr>
<tr>
<td>SF-10%</td>
<td>24.9 (3.2%)</td>
<td>3.4</td>
<td>0.96</td>
<td>20.6</td>
</tr>
<tr>
<td>FL-25%</td>
<td>22.7 (3.1%)</td>
<td>3.5</td>
<td>1.08</td>
<td>20.7</td>
</tr>
<tr>
<td>EM-25%</td>
<td>22.0 (5.1%)</td>
<td>2.9</td>
<td>1.08</td>
<td>20.7</td>
</tr>
<tr>
<td>SF-25%</td>
<td>23.7 (4.2%)</td>
<td>3.5</td>
<td>1.08</td>
<td>20.7</td>
</tr>
</tbody>
</table>
Figure 4-6: Fiber Morphology of three different types of fillers in 10% of concentration

From the fiber surface, include in Figure 4-6 (a-d), it was suspected that roughness could associate with the particle size especially when the dimension is no less than 10% of fiber diameter around 20μm. Specifically, since larger particle size is likely to be excluded out of
the fiber cylindrical perimeter. We believe the surface roughness of GCC filled fiber surface contribute to light scattering effect which remove the waxy feeling of the fibers. PCC fillers impose smooth without much protrusion outside of fiber. The importance exposing the surface roughness with other application, such as used for wipes when a scratching over counter surface may be accompanied by a bumpy surface. Sole and Ball point out talc filled polypropylene injection molding polymer processing has also performed lower wear rate than pure material, but 5μm CaCO₃ has higher wear rate than PP on both mild and coarse abrasive belt [10]. As expected, with increasing the filler weight fraction, the chance of flake caused from abrasiveness may peel off large particles that are sticky out of the perimeter. Rubbing filled fabric to counter top could result into flaking and an increased friction coefficient [10]. As shown in Figure 4-7 (a) and (c), two figures compare the fabrics containing with 10% of GCC to the level at 30%. The coarse particulate calcium carbonate tends to emerge onto the nonwoven and change the general texture and the light scattering on those roughened fiber surface. At higher loading, the relative movement of polymer and particles notch on polypropylene fiber surface along flow direction, whereas anisotropic fillers like EM can better align better with shear flow (Fig. 4-7 a. b). This is attributed to the aspect ratio of such rod-like fillers, where alignment lowers the flow resistance under the hydrodynamic force so that 0.25μm cross-section faces vertically to fiber cross-section. It is quite apparent to deduce from Fig. 4-7 (b) that a surface oriented particles in spunbond attenuated fibers, but compared to melt spun fibers shown in Fig. 4-6 where shows the cluster of tiny tip inserted vertically to spin direction of fibers. The phenomenon is attributed to the rotating motion of needle-like particles oriented minor axis on cross-section of fibers.
Figure 4-7: Spunbond fiber webs containing with 10% GCC (a) compare to (b) 10% EM; (c) 30% greatly roughen fiber surface with one spot of defect patch on spunbond fabrics (d).

Spunbond process encounter with melt dripping as concentration is above 20%. This phenomenon is related with long running that causes mesh screen blocking up inside of spinpack. Filter clogging problem not only block the flow entrance in the capillary, but also
weaken the polymer melt strength down the spinneret. Those broken filaments form ropy defects onto the spunbond web. As shown in Figure 4-7 (d), a fabric surface defect involve bundles of filaments that after being caught by broken filaments, the subsequent attenuation will form as a tie knot. Within the patch, fibers are bind together and directly laid down into the web. So fabrics lack of uniformity at those defects. As fiber surface become roughened by calcium carbonate fillers, fiber flexural rigidity increases the difficulty of fibers random web lay down formation. So fiber distribution uniformity issue comes along with adding inorganic filler particles.

4.3.3.1. Crystalline Structure of Melt Spun Fibers

Crystallization of polymer starts from nucleation and follow on with crystal growth. In a quiescent melt solution nucleation start sporadically from nucleation sites and grow outwards as spherulite. The size of spherulite is theoretically expanding all over the available volume if time is sufficient long, they will stop growing when they impinge onto each other \[15\]. However, lamellae is the dominated fiber crystalline structure since high shear stress induce row nuclei in fibers and lamella plane thickens during the subsequent spin-draw process \[12\]. Whether filler additives go in the compacted structure or not depends on crystal form of calcium carbonate, surface treatment on particle surface as well as particle size. GCC-FiberLink is calcite form with distinct cleavage plane, they act as single nuclei site but the number of nuclei which contribute to secondary nucleation still rely much on the row nuclei within the polypropylene melt. Both GCC and PCC have increased fiber crystallinity, just different at varying of loading within fiber. 2.5% of FiberLink narrow the endothermic
melting range from on-set to end-set point of $T_m$. At the same time, fiber crystallinity increases especially for 2.5% of FiberLink and Superpflex, both of which are in calcite crystalline form according to Figure 4-3. Kowalewski and Galeski brought up the interface phenomenon at calcite with polypropylene and found that the nucleation effect is associated with defects of calcite crystals $^{[11]}$. At large cleavage substrate, the crystallite nucleated initially will continue on growing parallel to flat surface, but may change the growing direction when come across with defects such as steps in the cleavage $^{[11]}$. Zoukrami and co-workers investigated the nucleating effect of CaCO$_3$ using low density polyethylene (LDPE), and discussed on crystallization temperature determined by filler particle size, and denied the cause from loading of CaCO$_3$ $^{[12]}$. Superpflex fillers barely change fiber crystallinity from 2.5% to 10%, while increasing concentration will narrow down the melting range and uniform the population of crystal size.

The melting range of endothermic peak becomes relative wider revealing crystallites lamellae spacing forming by secondary nucleation grow into a denser lamellae planes formed with monoclinic form of polypropylene appears. As claimed in previous work, aragonite form of CaCO$_3$ tends to form nucleus which help to reduce the inter-particle spacing in polypropylene $^{[11]}$. By a close compaction between those needle-shapes aragonite fillers along shear flow, the large specific surface area will entrap larger polypropylene molecules surround fillers. Then the distances between fillers can be narrowed to some extent that the lamellae fold chains in epitaxial alignment vertical to the long axis of EMforce filler. Higher fiber crystallinity of 10% filled EMforce indicate the efficiency of accumulating of nucleus
in polypropylene at particulate surface. From subsequent crystallization temperature (Table 4-5), it is found that EMforce fillers slightly increase the $T_{c-on-set}$ but less than 2°C, therefore, the nucleating effect of the CaCO$_3$ fillers is not significant in polypropylene. So we must regard the increased fiber crystallinity come from the shear-induced crystallization in polymer spin-draw formation.

Table 4-5: Melting Endothermic Peak Information and Crystallization Temperature:

<table>
<thead>
<tr>
<th>Filler Conc.</th>
<th>Filler Type</th>
<th>$T_m$-onset (°C)</th>
<th>$T_m$-end-set (°C)</th>
<th>Crystallites Melting Temp. Range (°C)</th>
<th>Crystallinity (%)</th>
<th>$T_{crystallization}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Polypropylene</td>
<td>152.4</td>
<td>182.2</td>
<td>29.8</td>
<td>52.1</td>
<td>125.2</td>
</tr>
<tr>
<td>2.5%</td>
<td>FiberLink</td>
<td>153.2</td>
<td>180.7</td>
<td>27.5</td>
<td>54.2</td>
<td>126.0</td>
</tr>
<tr>
<td></td>
<td>EMforce</td>
<td>151.1</td>
<td>181.7</td>
<td>30.6</td>
<td>53.1</td>
<td>126.0</td>
</tr>
<tr>
<td></td>
<td>Superpflex</td>
<td>152.4</td>
<td>179.6</td>
<td>27.2</td>
<td>54.0</td>
<td>126.2</td>
</tr>
<tr>
<td>10%</td>
<td>FiberLink</td>
<td>153.8</td>
<td>179.8</td>
<td>26.0</td>
<td>53.0</td>
<td>125.8</td>
</tr>
<tr>
<td></td>
<td>EMforce</td>
<td>153.3</td>
<td>180.2</td>
<td>26.9</td>
<td>55.8</td>
<td>126.6</td>
</tr>
<tr>
<td></td>
<td>Superpflex</td>
<td>153.2</td>
<td>178.8</td>
<td>25.6</td>
<td>54.4</td>
<td>125.9</td>
</tr>
</tbody>
</table>
Figure 4-8: Fiber crystallinity melt spun at 0.6ghm, contained with 10%.

Figure 4-9: Crystallization behavior at 10°C/min cooling rate of fibers contained with pure PP, EMforce, FiberLink and Superpflex all at 10wt. %.
4.3.4. Properties of Fiber Forming Spunbond

4.3.4.1. Melt Viscosity

Figure 4-10: Shear viscosity of polymer filled with EMforce and Superpflex two particle fillers.

In the polymer extruding from the spinpack, major problem in fine particle processing is the clogging in the spinneret. When filler concentration is more than 10%, the pump pressure is shoot up caused by over loading (>10%) of PCC, especially refer to Superpflex with finer spherical shape. While EMforce and FiberLink keep the pump pressure at relative stable range. EMforce at the same concentration, as shown in Figure 4-10, behave with lower melt viscosity than Superpflex. Adding 15% CaCO₃ with polypropylene melt behaves in higher melt viscosity at low shear rate 10 s⁻¹ ~ 300s⁻¹; while further raise up to high shear rate from
500 to 1,000 s\(^{-1}\) can align particles with anisotropic shape more uniformly along the polymer jet flow, with overlapping shear viscosity at high shear rate range (> 1000 s\(^{-1}\)). Loading spunbond extruder with up to 30% still keep at normal pump pressure level as shown in Table 7-11, Appendix J. The relatively easy packing of GCC allows the large interstice to be filled up with fine particle size, owe to its relatively larger size distribution. Mooney equation (5) explains viscosity as a function of volume fraction, shape factor, aspect ratio, packing characteristics and interaction parameters.

\[
\ln\left(\frac{\mu_c}{\mu_m}\right) = K_e V_f [1 - K_e (V_f/\phi_{max})]^{-1}
\]  

(5)

Where \(\mu_c/\mu_m\) is the ratio of the viscosity of the composite to that of unfilled matrix, \(\phi_{max}\) is the maximum packing factor, defined as true volume of filler/apparent volume occupied by filler, \(V_f\) is the volume fraction of fillers. \(K_e\) is geometric parameter known as the Einstein coefficient, which is depend on aspect ratio and degree of agglomeration \([1]\). Varying particle size distribution influences the true volume of fillers packing inside, therefore resulting in different \(\phi_{max}\). With size distributed in mono-dispersed, or in narrow distribution range, packing volume is restricted in the volume because there are relatively large gap in between each particle. Compare to GCC, the PCC fillers possess with fine and uniform particle size, and also cause more screen mesh clogging because of higher melt viscosity. Even though particles finer than 0.5 \(\mu\)m also account portion in the GCC size distribution (Fig. 4-2), those finer cubic can also form a combination in packing at higher loading that any large interstice between bigger particles may be filled out, which increase the ratio between true volume to the apparent volume \([14]\). This ratio represents the capability of inorganic fillers in occupying
into dense and compacted volume. A wide particle size pushes the ultimate value of $V_{true}/V_{apparent}$ ratio, therefore, reducing the filled polymer viscosity ($\mu_c$) based on equation (5).

4.3.4.2. Fabric Thickness

Long filaments layer up as fluffy volume in $z$-direction of the web, guided by parcel out of aspirator. Assumed fibers are with round cross-section, so varied fiber diameter spun from different particle type of CaCO$_3$ should result in a slightly different packing geometry of spunbond. As shown in Figure 4-11, the fabrics thickness varies with filler loading concentration, which increases up to 10% but then drops down. While for fibers filled with PCC at 5% and 10%, the different fiber diameters may directly result into the thickness of spunbond containing Superpflex increases to be standing out among three particle types (FiberLink and EMforce). As refer to Table 4-4, the needle-shaped particle EMforce tend to decrease fiber diameter and fiber linear density comparatively, resulting in a decreased spunbond thickness. That may impact the fiber opening and bundles filaments separation at laying down into the web, as shown in Fig. 4-7d. Also as fiber diameter is decreasing at higher loading concentration, so the fabric thickness decreases at 20% of loading. Addition of fillers at high than 10% causes thickness even lower than PP control level. But using SF particles at 10% will keep at rather high thickness level, may attributed to larger fiber diameter (Fig. 4-5) and less packing efficiency into the fabrics. It also indicates that with shear viscosity increases by loading with finer PCC-SF particles, polymer flow jet bear larger spinline tension but less elasticity to response to radius deformation. With EMforce maintain the polymer viscosity at similar level as polypropylene pure resin, then cross-sectional
dimension of fibers form by necking below the spinneret and develop molecular orientation by high pressure attenuation.

4.3.4.3. Tensile Strength

Single fiber tensile behavior describes polymer chains viscoelastic deformation under tension. Initial elastic region reflects Young’s modulus. We mainly discuss secant modulus at 5% strain because initial curve is deviated from a straight line with concave shape. Molecular chain orientation affect fiber modulus, while the spinline stress pulls on flow jet can make a difference for particulate fillers. As shown in Figure 4-12, stress-strain behavior yield at lower stress with an apparent smaller modulus. During following drawing, tie molecules between folded planes are aligned to the main axis of fibers, but stress concentrating on the

Figure 4-11: Fabric thickness of spunbond through 135°C calendar bonding.
rigid filler particles, when the molecular orientation is sacrificed by chains relaxation at the barrier of fillers. Although crystallinity in fibers could positively affected by fillers, polymeric orientation may be hindered by calcium carbonate. As filler concentration increases, the stress-strain curves for filler contained fibers reduce its stress in the plastic region. EMforce with high aspect ratio has elongated the fiber strain at breaking indicating the advantage of high specific surface area that may enhance the interfacial interaction during spinning. It also induces higher stress at breaking associated with less defects within fibers as shown in Figure 4-12 (b) comparing with SF and FL fillers with 25% of loading.

Semi-crystalline regions keep on orientating the lamellae crystallites as polymer go across the yield point. Extensional forces will gradually broaden the d-spacing between folded chains, by working on the highly compacted crystallites, and then pull out of polypropylene chains from the micelle compacted region until the crystalline lamellae are unraveled from the folding plane. During the chain opening, there are local filler particles acting as stress concentrators at random coils, crazing around the filler particles may collapse the lateral plane within fiber resulting in breakage. When particles are wetted perfectly by polymer, they will keep moving with inter-planer broaden along tensile stretch, until the strength is larger than the weakest spots within the lamellae linkage. Eventually stress breaks down fiber structure by ruptures residual fibrils in the shearing band left at the crazing phase.
Figure 4-12: Stress-Strain curves of single melt spun fibers PP containing with three different types of fillers with (a) 10% and (b) 25%.
Same trend was noticed in single fiber tenacity vs. filler concentration using FiberLink and Superpflex, while for EMforce at small loading at 2.5%, the tenacity is significantly larger than polypropylene. As concentration reaches to 10%, its tenacity lower down to the same level as FiberLink and Superpflex. At 25% of filler concentration, EMforce show 0.5 gram force per denier (gf/den) higher tenacity. As to fiber toughness vs. concentration in Figure 4-13 (b), the trend for FiberLink and Superpflex both decline with concentration. But for EMforce, the toughness first increases with filler concentration to 10%, then decreases at 25%. To specifying at the variation at 2.5% and 10% for EMforce, we can see that 2.5% has larger standard error, so that its toughness level did not significantly lower. Toughening effect for EMforce is representing in its higher breaking strength especially the stiffness at small loading level which reinforces fiber structure (Fig. 4-12a, Figure. 4-18). While for cubic shape GCC, there exist certain amount of defects surround particles, which result in decreased tenacity and toughness. Since larger filler particles debond in polymer strain deformation, so that the strain at breaking has significantly reduced (Fig. 4-12b). In another consideration, both PCC fillers possess with larger specific surface area and this enhances the relative movement along fiber deformation. Especially the high aspect ratio promotes the extra energy input to pull out of polymer matrix. Such feature also helps overcome the debonding at interface, and transfer the stress easily across the filler/polymer interface.
Figure 4-13: Single fiber tensile properties showing tenacity (a) and toughness (b).
Using particulate fillers in thermal calendar bonding could generate a different bonding efficiency by thermal treatment of polymer to give polymer recrystallization and form interfacial bonding across fibers. From a consistent bonding temperature (135°C), fabrics produced with pure PP fibers are mainly compared with 10% of calcium carbonate fillers contained fabrics. Their tensile strength and elongation at breaking in MD is seldomly varied with loading type (Figure 4-14a, b). Only results related with filler loading types is that adding GCC has decreased breaking strength significantly in CD. In contrary, PCC-EM positively improves tensile strength in CD and decreasing elongation at breaking comparing to PP fabric. The randomly distributed fibers could reorient from certain orientation distribution angle to the main force direction such as in MD, by rotating and friction movement and mainly transfer the stress to the bonding points. Since the fibers oriented in CD is not comparable to MD, fibers reorient and stress redistribution in stretching the fabrics.

Table 4-6: Single Fiber Tensile Properties Related with Types of CaCO₃ in Melt Spinning:

<table>
<thead>
<tr>
<th>Filler Loading Information</th>
<th>Secant Modulus at 5% (gf/denier)</th>
<th>Tenacity (gf/denier)</th>
<th>Toughness (gf/denier)</th>
<th>% Strain at Breaking</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP Fibers</td>
<td>16.7 (1.8)</td>
<td>4.0 (0.12)</td>
<td>4.4 (0.4)</td>
<td>162 (19)</td>
</tr>
<tr>
<td>2.5% FL</td>
<td>16.2 (1.0)</td>
<td>3.8 (0.13)</td>
<td>4.1 (0.1)</td>
<td>163 (18)</td>
</tr>
<tr>
<td>2.5% EM</td>
<td>26.6 (2.5)</td>
<td>5.4 (0.33)</td>
<td>4.1 (0.3)</td>
<td>119 (57)</td>
</tr>
<tr>
<td>2.5% SF</td>
<td>17.0 (0.6)</td>
<td>4.0 (0.05)</td>
<td>4.4 (0.12)</td>
<td>164 (19)</td>
</tr>
<tr>
<td>10% FL</td>
<td>12.0 (1.8)</td>
<td>3.0 (0.08)</td>
<td>3.2 (0.10)</td>
<td>166 (16)</td>
</tr>
<tr>
<td>10% EM</td>
<td>12.4 (0.4)</td>
<td>3.3 (0.07)</td>
<td>4.2 (0.2)</td>
<td>196 (24)</td>
</tr>
<tr>
<td>10% SF</td>
<td>14.5 (1.6)</td>
<td>3.3 (0.06)</td>
<td>3.3 (0.13)</td>
<td>155 (19)</td>
</tr>
<tr>
<td>25% FL</td>
<td>9.5 (0.4)</td>
<td>2.2 (0.04)</td>
<td>2.1 (0.04)</td>
<td>150 (12)</td>
</tr>
<tr>
<td>25% EM</td>
<td>11.1 (0.3)</td>
<td>2.6 (0.06)</td>
<td>2.9 (0.1)</td>
<td>169 (8)</td>
</tr>
<tr>
<td>25% SF</td>
<td>9.1 (0.2)</td>
<td>2.0 (0.04)</td>
<td>2.3 (0.1)</td>
<td>169 (15)</td>
</tr>
</tbody>
</table>
becomes closely related with the damping of fracture energy in the filled structure. The function of individual segment of filaments works towards to the extensional direction by connecting with large amount of unbroken fibers which assist to propagating stress efficient in the fiber network. Fiber structure that has been toughened by needle-shape fillers can mainly contribute its higher toughness to the fabric reinforcement as shown in Figure 4-13(b). From standard deviation data in the plots, we find PCC filled fabric obtains less variation compare to the other two types of filler, especially for the MD profile. As shown in Figure 4-16(c), we can see that uniformly dispersed EM particles exclude apparent large cracks, also indicate fiber polymers are melted and recrystallize sufficiently and form consolidated bonding structure. Because as previous fiber surface morphology indicated the long axis tends to anchor along the fiber direction, as there are fibril chains formed at fiber-fiber breaking phases, the possible result is from the filler assistant in polymer chain reputation across the fiber boundary. As a result, such relaxation in polymer chains entanglement will bridge those bundles of fibers and contribute to transferring the stress through the fibrous network. Contrarily, GCC FiberLink is with irregular cubic particle shape so it causes more uneven packing within the bonding area (Fig. 4-16d). Also the debonding in fiber stretching phases have include apparent large amount of voids around those particulate fillers (Fig. 4-16f).

During spunbond processing the PCC-Superpflex tend to cause severe pump pressure issue with 10% of loading in the extruder supplied to sheath of fibers, so above 135°C only spunbond with EMforce and FiberLink fillers above 10% are supplied (Fig. 4-15). To further
reveal the difference between GCC and PCC-EMforce, an advanced plot based on 145°C bonding temperature indicates the reinforcement is applicable for a wide range of EMforce loading from 2.5%~20%. This is because of single fibers filled with such needle-shape particles achieve to a high tenacity and toughness as we discussed previously. Below 20% both GCC and PCC filled spunbond keep its strength above the level of PP control fabric, and overcome the detrimental weakness caused by filler particles embedded in single fibers. Bonding energy from thermal calendar surface release partial set amorphous orientation in fibers, and form recrystallization of polymer across fibers, forming fibril like chain reptating and diffusing across fiber boundary.
Figure 4-14: Fabric grab tensile properties showing MD and CD breaking strength (a) and elongation at breaking (b) bonded at 135°C.
Figure 4-15: Toughening effect of EMforce fillers at 145°C bonding temperature compare to FiberLink Fillers.
4.3.4.4. Thermal Degradation

Thermal degradation properties of spunbond fabrics has been involved in weight loss (%) curves to temperature in Figure 4-18, results shows that loading in CaCO₃ particulate fillers inevitably increase thermal degradation rate and result the on-set degradation temperature raise up.
Figure 4-17: Filler loading effect on the thermal stability of polypropylene fibers under Nitrogen gas flow in furnace, at constant heat rate of 20˚C/min.

Table 4-7: 10% of Calcium Carbonate with Three Different Types on Thermal Degradation Properties of Fiber Polymers:

<table>
<thead>
<tr>
<th>CaCO₃ Filler Types</th>
<th>On-set Degradation Temp. (˚C)</th>
<th>Peak Weight Loss Temp. (˚C) vs. Weight Loss</th>
<th>End-set Temp. (˚C)</th>
<th>Residual (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP Control</td>
<td>409.1</td>
<td>449.9 (19.3 %)</td>
<td>459.4</td>
<td>0.3</td>
</tr>
<tr>
<td>EMforce</td>
<td>453.5</td>
<td>484.6 (34.2 %)</td>
<td>496.7</td>
<td>9.3</td>
</tr>
<tr>
<td>Superpflex</td>
<td>427.4</td>
<td>457.7 (39.2 %)</td>
<td>473.6</td>
<td>8.4</td>
</tr>
<tr>
<td>FiberLink</td>
<td>410.4</td>
<td>441.6 (37.6 %)</td>
<td>455.1</td>
<td>11.3</td>
</tr>
</tbody>
</table>
Thermal degradation properties of spunbond fabrics has been involved in weight loss (%) curves to temperature in Figure 4-17, results shows that loading in CaCO$_3$ particulate fillers inevitably increase thermal degradation rate and result the on-set degradation temperature raise up. Precipitated calcium carbonate delay the degradation on-set points much greater than ground calcium carbonate. This means polymers structure can undergo a higher thermal resistance above 400°C with finer calcium carbonate particles, as included in Table 4-7, on-set degradation temperature ($T_{d-on-set}$) of PCC is 20~40°C higher than polypropylene control, and peak degradation temperature ($T_{d-peak}$) also raise up by 10~35°C. While the event occurrence temperature for PP control did not expect much variation from GCC filled polymer. Peak temperature is slightly lower after incorporated with GCC, which can be reflected from the weight loss derivative curves. Peng and Kong have demonstrated that polymer/inorganic nano-composites perform good thermal resistance due to carbonaceous char built up at filler particle substrate, like on clay and on silicate layers, further provide a transfer barrier during burning and shield underlying flammable material from heat $^{[15]}$. The reasonable mechanism on improve thermal stability by particulate fillers is to restrict the diffusion of volatile decomposition products in the degrading process $^{[16]}$. Heat capacity of two different PCC relates with the peak heat release rate, as the PCC-SF has much finer particle size and its network in stacking will diffuse the heat by inter-particle conduction. Chars forming on PCC fillers particles are covered to a higher covering density because the relatively larger specific surface area of PCC. So the insulated structure delays the rest of polymer exposing to the higher surrounding temperature. Due to lower specific heat (shown in Appendix I) of SF than EM, the EM filled polymer show higher heat release rate than the
SF filler, also with the peak heat of derivative curve comes at higher temperature than SF. While GCC fillers show less impact on degradation resistant, mainly due to the larger internal microvoid around polymer-filler interface which reduce the efficient heat transfer out of the polymer. Therefore, it causes pyrolysis accelerate at the heterogeneous interphase when heat is accumulated at the polypropylene materials.

4.4. DISCUSSIONS

The key factor in spunbond fabric property is fibers forming structure, particularly in an interaction with calcium carbonate fillers that help fiber develop crystalline and orientation that impact the spunbond structure formation. Spinning start to deform polymer jet into a very small cross-section, so characterization focused on fillers particles dispersion and fiber internal morphology reveal the accumulation of agglomerations that potentially form as potential weakest spot (Fig. 4-19). Adding GCC –FL according to the discussion in Chapter III, the top cut also form as potential weak link structure in melt spinning, accompanied by a debonding at weak interfacial links. While mineral fillers selected from two precipitation CaCO$_3$ types outstand in modifying single fiber tensile properties. Needle-shape EMforce, with aragonite crystal form, is supreme in fabric reinforcement because of its high specific surface and larger aspect ratio. Such filler not only promote high modulus but also a high breaking strength of fiber with a larger toughness. As Figure 4-13 results shown, EMforce has improved in tenacity in only 2.5% which corresponded to its substantial toughening effect. Such effect can be described from single fiber stress-strain curve, as shown in Figure 4-18, high modulus with low strain at breaking indicates highly oriented crystalline. In that
orientated lamellae crystals, the effect of small loading of finer precipitated CaCO$_3$ particles is promoting the growth of crystalline orientation along the spinning of fiber polymers. The likely epitaxial growing along the fillers long axis forms closer packing of crystallites to assist to chain alignment during shear deformation. This substrate could be referred to a cleavage plane in GCC, or the periphery of PCC-EMforce. Particle shape with high aspect ratio assists for filler orientation in fiber spinning. The single fiber tensile behavior which shows improved fiber modulus and toughness elucidate the EMforce possess supreme load transfer functionality. Since by the shear stress in fiber spinning may preferentially induce long axis keep the same orientation as polymer melt flow, the crystal growing in the spinning incline to have more fiber axis oriented. As fiber orientation is enhanced at 2.5%, the fiber modulus, yield strength increases, but elongation at breaking decreases that resulted into high modulus-low compliance, high strength-low strain of fibers. For fibers contained with PCC-SF fiber polymer orientation is regarded to reach to a higher level, there is one reason from the higher toughness at 2.5%, but also from the outstanding fiber modulus with 10% of loading (Table 4-6). Large specific surface area relatively overcome the craze forming at the perimeter of fillers; especially reduce the amount of cavity forming in melt spinning around cubic fillers.

We hypothesize filler particles are able to freely flip in 360° in a low viscous polymer melt, and assume material of calcium carbonate withstand shear deformation so that can be regarded as rigid needles or spheres. So as polymer jet flow are spinning from spinneret to the high pressure aspirator chamber, the particle with momentum to move downward even as
polymer is softened. In the subsequent drawing, polymers underwent a plastic deformation, with the rigid particles anchored inside of each fiber. Both momentum motion and shear deformation in spinning crack polymer materials around rigid CaCO$_3$ particles, forming shallow split as shown in Figure 4-7(c) and (d). Filler hardness is important in composite failure mechanism, according to George, hard spheres like glass beads exert different bonding mechanism with polymer matrix from soft particles like rubber $^{[25]}$. It was found that stress tend to transfer through the hard particles from the matrix as opposed to a little transfer with soft ones. In rubber spheres reinforced epoxy composite, based on Guild and Young, rubber modulus gives a slight impact on the composite modulus, but more act as holes within the epoxy with a debonding tendency as matrix are easily deformed $^{[26]}$.

![Stress-strain behavior of three types of filler at loading of 2.5%](image)

Figure 4-18: Stress-strain curves of single fiber tensile containing 2.5% of fillers: EMforce (EM), Superpflex (SF) and FiberLink (FC).
In polymer elongational deformation, phase separation at filler/polymer may occur ahead of time before the polymer is eventually broken down. This separation initializes at the pole direction along the tensile force direction \cite{9}, and starts from the relative weak interphase region where matrix is not capable to hold with particular fillers. As shown in Figure 4-4 (a) and 4-16 (f), there are micro-voids embedded in the GCC filled fiber samples. This phenomenon, according to previous works, is referred as filler debonding \cite{9, 27}, that separation of filler from matrix occur before shear yielding of polymer and further strain of blended phases cannot keep simultaneous elongation as polymer phase because they have apparent different Poisson ratio. This phenomenon also happen during the following single fiber tensile behavior that stretching the ligament out of the folded lamellae phases reform the status in stress distribution around fine particles, mainly perform multiple voids around the dispersed particles (Fig. 20.a). The interfacial voids overcome the stress concentration during stretching, and the following debonding with relative movement between polymer chain segments sliding through rigid particles, such defining shear yielding will dissipate fracture energy to avoid devastating breakage \cite{28}. That larger particle size with smaller specific surface area tend to weaken the interfacial bonding that cause debonding during the subsequent drawing of fibers. While for finer particles, the relative contacting area could reach down to nano scale that compare to the micron size range of fiber diameter. As compare GCC with PCC-Superpflex, filler size $d_{50}$ to $d_{90}$ drops down from 2.3 to 5.2μm to 0.38 to 1μm, accompanied with fiber tenacity weaken severely at 2.5% and 10% for GCC (Figure 4-13). From fiber surface bumpiness of GCC filled PP, top cut or cluster of larger ones bold out from certain cross-sectional phases in spinning, resulting in spinning strength
declines. While the tenacity of PCC spherical fillers with 0.38μm, still maintain relative higher fiber tenacity up to 10% indicating less interfacial weak linkage existing inside of fibers. However, keep increasing loading of fine particles resulted into severe deterioration in tenacity of fibers as appeared with 25% of PCC-SF in the spinline (Fig. 4-13a, Fig. 4-19a). This should because of accumulated of small voids forming such interconnected pore canal, because of the isotropic feature of SF fillers, those pores could be distribute tri-axially inside of fiber, which eventually resulted stress amplify along the plane bearing larger amount of clusters [27, 34]. While for PCC-EM the internal long slit form of voids tend to perform certain anisotropic characteristics as shown in Figure 4-20 (b), lateral compression from the polymer to the filler will mainly bear craze along the pole of the needle-like particles.
Figure 4-19: Filler particle interface with polypropylene matrix with microvoids surround filler particles.
Figure 4-20: Cavity formation as debonding occurs at interface of spherical particles (a) and needle-shape particles (b).

Fiber tensile breaking represent spin forming fiber polymer structure mingled with types of CaCO₃ at varying of filler particle size. Superpflex improve fiber tenacity with a decreasing void size surround those fine particles. If assuming filler loading concentration is constant at the same level, loading above 10% reduce fiber tenacity because of more fiber defects inside of structure. Since fillers are interacting with polypropylene matrix at certain volume range, it is regarded with high specific surface area for smaller particle size that will provide more interactive area within the polymer matrix. It has been claimed that mineral fillers volume fraction, particle size and surface chemistry will all contribute to a particular filled polymer molded composite [29, 30]. Elastic modulus of plastics filled with inorganic fillers increases, but the breaking strength is decreasing with filler loading [1]. From point of particle inertia in polymer jet flow below spinneret, with higher density and comparatively larger particle size,
the flow pattern around main plane of fillers tend to be rearranged which will have dominant 
\( z \)-axis pattern extended along spin direction.

\[
\sigma_T = \sigma_{T0} \lambda^n \frac{1 - \phi_f}{1 + 2.5 \phi_f} \exp \left( B_\sigma \phi_f \right) 
\]

(5)

\( \phi_f \) is the volume fraction of the filler, \( \lambda \) is relative elongation, \( \lambda = L/L_0 \); \( \sigma_T \) is true stress of materials; \( \sigma_{T0} \) is the true tensile strength of the matrix polymer; \( n \) characterizes the strain hardening tendency of the matrix. Parameter \( B_\sigma \) reflects the effect of the interaction between filler and matrix, included in the equation:

\[
B = (1 + A_f \rho_f l) \ln \frac{\sigma_T}{\sigma_{T0}} 
\]

(6)

where \( A_f \) is specific surface area of filler, \( \rho_f \) is the filler density, \( l \) is the thickness of interface. Surface coating applied to filler particles is aimed to solve the dispersion problem in miscible system and enhance interphase interaction between polymer and inorganic fillers. Surfactant or coupling agent is help with associate two phases and disperse particles into the non-polar polymer solution. From the good dispersion as shown in Figure 4-4 and 4-19, there must be sufficient wetting on GCC and PCCs in the melt blending and extruding. Based on factory supplied masterbatch, FiberLink 201S is treated with 1-1.5\% of stearic acid. Superpflex 200 is treated with 2\% stearic acid. From the patent by Wernett, coating to EMforce is preferably with fatty acid as well in 2.4~4.3\% which is larger than Superpflex \cite{18}. So we interpret the better toughening effect to EM than SF is not just contributed to the larger specific surface area, also the fatty acid coating generate such densely packed alkyl branches which absorb polypropylene chain molecules in the polymer melt. Wernett and Fekete both pointed out tensile strength of composites decreases with increasing surface
coverage of stearic acid; however it obtain higher ductility in the deformation which means the elongation at breaking increases correspondingly \cite{18, 20}. In our result, tensile behavior of fiber material is corresponded to the ductile performance at spherical SF fillers embedded up to 25\% (Table 4-6, Figure 4-12b), that fiber material with much finer cross-section achieve longer extension at same testing condition is attributed to the larger specific surface area where larger amount of stearic acid will connect with polymer wormlike reparation and form an immobilized interphase protection. Nakatsuka et al. have claimed an interfacial bonding form after surface treating with phosphate coupling agent which should be regarded as the dominant factor for GCC (7.74 m\(^2\)/g) reinforcement to vulcanized styrene-butadiene rubber \cite{21}.

Melt viscosity at fiber spinning associate with viscoelasticity of polypropylene with the filler particle size, shape and the interfacial adhesion. Stearic acid coated calcium carbonate particle can overcome the cohesiveness in the hydrophobic solution, and the dispersed filler system is an assumption to estimate the filler concentration effect on the shear viscosity under steady state polymer. The melt viscosity of zero viscosity based on Einstein theory is related to the volume fraction (\(\phi\)) of spherical particles.

\[ \eta_c = \eta_m(1 + 2.5\phi) \]  

(7)

However, this equation is only applicable to suspensions where particles are not interacting in behavior as Newtonian liquid. In non-Newtonian behavior such as shear thinning in fiber melt spinning, high shear rate can influence the melt viscosity of blended phase; even though
suspended particle tend to form interparticle steric repulsion after surface treatment, they are still increase the melt viscosity as hinder from those suspended particles on the flexibility of chain molecules, especially when polymer is less oriented at low shear rate. Such hindering mainly behave as the normal stress impose onto the wormlike polymer molecules. The true loading $\phi$ is related to the relaxation time $\tilde{\tau}$ as well as normal stress in the flow jet:

$$\frac{\tilde{\tau}(\phi, \dot{\gamma})}{\tilde{\tau}(0, \dot{\gamma})} = 1 + A(\dot{\gamma})\phi + B(\dot{\gamma})\phi^2 + \cdots$$  \hspace{1cm} (8)

And normal stress coefficient $\Psi_1$ is also shear rate $\dot{\gamma}$ dependent, that at fixed $\dot{\gamma}$, increasing the filler loading $\phi$ result in a higher $\Psi_1$, but reduce the elastic memory of polymer melt, so that relaxation time for filler contained system will be extended with high $\phi$. It was also found by Minagawa and White that addition of fillers decreases the melt elasticity, reduce extrudate swell and smoothen the polymer flow, therefore modify the extrudate distortion in polymer extrusion \cite{22}. As shear rate is swiping up to 10,000 s$^{-1}$, the range above 1000 s$^{-1}$ is approximately mimicking fiber extrusion related problem in the elongation viscosity. The elongation viscosity is greatly decreased as temperature cool down in the quenching chamber. With $\phi$ increase, polymer volume $(1-\phi)$ decreased, so the viscoelastic motion of polymer jet start to surrender with a viscous flow with less flexibility. Up to certain points, further loading $\phi$ will cause the spinning instability such as fiber breakage and melt dripping; practically the weight fraction usually comes at 10\% for PCC and 30\% for GCC.

The particle size distribution determines packing geometry within polymer. Maximum packing fraction $\phi_{max}$ of polydispersed suspension describes the true volume of particles
divided by apparent volume occupied in the system, based on equation (5), the larger the \( \phi_{max} \), the lower the polymer viscosity at same \( \phi \)[23]. In a bimodal distribution, particle size composes of relatively large size particle portion and a fine size portion. Inter-particle spacing is proportional to filler particle diameter, so those larger spaced left by the stacking of larger fillers could be filled out by finer fillers. The efficiency of filler particle packing is a predominant factor to increase the true loading volume in fibers. Usually, mono-disperse particles fillers has the lowest pack fraction at maximum. As to PCC-SF, as its particle size distribution is narrow and less than 0.6μm, resulting in polymer extrusion evoke some agglomeration issue dependent on \( \Phi_f \). It is estimated that bimodal GCC (1μm) reach to 0.55 maximum packing fraction in mineral oil, GCC (3μm) can pack up to 0.59; while mono-model PCC (1μm) only can reach maximum packing at 0.44 compare with 0.6μm PCC packed as low as 0.3 [24]. Theoretic results show that the \( \phi_{max} \) is dependent on polydispersity, from minimum to maximum packing fraction are in a sequence as mono-dispersed < bimodal dispersed < tri-modal dispersed system, according to Genovese [23].

\[
\ln \frac{\eta}{\eta_0} = \frac{[\eta]\phi_n}{\sigma-1} \left( \frac{\phi_n-\phi}{\phi_n} \right)^{1-\sigma} - 1
\]  

(9)

where \( \sigma \) is particle interaction coefficient, \( \eta \) is the suspension viscosity, \( \eta_0 \) is medium viscosity, \([\eta]\) is the intrinsic viscosity, \( \phi_n \) is the particle packing fraction. During fiber spinning process, when loading is exceeding certain level strain hardening may happen due to higher elongation rate, which may cause melt fracture below the spinpack [12]. With a sufficient packing of particles in polymer extrusion, as GCC fillers loaded up to 20~30 wt. %
of loading, polymer jet is keeping a flexible elongation deformation without much instability at the spinneret. As shear rate $\dot{\gamma}$ shoot up, the particulate fillers undergo compaction that different particulate shape respond to jet strain with a consolidated packing into an interconnected filler network in fibers. At this time, anisotropic filler particle, such as EMforce, may run the main axis compliance to the shear stress. One of the features of inorganic particulate fillers, aspect ratio, dominates the spinning filler alignment and further impact the filler reinforcement in fibers. As previously mention, EMforce has toughened the polymer structure and performed larger tensile strength. This mainly contributed to the uniform alignment of needle-shape particles along spinline which enhance polypropylene molecule orientation and shear-induced crystallization. Although shear viscosity for EMforce filled is above GCC filled, but at high shear rate, the evidence shown in Figure 4-21 has strongly indicated overlapping on the viscosity curve of PCC above 2000 s$^{-1}$ as GCC-FL show in the plot. This could because of a better alignment along the flow curve for such needle-shape particles that reduce the friction with polypropylene, especially when elongational stress highly oriented molecular chains along the flow jet, this help with the needle shape particle to anchor along the fiber direction.
When fillers go into fibers and with fiber laid into nonwoven webs, the bonding strength at 135°C has not differentiate the average tensile strength among the different types of CaCO$_3$ fillers. However, larger standard deviation comes along with 10% loading of GCC in MD strength with the peak load increase up by 5 lbs comparing to without additive loaded. It elucidates the function of using such fibers with its surface roughened lay down into nonwoven convey belt by forming a changed fiber-fiber friction which may reinforce the packing within the web. So that when pulled fibers out of the structure, the larger restriction from fiber to fiber interlocking by increasing the coefficient of friction become the possible reason to improve the peak load for GCC contained fibers. Large particle size modify the

Figure 4-21: Shear viscosity of polymer filled with 5% FiberLink, 2.5% EMforce and 5% Superpflex compare with polypropylene control resin.
attenuated fibers by forming a conjugated structure in 16μm circular dimension with 2~10μm inorganic phases randomly distributed within. Unless a significant weak spots appears fabrics will keep the breaking strength even if fibers are deteriorated (Fig. 4-15). On the other hand, we notice a different breaking mechanism for CD and MD as shown in SEM graph in Figure 4-16 (a) and (b), bonds stretch in accompany with stress pulling onto bridge fibers when any singular fiber broken will not affect the stress transfer in the assembly of fibers. Ruptured bonds may eventually break fabrics in MD, however the stress propagation in CD will be faster because of less fiber oriented distribution. Thus the fiber internal defects result into fabric strength deterioration in CD, especially for GCC fillers when the stress concentration increases which significantly increases fraction of top cut above 10μm. Such defects have been already revealed in melt spinning, which mainly involved in FiberLink filled PP fibers showing dispersed cavities around fillers. Therefore, fiber toughness and tenacity decrease as at smaller carrying area stress concentrated on the limited cross-sectional compartment, which form discontinuous phases if those cavity around separate the interfacial linkage.

4.5. CONCLUSION AND SUMMARY

We approach to the structure-properties study by conducting fiber melt spinning containing a type of GCC and two types of PCC. The particle size distribution for GCC ranges from 0.5 to 10μm, while PCC particle size is less than 1μm, among them the one with larger aspect ratio significantly improve single fiber modulus, tenacity and toughness. Fabric tensile strength in cross direction is also reinforced by adding the filler particle with large aspect ratio. While the other PCC with 0.38μm average diameter can effectively decreases the voids dimension
at interfacial between spherical particles embedded in fibers. The toughening effect on fiber structure mainly behave with higher tenacity and toughness at lower than 10% of loading, which already form large amount of microvoids in GCC filled fibers. Although SF possess with finer particle size than GCC, from single fiber tensile strength both fillers induce similar mechanism, while SF filled fiber tend to behave with higher modulus especially at 2.5%~10% and larger fiber diameter as well. It indicated the fillers particle function as reinforce agent in thermal calendar bonded fabrics, polymer chain elongation slide with the high specific surface area of particle fillers by pulling out sufficient strong fibrils surround the filler area (Fig. 4-16).

GCC has mainly generated an abundant amount of microvoids around fillers embedded in fibers, although yield interfacial adhesion and cause decrease in fiber tenacity, fabric tensile strength is maintained after thermal bonding. Comparing to PCC, GCC is capable to be added increased level of loading up to 30% without causing severe high pump pressure issue caused by high shear viscosity. Although the melt viscosity of needle-shaped PCC is higher than GCC in low shear rate range, as shoot up the shear rate, it almost reduced the polymer shear viscosity at the same level as GCC contained polymer. Thermal stability of polymer is also improved with loading with inorganic fillers calcium carbonate, especially to PCC-EM, mainly resulted in higher on-set degradation temperature.
REFERENCES


CHAPTER 5  Bonding Mechanism Study based on Inorganic Particulate

Filler added Spunbond Nonwoven – Processing, Bonding Structure and Mechanical Property

ABSTRACT

Spunbond nonwovens combine thermoplastic polymer material adding with functional additives, pigments and fillers, changing web bonding structure and producing a variety of fabric products meeting with certain applications. By web formation and thermal bonding, fibers transform from singular cylinder geometry into two to three-dimensional fibrous web, each unit of fibers in isotropic distribution contribute to the whole structure integrity of fibrous geometry. Thermal calendar temperature varies from 130˚C to 150˚C gives spunbond a different melting and recrystallization behavior. Our primary results show loading CaCO$_3$ from 2.5% to 20% keep at the optimum tensile strength, while decreasing tear strength. Filler adding with polypropylene has lower heat capacity which transfer heat efficiently and lower the calendar bonding optimum temperature. Heat capacity is characterized by using Modulated Differential Scanning Calorimeter (DSC). Bonding structure is mainly studied by using scanning electron microscopy (SEM) that reveal the impact of heat on bonding area from different bonding mechanism influenced by temperature.

Key Words: Calcium Carbonate Filler, Spunbond, Thermal Calendaring, Bonding Mechanism, Heat Capacity
5.1. INTRODUCTION

Spunbond is a traditional technique in nonwovens that polymers such as thermoplastics undergo a continuous process from spinning, quenching, attenuation, web laid down formation and web bonding in fast speed and low energy cost. Mechanical bonding, thermal bonding and chemical bonding offer different options in web bonding process, and its structure and property both influenced by the interaction between fiber material and porous structure formed by consolidation methods. Additives are mainly applied as processing agent, thermal stabilizer, or nucleating agent to support required property improvement for polymer resin, which include but not limited to Polypropylene (PP), Polyethylene (PE), Polyester (PET), nylon, elastomer and co-polymer. In some cases, adding inorganic fillers is for the purpose of lowering cost of raw material. Since spunbond with high output, low cost, very flexible to different species of polymer material, which gives broad options for adding innovative additives to aiding the process. Previous work has mentioned by combining inorganic particulate fillers such as titanium dioxide with thermoplastic polymers will achieve the desire brightness to the nonwoven fabrics \cite{8,10-11}, which add value in cloth-like fabrics by using inorganic filler particles.

Calcium carbonate (CaCO$_3$) fillers is regarded as a cost efficient filler applied in plastic molding \cite{1,2}, film extrusion \cite{3,4}, papermaking \cite{5}, painting and coating \cite{6,7}. More than that, previous arts in patents and literatures involve a number of techniques that applied inorganic fillers in fiber spinning and spunmelt. Nonwoven is seeking for the economic benefit from inorganic fillers that has lower cost than resin cost, at the same time advocating the lower
carbon footprint of CaCO₃ fillers over petroleum based polymer resins [11]. Products relevant to wipes, hygiene, masks and many kinds of disposable nonwovens will be potential market to adding in the value of CaCO₃ to the vast scale of production. Because more significantly, fillers may give cloth-like soft to fabrics with comparable brightness and whiteness as other more expensive additives such as titanium dioxide [8-11]. However, the spunmelt processing confront challenge in how to minimize the deterioration in fiber structure and obtain the desired fabric performance without sacrificing the processability. In this category, incorporated with CaCO₃ fillers into spunbond fibers could break in the continuity in polymer extrusion, cause low melt strength and frequent breakage. Some of pioneering works have mentioned about spunlaid by McAmish and spunbond technique by Borneman and Harberer [11, 26], as well as flash-spun by Rollin [9], but more unsolved problems still existed in specific structure-property relationship, especially on mechanical property related to different loading of CaCO₃ fillers. Mineral filler CaCO₃ are with higher density 2.7 g/cm³ compare to polypropylene at 0.9 g/cm³, resulting in theoretical density of polymer blend should be increasing with filler loading concentration. However, previous characterization based on biaxial drawn film indicated structure become thinner and lighter because an inter-phase debonding at periphery of particles, generating microporous structure [4, 12-13]. It is suspected that adding higher density filler particles affect fiber theoretical density and particle packing density in fiber spinning, then when these fibers form into web, the web will perform differently based on the thermal bonding conditions. Therefore, the relevant mechanical properties of thermal bonding fabrics should be closely related with the amount of inorganic particles loaded in fibers and calendar bonding condition [18].
In thermal bonding, inorganic fillers have impact on polymer melting and crystallization behavior because of the heterogeneous in nucleating and crystal growing. Upon heat, the crystal with less perfection in fibers are melted and recrystallized into larger crystals. As studied before in injection molded plastic, adding inorganic particles such as mica and talc change polymer thermal conductivity and greatly increase melting-cooling-melting circling time, and greatly shorten the time for de-molding\textsuperscript{[14]}. It should not be missing one point in the nucleating ability of fine particles on polymer crystallization\textsuperscript{[15]}. Thermal bonding fabrics from previous study cover a variety of processing parameters –calendar roll temperature, line velocity, calendar pressure and calendar emboss coverage\textsuperscript{[16, 17]}. Different factors affecting fiber polymer crystalline and fiber stress distribution in nonwovens were investigated to explain fabric failure mechanisms\textsuperscript{[18, 19]}.

Furthermore, two phase system in thermal calendar bonding must also be taken into consideration of crack formation at weak interphase at filler-polymer mixing phase\textsuperscript{[24]}. Fiber strength distinctively drops with filler concentration, that initially partially decreases up to 5 wt. % followed by deterioration above 20 wt.\% in previous discussion. The prominence work by Farukh et al. applied finite element model to characterizing breakage of thermal bonded fabrics by considering fiber to fiber interaction as well as fiber orientation distribution in the spunbond web\textsuperscript{[20]}. What accepted in theory of composite material is that stress concentration followed by debonding influence the mechanical property from micro scale to macro scale. At bonding points, calendar rolls conduct heat by emboss area that partial melt polymers
chains in fibers and join together upon cooling and recrystallizing. The bonding periphery performs with structural gradient within the transforming region where fiber lamellae crystalline structure is gradually softened and reformed into larger crystallites \cite{17, 18}. The periphery regions could result into stress concentration that initialize crack around weak fiber bundles. However, there have not implied any fabric breaking mechanism regarding to inorganic component of CaCO$_3$ filler thermally bonded nonwoven structure. Although weakened interface forms in fiber material with CaCO$_3$ incorporation as discussed in previous chapter, the contribution to fabric strength is a combination of fibers as well as bonds. In this paper, the main goal is to find the breaking mechanism of inorganic fillers added spunbond nonwoven structure, and to obtain insights in spunbond fabric structure and mechanical properties added with CaCO$_3$ fillers.

5.2. EXPERIMENT

5.2.1. Mono-component Spunbond

Web is formed by 0.5 Meter Bicomponent Spunbond Line (Hills - Nordson) in the pilot plant of The Nonwovens Institute (Raleigh, NC). Two extruders convey polymer material into spinneret. Polymer is blend with calcium carbonate masterbatch in certain ratio, melting and mixing in screw extruder, and filtered out of any impurities, thereafter, the polymer is pumped out at 0.6 ghm to the spinneret. Technical index of spunbond process include speed, temperature and pressure of calendar are included in Table 5-1. Calendar rolls is connected with web forming belt which mainly conveys web into thermal bonding regions. Calendar is controlled at five temperatures levels: 130°C, 135°C, 140°C, 145°C and 150°C. Double-roll
calendar has one embossed roll with oval pattern nips at 18% of point coverage, and another smooth roll has equal calendar temperature as the embossed roll.

Calcium carbonate filler focus on using GCC filler types - FiberLink (FL). Filler weight concentration varies from 2.5%, 10%, 20% to 30%. Web bonding takes place at each of five levels of calendar roll temperature and the bonded fabrics are first cooled down to room temperature followed by a winding up into rollers. Fabric spunbond into 50 gsm and 100 gsm, composed with fibers made with constant mass throughput (0.6 ghm) but varied in volumetric throughput after taking the melt density into account (Appendix Table 3-8). A higher throughput level is set at 0.8 ghm only produced for 50 gsm fabrics.

Figure 5-1: Schematic graph of spunbond (Hills - Nordson with Bicomponent Technique) [22]
Table 5-1: Temperature and Speed Profiles of Spunbond and Calendar Bonding:

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>Primary core</th>
<th>Secondary sheath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruder Zone 1-Zone 6</td>
<td>Zone 1-Zone 5</td>
<td>Zone 1-Zone 5</td>
</tr>
<tr>
<td>Spinhead</td>
<td>465</td>
<td></td>
</tr>
<tr>
<td>Quench air</td>
<td>40%</td>
<td></td>
</tr>
<tr>
<td>Speed</td>
<td>Throughput</td>
<td>0.3 ghm</td>
</tr>
<tr>
<td>Quench air</td>
<td>25%, 1055 RPM</td>
<td></td>
</tr>
<tr>
<td>Aspirator Fan</td>
<td>45%, 1619 RPM</td>
<td></td>
</tr>
<tr>
<td>Calendar pressure</td>
<td>750 psi</td>
<td></td>
</tr>
</tbody>
</table>

5.2.2. Fabric Characterization

Grab Tensile Behavior

Five samples for each MD and CD are tested using the United Grab Tensile Tester based on standard ASTM D5034. Testing used the type of CRE operating at speed of 300mm/min and tester records the breaking strength as well elongation at breaking for each sample.

Tongue Tear Test

Tongue tear strength is also tested on United Tester with an 8 inch gape length. The testing method is according to ASTM D 5737. Samples were measured on MD and CD two directions in 8 by 3 inch. At least five samples were tested and record the tear strength.
**Scanning Electronic Microscopy (SEM)**

Fiber spunbond structures are imaged using Phenon SEM from the Nonwovens Institute physical testing lab. From platinum coated fibrous samples, we are able to measure fiber diameter using Image J from the SEM pictures. Bonding structure is also characterized both from top view and lateral view. The breaking spot of those tensile test fabric samples are evaluated as well. From varying of magnified from 400x to 20,000x, our view perspective covers from a general fiber orientation to particulate fillers hanging on fiber surface. On web bonding morphology, one interesting part is the cross-section to view the web mid-plane under embossed region. So by using liquid nitrogen, fabric samples are cut in transverse direction across several patterned bonds.

**Differential Scanning Calorimeter (DSC)**

The melting and crystallization behavior of the filaments samples were analyzed by Discovery TA Instrument Differential Scanning Calorimetry (DSC). All samples were first heated at 10°C or 20°C/min from 25°C to 195°C, followed by cooling at 10°C/min rate. Thermograms were obtained from DSC analyzed with the Trios software. Crystallinity is calculated from endothermic peak, which reveal fiber crystallinity developed in spinning. Crystallinity is calculated based on equation:

\[
\chi_c (% \text{crystallinity}) = \frac{\Delta H_m}{\Delta H^0_m} \omega \times 100\%
\]  

(1)
Where $\Delta H_m^0$ is the heat of fusion (165 J/g) for 100% iPP; $\Delta H_m$ is the heat fusion per unit gram of fiber sample; $\omega$ is weight concentration of PP added with spunbond fiber.

**Modulated DSC**

Calibration of MDSC used sapphire on TA Discovery DSC instrument. Fiber samples weighing of 10~15mg are prepared using aluminum pan. Modulation method based on ASTM E2716, setting heat rate at 2°C/min, 100s modulation period, ±1°C amplitude, and ramping from 25°C to 230°C. Then we record the normalized modulated heat flow curve and using derivative of modulated temperature curve, thus we have the amplitude of heat flow (W/g) and amplitude of heat rate (°C/min).

Heat capacity of PP fibers is measured as control, and ground calcium carbonate raw material with stearic acid coating was measure as 100% of filler, and PP with different amount of calcium carbonate filler (5~30%) was measured and compared with the values calculated based on the Rule of Mixture:

$$C_{p-k\%} = C_{p-PP} \times (100 - k) + C_{p-c\text{aCO}_3} \times k$$

(2)

Where $C_{p-k\%}$ is the specific heat capacity of PP containing with k% (wt.%) of calcium carbonate filler. $C_{p-PP}$ is the specific heat capacity of PP fiber, and $C_{p-c\text{aCO}_3}$ is the heat capacity of calcium carbonate powder.
**Thermal Gravimetric Analysis (TGA)**

Fiber thermal degradation property was tested using TA TGA Instrument. A fabric sample, around 10mg, was put into a platinum plate which is attached to a micro balance. Samples were heated up from 25°C to 600°C in a rate of 20°C/min with a gas supplement using nitrogen. Then sample weight in percent is plotted with increasing temperature, which illustrates the thermal degradation behavior.

**Fabric Bending Rigidity**

Flexural rigidity characterizes fabric stiffness in bending along MD or CD. A sample overhang length is measured when tip of sample touch down to a slope which has 45° angle with horizontal platform. Four measurements record the value to make sure every time reverse specimen from the front or the back. This avoid error during testing because some fabric may double surface effect. For each sample, four specimen for MD and CD, in sample size 8”by 1” (200mm by 25mm) based on ASTM D-1388-14. After testing, sample weight is measured as $W_0$ and result into basis weight $W$ (g/cm²) based on calculation.

$$ W = \frac{W_0}{5.1628} \quad (4) $$

Bending length is related with overhand length as $c=O/2$. Where $c$ is bending length (mm); and $O$ is overhang length, both in mm. Flexural rigidity is calculated from equation

$$ G = 1.421 \times 10^{-5} \times W \times c^3 \quad (5) $$

Where $G$ is under unit of μjoule/m.
5.3. RESULTS AND DISCUSSION

To begin with fiber web mechanical properties, let us first consider about friction force by pulling single fiber out of a consolidated web structure. This fiber swirls in a random path that as long as it spun from the spunbond system. As many of these embedded in a nonwoven structure, loading CaCO₃ fillers into melt extrusion not only change fiber structure, but also change whole fabric structure. Nonwoven with thermal point bonded patterns respond to deformation with fiber reorientation in the web. As calendar temperature is close to on-set melting temperature of polymer, fibers under embossed compression are melted and those imperfect crystalline phases recrystallized upon cooling. The reformed polymers will be melting fiber crystals and recrystallize into new form of big crystallites. Synergetic effect of fibers and bonds define the fabric failure strength and how much extension fiber pulled apart before maximum load is reached.
What has been found in previous chapters that fiber polymeric structure is influenced by loading GCC FiberLink (FL) which has a cubic particular shape with an average particle size of 2.28μm. In varying of concentration from 5%~30%, fiber tenacity is continuously decreasing but the strain at breaking is unaffected up to 15%. Lower value in fiber tenacity indicated adding filler caused structural defects that increase the possibility of breakage, so that fiber breaks at lower tensile strength. But stress reduction in a strand like element must be put into a two dimensional webs that transfer through the connections with those bonds. In between bonding regions, bridge fibers functional as transverse connection which will mainly conduct the stress transfer through the fiber network.

Figure 5-2: Single fiber tensile properties with varying level of GCC-FL concentrations.
5.3.1. **Grab Tensile Behavior**

Optimum bonding effect achieve at different calendar temperature for varying of loading concentration of CaCO$_3$ fillers. Tensile strength after incorporating of CaCO$_3$ fillers is keeping at same level as polypropylene fabrics as shown in Figure 5-5. Melted fiber junctions under point nips form with stronger bonds as temperature increases and improve tensile strength (Figure 5-3). At higher temperature over-bonding may cause fabric strength level down at higher strain at breaking, especially when concentration reaches to 30% (Figure 5-4). This over-bonding mechanism occurs most likely when loading amount of CaCO$_3$ exceed 10%, at temperature at 140~145°C, as bonding. When heat diffusion transfer through the emboss area at 140°C~150°C, Polypropylene control keep leveling up the strength up to 150°C, but 10~20% of CaCO$_3$ in Polypropylene already achieve the optimum bonding at 140°C. Optimum of PP fabric strength hit at 72 Lbs in MD comparing to PP containing with 20% CaCO$_3$. If define the temperature achieve optimum bonding condition as $T_o$, then calendar temperature $T_c$ will cause reduction in strength and elongation where $T_c$ is higher than $T_o$ because of over bonding. For CaCO$_3$ filler contained spunbond fabrics, same bonding strength with higher elongation will be achieved at lower $T_o$.

Therefore, bonding mechanism of fiber web is determined by polymer morphology deformation in compatible with filler particles. Without sufficient bonding temperature, fibers will not completely soften its crystallites but only partially melt the smaller crystals and amorphous. But adding inorganic fillers tend to randomize polymer chain orientation in fibers, which give higher probability to soften the semi-crystalline at a lower calendar
temperature \(^{[17]}\). Polypropylene chains overcome the steric barrier from fiber structure with inner energy increase, forming reptation across fiber to the adjacent fiber at contacting points. On another point, the tacky polymer molecular chains which are released from crystallites will respond to heat much faster especially under the compression. As we know, thermal point bonding at the \(T_o\) is lower than the melting temperature of the fibers. For example, DSC melting peak find polypropylene spunbond is with melting temperature \((T_m)\) at 159°C (Table 5-3). Fabrics failure comes earlier as mentioned at over-bonded temperature (145~150°C), even undesired rigidity and sticky plastic-feel of fabric replace of softness contacting to skin \(^{[8]}\). Adding CaCO\(_3\) fillers contribute to modify fiber surface texture and improve softness by “feeling” the rubbing from skin to uneven fibers and roughen fabric structure. Furthermore, since bonding temperature is relatively lowered by adding calcium carbonate so that fabric stiffness is replaced with softness.

Bonding structure of spunbond fiber web can also be interpreted from the lateral view of the webs. It defines three possible mechanisms: under bonding, optimum bonding and over bonding. If we define mid-plane fibers as those keep farthest from heat sources (calendar surface), which stay covered relative to an upper layer of fibers connecting to embossed points and bottom layer contacting with the smooth calendar roll surface. As shown in Figure 5-6, inorganic filler as to fiber web is like a thermal conductive carrier which stimulate bond forming dense locking from each side of the layer to the mid-plane, then fibers in the mid-plane are fused sufficiently and form into an integral with plastic bonding area. Under-bonded fabric structure does not restrict fibers from segregating from bonding region, as PP
fabric bonded under 145°C which cause fiber directly segregate out of the bonding region. Adding fillers into fabrics help to transfer load within the web by fiber to fiber friction, as fiber possess with rough bumpy surface illustrated in Figure 5-9 (e, f). An effective bonding can form with loading of 10-20% of fillers at 140 °C in 100 gsm fabric, comparatively, as thickness for 50 gsm fabric is decreasing, impact of heat through the bonding region is enhanced so that 135°C can be applied for 20% of CaCO₃ (Table 5-2). Inorganic fillers help develop a well bonded fabric through lateral dimension to the mid-plane of the fabric, which start to be effective for 2.5% of filler in 50 gsm and 10% of filler in 100 gsm fabric. We found that $T_o$ decrease by 5°C at a little filler incorporate (2.5%) made into 50 gsm PP spunbond fabric. Compare with PP (50 gsm) fabrics, tensile curves included in Figure 5-7 (a, b) support the strength as fabric stretch to the peak load can be reinforced by loading a small amount of fillers, which extend the strain at breaking compare with PP fabrics. In both situations, the peak load and strain over the peak stress support the function of CaCO₃ fillers to enhance the fibers entanglement. As previously results indicated shown in Figure 5-8, deterioration in secant modulus and yield strength both start from a small loading of CaCO₃ in single fibers. So in a fibrous structure, a fiber may yield to extensional and shearing force during fabric deformation relatively easily than fibers with higher modulus. That dominates in improving fabric deformability and flexibility in the grab tensile behavior in the bonded fabrics.
Figure 5-3: Grab tensile strength of spunbond containing with different amount of FL, compare to PP fibers (○), 2.5% (■), 10% (▲), 20% (●) and 30% (▲▲).
Figure 5-4: Fabric tensile % elongation at breaking at levels of bonding temperature. (Symbols are same as Figure 5-3)

Table 5-2: Temperature Profiles for Thermal Calendar Bonding Achieve at Optimum Fabric Breaking Strength:

<table>
<thead>
<tr>
<th>Optimum Bonding Temperature (°C)</th>
<th>PP</th>
<th>FiberLink GCC Concentration (°C)</th>
<th>2.5%</th>
<th>5%</th>
<th>10%</th>
<th>20%</th>
<th>30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 gsm</td>
<td>150</td>
<td>145</td>
<td>-</td>
<td>140</td>
<td>135</td>
<td>135</td>
<td></td>
</tr>
<tr>
<td>100 gsm</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>140</td>
<td>140</td>
<td>135</td>
<td></td>
</tr>
</tbody>
</table>

* 155°C for 100gsm has breaking strength at 74.92 Lbs with 35.6% compare to 150°C which has 75.96 Lbs with 37.1%.
Figure 5-5: Filler concentration effect on fabric optimum bonding strength and elongation at breaking, according to Table 5-2.
Figure 5-6: Schematic graph of lateral view of thermal bonded fabrics into mid-plane (a); Lateral view of 50 gsm spunbond SEM at 135°C bonding temperature with 10% of CaCO₃.
Figure 5-7: Tensile behavior of spunbond influenced by (a) and (b) 2.5 wt.% CaCO₃ filled fabrics at 135°C and 140°C; (c) and (d) compare PP with 10 wt.% CaCO₃ filled fabrics at 140°C and 145°C.
5.3.2. Heat Transferring Over Bonds

Adding fillers assist heat conducting through fiber material, which lowers the amount of energy to raise up the temperature of polypropylene to its melting temperature. Thermal conductivity for polypropylene and calcium carbonate are 0.5 W/(m·K) and 2.7 W/(m·K) respectively \textsuperscript{[14]}. From the view of lateral direction, as shown in the schematic graph in Figure 5-6, heat conduction from calendar surface to the web mid-plane in a faster pace so that decrease the energy input requirement. Heat transfer to polymer material respond to conformation relaxation in molecular level that adding particulate fillers increase the entropy level as that imposed by using higher bonding temperature. Calendar temperature is the
dominant factors as bonding regions composed of fibers tend to have a temperature-dependent viscoelasticity. If temperature is lower than the optimum temperature, chain molecules cannot be fully released to form the bonding, as shown in Figure 5-6 (b) behaves like insufficient melted fibers. The heat transfers through fabric thickness deform semi-crystalline structure, decrease the molecular orientation within the bonds \[18\]. Fusion of polymer not only penetrated into the mid-plane, but also expanded the whole bonding region. Web strength will be correspondingly improved with more fiber interlocking to form optimum strength level, as results showed in Figure 5-3 and Table 5-2. We also notice a reduction in strength at even higher loading at 30 wt.%, at which level the bonding temperature 135˚C is already high enough to form the bonds. Reduction in fabric strength is due to fiber structure defects at inorganic/organic interphase. Such defects behave as the over-bonding induced weak periphery around the bonds where polymer orientation gradient is sharply transit from higher orientation in fibers to a lower orientation in the bonds.

Between two bonding points of fabrics, heat expanded in different conducting rate out from center of embossed region. As heat transfer to fibers is dominated by contacting transfer from embossed metal surface to fibers by thermal conduction, then those bridge fibers located in in the valley between two embossed region, are impacted under thermal convection and radiation. Previous study by Michielsen et al. gave estimated duration time of fabrics in between calendar roll, is about 6.0-60 ms, or 8-20 ms in commercial scale \[17\]. Higher heat flux traverse through particulate added polymer will relatively increase heat transfer coefficient reach to the melting point. It has been estimated the time it takes for isotactic
Polypropylene webs mid-plane reach to 132°C is 7.3 ms and 6.0 ms as to calendar bonding under 143°C and 151°C, respectively \[17\]. Previous results by Wang and Michielsen has indicated higher point-bonding temperature caused reduction in mechanical strength substantially \[23\]. Because after polymer recrystallized the original lamellae structure in fibers cannot be regained, and fiber molecular orientation is destructed with no longer persistence in tensile strength. Therefore, web structure becomes less continuous from bonding area into bridge fibers, which may raise high risk of breaking at bonds periphery region. Continuous reduction in optimum bonding temperature for spunbond with different basis weight at 50 gsm and 100 gsm (Table 5-2), indicate if process spunbond web contain with CaCO\(_3\) but still at constant calendar roll temperature as same as PP fabric, bonding periphery region will have high probability to form weak structures. So calendar temperature should be adjusted to at least 5~10°C lower to keep a continuous orientation gradient decrease from bridge fibers into bonding regions.

Higher thermal conductivity is attributed to lower heat capacity of the blend phase of inorganic particles in polypropylene. Based on the rule of mixture in equation (3), polymer/filler blend ratio and the heat capacity of each part will add to the composite \(C_{p-composite}\), Figure 5-11. It was found the material heat capacity at specific temperature level is decreased with filler concentration. The experimental results is well manipulated by the rule of mixture when filler concentration above 10%.

\[
C_{p-composite} = \phi C_{p-CaCO_3} + (1 - \phi)C_{p-PP}
\]  

(3)
$C_{p-caco_3}$ is the heat capacity of powder form calcium carbonate which is 0.86 J/g·°C at 50°C, comparing to 1.96 J/g·°C for PP. $\phi$ is the weight fraction of CaCO$_3$ fillers. $C_{p-composite}$ is plotted in Figure 5-11 as theoretical heat capacity of calcium carbonate contained fiber samples. Roussell et al. reported that calcium carbonate fillers is with specific heat of 0.9 KJ/(Kg·K) whereas polyolefins is within the range from 1.8 to 2.4 KJ/(Kg·K)\textsuperscript{[14]}, which is consistent to our results characterized by modulated DSC. In the DSC the heat capacity is characterized from reverse heat flow that is related to the amplitude of oscillating heat flow curve to the amplitude of heat up rate. Lower heat capacity associated with amount of inorganic fillers that estimate how much thermal energy is reduced to raise up the system temperature by one unit of kelvin. Therefore, calcium carbonate fillers incorporation with polypropylene can induce more thermal energy transfer through the webs through the calendar nip regions. The temperature reach to on-set melting temperature will efficiently melt and bond polymer material underneath the bond. If we denote mid-plane temperature as $T_{mp}$, which is rising as embossed region started receiving heat diffusion through the web thickness in a finite amount of time. $T_{roll}$ as the calendar surface temperature, $T_{initial}$ gives spunbond initial temperature when it arrives at bonding regions between two calendar rolls. Then the temperature relationship can follow the model in equation (6).

$$T_{mp} = T_{roll} + 1.2733 \ (T_{initial} - T_{roll}) e^{-\pi^2a^2t/4L^2}$$  \quad (6)$$

$$\ln(T_{roll} - T_{mp}) = \ln1.2733 + \ln(T_{roll} - T_{initial}) - \frac{\pi^2a^2t}{4L^2}$$  \quad (7)$$

$$\alpha = \frac{k_p}{C_p}$$  \quad (8)$$
Based on equation (6), mid-plane temperature will eventually reach to the maximum temperature with time $t$, which at $t=0$ those fibers are still undisturbed by heat. $L$ is the half thickness of nip, $\alpha$ is the diffusivity, $C_p$ is heat capacity, $k$ is thermal conductivity, $\rho$ for iPP is $0.9$ g/cm$^3$, for $10\%$ CaCO$_3$ contained PP is $0.95$ g/cm$^3$.

Table 5-3: Temperature Profiles of Spunbond Webs in Calendar Nip Bonding Region:

<table>
<thead>
<tr>
<th>$T_{roll}$ (°C)</th>
<th>$\alpha$ (m$^2$/s)</th>
<th>$T_{initial}$ (°C)</th>
<th>$T_{mp}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>145</td>
<td>iPP=$2.9 \times 10^{-7}$</td>
<td>60</td>
<td>145</td>
</tr>
<tr>
<td>135</td>
<td>CaCO$_3$=$1.1 \times 10^{-6}$</td>
<td>60</td>
<td>135</td>
</tr>
</tbody>
</table>

We estimate the time duration time under nip pressure in calendar region is 60ms, and thermal diffusivity is calculated based on $10\%$ CaCO$_3$ filled fibers, difference between PP and CaCO$_3$ influences the heat penetration into mid-plane, but it is equilibrium at same level as $T_{roll}$, including in Table 5-3. We realize the amount of heat is sufficient to rise up the temperature to the same level as calendar surface at 60ms time window. So extent of bonding is determined by the subsequently cooling process after leaving the calendar region, when the relaxed polypropylene chains reduce the free energy level by forming into compacted crystallites. At lower temperature, polymer lamellae crystallites has not intact much but only modify partial small crystallites. Temperature derivative to time is a partial derivative of $r$ and $l$ as shown in equation (9):

$$\frac{dT}{dt} = \frac{k}{C_p \rho} \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial l^2} \right)$$
where \( r \) is the fiber radius and \( l \) is the fiber length throughout the bonds. Heat conducting along long strands of fibers also impacts the on-set crystallization temperature of impacted fibers. Polymer crystalline structure undergoes recrystallization process after web leaves from bonding region. With polymer form into different geometry of bonds, as shown in Figure 5-9, the evidence pointed that another possible correlation with filler loading concentration is the bonding region area. As fillers concentration goes up to 10%, the heat generated from crystallization transfer through the filler particles outwards, which may soften the fibers outside of perimeter (Figure 5-9 b and f). In this case, the on-set crystallization temperature will increase a couple of Degree Celsius, and will cause the polymer crystallized into smaller crystals. It is also attributed to heat radiation from calendaring that expands the bonding area that the released heat energy will impact the perimeter regions in the bonded fabrics (Figure 5-10). Heat radiation indirectly contributes to increase the entropy of the polypropylene fibers, especially when the calendar temperature is relatively higher, which increase the temperature at those bridge fibers and cause melt range expanded as shown in Figure 5-9c.

\[
q_{A\rightarrow B}^n = \beta (T_A^4 - T_B^4)
\]  

(10)  

\( \beta \) is heat radiation coefficient, \( T_A \) is the temperature of heat source, and \( T_B \) is the temperature of fabrics before calendaring. Amount of fusion correlated with temperature and weight fraction of filler comparably, fillers loading to 20% respond to more affected periphery fibers than 10% filled case.
Figure 5-9: SEM pictures of spunbond made of PP (a); 10%~30% CaCO₃ in PP (b) (c) (d); Bonding at 135°C in 50 gsm. Melt spun fibers roughened by 20% CaCO₃ loading (e). The bridge fibers (10%) with local fiber morphology changed due to heat radiation (140°C) (f).
Most of bridge fibers stay far from bonding regions do not go through chain relaxation even after exposure to thermal radiation. Bridge fibers maintain the fabric structure integrity as a soft and flexible medium, and functionalize as the stress transfer links between bonds. Since there are filler embedded inside of fibers, the heat conducting in plane will be conducted through those fibers. In the Figure 5-10, we can image the impact of heat from embossed area in a radial expansion to the adjacent bridge fibers, if without any inorganic component inside of polymer material, thermal energy from emboss metal surface will be dissipated quickly that only change structure beneath nip region, forming into the oval pattern of bonds. Whereas thermal conductivity from CaCO₃ fillers change the heat diffusion impact region from oval pattern to a circular region outwards. The imaginary circle is expanding from small area C1 to a relatively larger area C2, dimensions shown in Figure 5-10 is based on the assumption that heat transfer normal to major axis is supreme to the transverse along main axis, because the heat flux from center of ellipse encounter with larger resistance when it moves along major axis to the perimeter region.

Figure 5-10: Heat conducting from emboss pad center of bonding point to outside.
We found that sample melting temperature did not vary too much with filler concentration, peak width gradually narrow down a bit, with the fiber crystallinity at 140°C first incline up to the maximum at 10% and then decrease. The calendar temperature effect on fabric crystallinity is first increase from 130°C to 140°C, then decreasing as temperature up to 150°C. The optimum bonding temperature 140°C achieve larger fabric crystallinity, since recrystallization of bonded fibers grow into larger crystallites by packing regularly that transform part of amorphous regions into crystalline region. However crystallites phases in fiber structure keeps with higher crystallinity than recrystallized spunbond with a much lower level in $X_c$ (%) above 140°C. This phenomenon reveal that crystallinity get to the ultimate level at the optimum bonding temperature, above that temperature fiber crystallites melted but formed into a less amount of crystallinity into the bonded structure. Our results is in contradictory to the conclusion from Najudappa and Bhat who claimed both crystal size and crystallinity of bridge fibers become smaller than bonded fibers after bonding [18], they neglect the temperature effect on the overbonding of fibers that may reduce fabric crystallinity. However, the consistence result in smaller crystal size is confirmed from our WAXD in Figure 5-13, diffraction peak height is significantly sharper after fibers are bonded into fabric, which means the perfectness of crystallites are formed accompanied by the crystal size increases from 86Å to 180Å. In the bonding procedure, crystal size grows larger by continuous reorganizing and folding of amorphous chains around lamellae crystalline region in fibers. With temperature keep increasing to over-bonding temperature, exposure to heat can break down the crystalline lamellae formed in spin-drawn fibers. Meanwhile, the polymer crystallization temperature is also impacted under different concentration of loading,
that these calcium carbonate filler particles provid some potential nuclei in polypropylene melt for lowering the kinetic energy in crystallization. This is confirmed from increasing crystallization temperature when concentration is above 10%, it moves up by 2°C, include in Table 5-4. Impact of calendar roll temperature (120-150°C) on varying crystal size is more significant on bridge fibers than bonded area [18]. Crystal size of polypropylene bridge fibers increases with temperature up to 140°C, and then decreases with higher temperature [18]. We also interpret from our results based on 130~150°C bonding temperature on 10% of filler loading, that the on-set melting time only increases by 0.5°C when bonding temperature is around 135~140°C, but the on-set melting time is delayed by around 5 seconds, indicating the crystallites formed at optimum bonding temperature will be more densely compacted. As temperature goes up from 130°C to 140°C, the on-set melting time postpone, while further rising up bonding temperature advances the on-set occurring time. This means crystallinity grows to the largest at 140°C for 10% loading concentration, which is also the optimum bonding temperature for the spunbond fabrics.
In a specific question on fabric breaking mechanism, the extent of fabric deformation in response to tension, stretching or tearing is dependent on the relative freedom of fibers under bonding regions. In previous discussion on elongation at breaking, fabrics stretch can withstand higher strain from 130~140°C. But above the optimum bonding temperature the strain to break is greatly reduced, drop in elongation indicated overloading effect of fabrics that accumulated particles in fiber cross-sectional plane cause fatal weakness at boundary perimeter. This region is as we discussed above in Figure 5-9 (c-d), heat diffusion will cause the over-melting of bonds with its topography cave into a lower horizontal plane, squeezing
polymer material out of the bonding area into the periphery region that hinder the elastic deformation. As shown in Figure 5-12, polypropylene fabrics breaks by rupturing the bonds, while for 30 wt.% contained with CaCO₃, 145°C has caused weak interfacial connection thus resulted fiber breakage occur at the bridge fibers. Previous work by Dharmadhikary et al. revealed a similar issue related to thermal bonded polypropylene fabrics that overbonding may have a stress concentrating effect at periphery region. Dharmadhikary claimed there was no apparent loss in birefringence of periphery fibers from 149°C to 160°C, but higher bonding temperature resulted into even bigger difference in birefringence between fibers and bonds [19]. At periphery, some bridge fibers can be softened and flatten when calendar roll temperature is sufficiently high [17-18, 22]. Fiber mechanical properties undergo a dramatic decrease from bridge fiber to bonding area, cause even a stronger bonding pad at higher calendar temperature, however the weaker fiber structure will not be regarded functioning to the maximized strength of the bonds, so bridge fibers will break first (Figure 5-12b).

Figure 5-12: Breakage at spunbond calendar bonding regions for 50 gsm fabrics at 145°C.
Table 5-4: Polymer melting and cooling data profile for each spunbond samples with certain amount of fillers and bonding temperature:

<table>
<thead>
<tr>
<th>Sample ID 50gsm-spunbond</th>
<th>Filler Conc.</th>
<th>T_{on-set} melting (°C)</th>
<th>Peak width at 1/2 height (°C)</th>
<th>$\chi_c$(%)</th>
<th>t_{on-set melt} (min)</th>
<th>T_{peak-crystallization} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-140°C</td>
<td>0</td>
<td>160.2</td>
<td>10.1</td>
<td>53.7</td>
<td>14.18</td>
<td>120.2</td>
</tr>
<tr>
<td>FL2.5-140°C</td>
<td>2.5</td>
<td>160.6</td>
<td>10.1</td>
<td>53.4</td>
<td>14.22</td>
<td>119.4</td>
</tr>
<tr>
<td>FL10-140°C</td>
<td>10</td>
<td>160.5</td>
<td>9.6</td>
<td>54.5</td>
<td>14.21</td>
<td>121.5</td>
</tr>
<tr>
<td>FL20-140°C</td>
<td>20</td>
<td>160.5</td>
<td>9.3</td>
<td>51.9</td>
<td>14.21</td>
<td>122.4</td>
</tr>
<tr>
<td>FL30-140°C</td>
<td>30</td>
<td>160.5</td>
<td>8.7</td>
<td>49.9</td>
<td>14.21</td>
<td>122.8</td>
</tr>
<tr>
<td>FL10-130°C</td>
<td>10</td>
<td>160.0</td>
<td>10.6</td>
<td>53.1</td>
<td>14.16</td>
<td>120.7</td>
</tr>
<tr>
<td>FL10-135°C</td>
<td>10</td>
<td>160.4</td>
<td>9.6</td>
<td>51.8</td>
<td>14.20</td>
<td>122.3</td>
</tr>
<tr>
<td>FL10-145°C</td>
<td>10</td>
<td>160.2</td>
<td>10.1</td>
<td>51.5</td>
<td>14.18</td>
<td>120.4</td>
</tr>
<tr>
<td>FL10-150°C</td>
<td>10</td>
<td>159.9</td>
<td>9.9</td>
<td>50.9</td>
<td>14.15</td>
<td>121.4</td>
</tr>
</tbody>
</table>

Figure 5-13: WAXD diffraction patterns of spunbond crystalline structure (whole fabrics: solid line; drawn fibers: dashed line) filled with 5% of calcium carbonate, bonding temperature 140°C.
5.3.3. Fabric Breaking Mechanism

Mechanical property of fibrous structure represents an alternative of bonding with fibers interconnected through the bond geometry. Based on shape and coverage of embossing regions, as appear in fabric structure in Figure 5-14 (a), fibers are restricted at those bonding area. To rupture a piece of fabric, it must overcome the shear resistance from the fibrous network. The orientation of oval pattern on the web may affect the stress strain behavior in either MD and CD of a spunbond fabrics. Since fibers orientation in the spunbond process has MD dominant over CD, so that tensile breaking strength is larger in MD, as Figure 5-15 plotted. With reduced calendar temperature below 140°C even though 100 gsm fabric can keep at constant breaking strength, however, reducing the fabric basis weight to 50 gsm did not keep the strength in fabric. Peak strength shows with a narrow bonding window of the fabrics comparing 20% of GCC fillers compared to PP control fabric. It is modeled by Rawal et al. that the reorientation of fibers along MD tensile mostly occur at low strain 3~5% [24].

The stretching force starts to reshape those bonds as shown in Figure 5-14 (b) by elongating, flattening and peeling off fibers from bonds. When all fibers are bonded strongly to resist stretching out from the bonds, single fibers can be tightened to a large extent of elongation. However, since polymer only partially melted at 135°C, some fibers under the calendar is not fully fused together with the main layer of the bonds, as a result, they are peeled out of the bonds shown in MD loading direction with Fig. 5-14 (b). While the grasping force from adjacent fibers will fail to hold the peeled piece in place before they reach to the maximum level because those bonding regions are relatively weaker at 50 gsm thinner fabrics. The brittleness at higher than 145°C should be due to the fast heat transfer that melt down the
fiber lamellae too much to deteriorate fabric mechanical property. In Fig. 5-15 at bonding above 140°C, MD tensile strength sharply turns down because of stress concentrate effect at bonding perimeters. Friction from fiber distributes the stress throughout the two dimensional fiber webs and avoids the load concentration on specific points. Such as in CD (Fig.5-14c), pulling fibers bundles and opening up the bonding regions will dissipate a lot of fracture energy.

Figure 5-14: Bonding patterns of spunbond fabrics (a), and fiber morphology after loading bearing in spunbond tensile test in (top and bottom) and c (top and bottom). Tested fabric are 50 gsm contained with 20 wt.% of calcium carbonate fillers bonded at 135°C.
Figure 5-15: Tensile strength in both MD and CD, comparing 50 gsm PP spunbond to 20% CaCO₃ contained in the fabrics.

5.3.4. Thermal Stability

Thermal degradation property of polypropylene reflect a potential functionality of adding inorganic fillers could bring up, that flame retardant additives would give direct improvement on material thermal stability. Previous research have investigated the flame retardant performance of specific system, such as halogen-free flame retardant system using ammonium polyphosphate containing with zinc oxide and processing agent [27], with performance improved on limit oxygen index and decreased total heat release rate. The direct and efficient way to characterize the thermal degradation property of polypropylene is by using TGA with nitrogen gas supplement, which weigh the loss in polymer material with furnace burning the material at a constant heating rate. Traditionally functional additives
such as montmorillonite, silicate, bentonite, magnesium hydroxide, carbon fiber and many kinds of compound assist char forming and mainly guide internal heat conductive pathway to remove heat away from combustible yarns [1, 2, 30, 31]. Polypropylene start degrading above 370 °C, followed by a fast declining in the polymer weight by chain scissoring at temperature around 375°C to 450°C. Loading calcium carbonate particulate fillers can change the on-set degradation temperature as illustrated in Figure 5-16 and Table 5-5. Increased on-set degradation temperature from 382°C to 417°C, is responding to an improved thermal stability. This comes from a heat dissipation mechanism forms at CaCO$_3$ fillers interface with polypropylene. After fillers forms into a heat conductive network, the heat will be conducted fast throughout the sample, which helps overcome local overheating caused by accumulation of heat and accelerating the scissoring of polymer chains. Especially when increase up the concentration of fillers, increment with 14°C~40°C increasing on on-set degradation temperature with the concentration added from 10% to 30%.
Figure 5-16: Degradation percent weight curve with temperature from 20°C to 650°C.

Table 5-5: Degradation Performance of Fabrics Containing with 2.5% to 30% of GCC-FiberLink (FL):

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>On-set Degradation Temperature (°C)</th>
<th>Residual of CaCO₃ (%)</th>
<th>Targeted CaCO₃ (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP Fabric</td>
<td>382.7</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>FC 2.5%</td>
<td>377.8</td>
<td>2.4%</td>
<td>2.5</td>
</tr>
<tr>
<td>FC 10%</td>
<td>391.3</td>
<td>10.7%</td>
<td>10</td>
</tr>
<tr>
<td>FC 20%</td>
<td>403.2</td>
<td>21.7%</td>
<td>20</td>
</tr>
<tr>
<td>FC 30%</td>
<td>416.8</td>
<td>31.3%</td>
<td>30</td>
</tr>
</tbody>
</table>
5.3.5. Mechanical Properties

5.3.5.1. Fabric Modulus

When stretched nonwoven fabric the ease of deformation reflect in its modulus. As to thermal bonded nonwoven structure, external straining should be able to concentration on film like bonds. Spunbond fibers interwines at oval pattern bonds at intersections where load is transferred through the network. Previous model use finite element methods to consider fiber micromechanical properties as well as percentage of bond coverage on the mechanical property of nonwoven fabrics [20]. Fabric modulus, affected by multiple factors in fabric web, enhance in point bonding regions by a high filler loading. At same bonding temperature, modulus for different web materials keep at same level as loading increases from 2.5% to 30%, even with single fibers weakened in their secant modulus. It is unexpected that modulus first ramp up with filler loading concentration to 10% then lower down from 20% to 30%, which indicated a better structure integrity as CaCO_{3} loading is at 10%. From our previous observation 10°C lower in optimum thermal bonding temperature could be achieved for PP control even being loaded with 10% and 20% of CaCO_{3} fillers. For polypropylene or fibers containing with small amount of fillers (2.5%), point bonding below 150°C still stay below bonding level when fibers are freely jointed by partial melted fibers. This represents the initial modulus is influenced by bonding temperature. 10% has induced more MD orientation than PP, 2.5% and 30% filled fabrics. As a valid evidence, the fibers containing with 10% of CaCO_{3} can be predicted orient more in MD in web lay-down process. Since the laid down orientation in the web structure is controlled by fibers stiffness and bending flexibility, that
more crystalline orientation which has larger stiffness could possibly induce more MD orientation domination comparing to fibers with more amorphous orientation.

![Concentration Effect on Fabric Secant Modulus (140°C)](image)

Figure 5-17: Secant modulus at 5% strain of spunbond fabrics.

As mentioned, material specific heat actually cause material melting fast upon conductive heat from emboss calendar pattern. Material without directly contacting with calendar roll surface is also influence by planar heat transfer through adjacent molten fibers. At the same time, heat radiation and convection partially melt polymer in bridge fibers, which composed of 82% of spunbond web. Fibers surrender its polymer orientation developed in fiber processing to the radiated heat. We can see from fiber morphology that surface polymer adhesion occurs at certain joints of fibers, in the form of polymer chain entanglement at those joints. According to Pai et al., intrinsic property of fibers govern the nonwoven structure and
property in elastic modulus, and such property is determined by average fiber diameter, curvature of fibers in the mat and the distance between fiber to fiber junctions \[^{[29]}\]. The strain energy from single fibers \(u_f\) and from the junction of fiber-fiber bonding or entangling is \(u_{junction}\), the Young’s modulus of nonwovens can be expressed from the stretch flexibility in uniaxial deformation averaged over the distribution of fibers in the initial web structure based on model:

\[
E_{mat} = \frac{\nu k_f r_0^2 (\sin^2 \theta_0)}{t_{mat}}
\]  

Where \(t_{mat}\) is thickness of nonwoven mat, \(\nu\) is areal density that number of fiber per unit area, \(k_f\) is fiber axial stiffness, \(r_0\) is the distance between two junction points along a fiber, \(\theta_0\) is the angle between initial fiber orientation to the CD direction.

\[
k_f = E_f A_f / r_0
\]

Where the single fiber axial stiffness is related to fiber Young’s modulus \(E_f\), fiber cross-sectional area \(A_f = \frac{\pi d^2}{4}\). Fiber strain energy \(u_f\) is related to fiber axial stiffness \(k_f\) because the initial straining of single fibers mimic the Hooke’s model connecting with bonds. At the fiber-fiber cross-sectional regions, the strain energy is correlated with effective torsional stiffness \(k_{junction}\):

\[
u_{junction} = \frac{1}{2} k_{junction} (\theta - \theta_0)^2
\]

Therefore, as increasing the fiber density with loading concentration of 2.7 g/cm\(^3\) part of inorganic fillers replace partial 0.9 g/cm\(^3\) of PP, the number of fibers per unit area reduces since fiber diameter increases up as shown in Figure 5-20, which affect the number of fibers
at the junctions. Based on the understanding that fiber bending flexibility is related with fiber diameter, in some occasions those enlarged fibers are tightened in between two junction points or even bind several fibers into rope like bundles, which reduce the $r_0$ and increase the $k_f$. It is important to keep investigating on bending performance of fabrics as well as the fiber orientation distribution when increases the loading concentration of CaCO$_3$ particles.

5.3.5.2. Bending Rigidity

Bending rigidity reflect fabric stiffness in certain direction. The testing direction is MD and CD that main fiber distributed direction is in MD in spunbond processing because moving belt impose momentum towards the MD when fibers falling down at belt flat surface. General trend is loading fillers can reduce bending rigidity of fabrics since single fiber reduce its modulus at higher filler loading. We also noticed at 10%, the fabrics tend to improve its bending rigidity as shown in Figure 5-18. The special fiber orientation in web formation might cause the peak out value at 10%, this may be due to improved bonding that result into less drapery effect in MD. It has been found the capacity to drape is based on the resistance from fiber forming fabric structure to a small amount of deformation$^{[29]}$. Bending rigidity correlate with bending length in cantilever, usually the extent of fiber compliance in bending resist the over-hang fibers outside of cantilever. The short bending length indicates the fabric has a better bending flexibility rather than hindering from a rigid wire network bond on fiber assembly along certain direction. When CaCO$_3$ filler concentration reaches at 10%, there are a increasing among of fibers dominate in MD which cause a significant higher flexural rigidity value in MD from Figure 5-18 and Figure 5-19.
Figure 5-18: PP spunbond filled with FiberLink fillers in 2.5% to 30%, bending rigidity shows the trend of fabric stiffness in MD and CD with amount of filler loaded in fibers.

Fiber formed by loading CaCO₃ in a varying of concentration may impact single fiber torsion rigidity and flexural modulus, therefore orientation on spunbond web may not consistently as same as when spun the polypropylene fibers. As fibers are increased with CaCO₃ loading the fiber volume swelled even though the volumetric throughput was decreased. The fabric anisotropy was expected to be correlated with ratio of the strength and modulus in machine direction to the corresponding value in cross-section [17, 20]. We regard the reduced bending rigidity with higher loading concentration due to a decreased fabric thickness that reduces the support over the 50 gsm fabric. At 140°C such 50 gsm fabrics have already been sufficiently bonded by thermal points to form stiff on the axial drapery tendency under gravity. Those
fibers under bonded are thoroughly deformed into plastic oval points with periphery regions even impacted by thermal conduction effect. Even though bonds become stiff, the bridge fibers become finer and less supportive as interconnected network against deflecting of the fabrics under gravitational force. It was also noticed spunbond webs tend to have less MD dominant distribution when CaCO$_3$ is loaded up to 20-30 wt.%, as expectedly, that finer fibers fall down to moving belt more randomly. This is because the momentum behavior will dominate over drawn fiber lay down movement onto the belt with velocity $v_{belt}$. Stronger momentum of inertial of fibers contributed to higher CaCO$_3$ loading concentration will compete with $v_{belt}$ which pulling the free fibers more on MD than CD.
Figure 5-19: The ratio between fabric breaking strength in MD to CD averaged over three bonding temperature from $T_l$ set from 135°C, 140°C to 150°C.
Figure 5-20: Fiber diameter of spunbond filled with different concentration levels of GCC-FiberLink in mono-component with constant mass throughput 0.6 ghm.

5.3.5.3. Tear Strength

Tear strength of fabric is dependent on effect of thermal point bonding that form a locking of fibers under the plastic bonds. Similarly, there is an optimum temperature for tear strength to reach to its maximum tear strength and then followed by a reduction, when fabrics thickness significantly reduces with temperature. Tearing resistance can work to the maximum only if long fibers will undergo largest torsional rigidity of fiber bundles. As 10% filled with fabrics still keep the tear strength increases up to 140°C and then start to drop above that temperature, which significantly decline to a much lower level compare to PP control fabrics. When keep increasing concentration, tear strength is severely deteriorated as overbonded
fabrics increase the bonding area. From the above analysis on fiber diameter (Fig. 5-20), fiber rotation torque could increase up with fiber diameter up to 10%, so that we expect that tear strength is maintained. But higher loading concentration 20~30% may result granule embedded in polymer matrix cause stress concentration at fibers and bonding pads. Those internal micro voids can be regarded as initiator of craze formed in the thin plastic bonding, accelerate the tearing deformation. According to reason from over-bonding or internal defects in polymer material, tearing ruptures rather easily for fabrics containing with more than 10% of fillers.

In previous discussion on thermal point bonding, the oval patterned bonds are with their long axis align in the MD direction (Figure 5-14). Tearing along MD is easily affected by thermal calendaring temperature. When the 18% covered bonding area expand, the real cross dimension in the oval points is impacted by heat transfer from long axis of oval to periphery region as shown in Figure 5-14. Tearing initialize at breaking fibers at slit opening regions, and will expand onto film like bonding regions. Another finding on fabric tongue tear strength is that the dependence on fabric basis weight. From Figure 5-21b, both 50 gsm and 100 gsm samples have declined in optimum tear strength with the concentration goes up. That fabrics with more than 10% of CaCO₃ of loading undergo dramatic decreasing in tear strength. Since heat conduction effect at bonding regions enlarge bonding area as shown in Figure 5-9 (c-d), tongue tear easily rupture along the flat and thin bonding regions. Resistance to tear strength comes from the free rotational movement of strands of bridge fibers, mainly referred to those align vertically to the tearing slit. When tear force starts
breaking the interconnecting fibers to those bonds, weakened fiber will break along the craze around the stronger bonding periphery and eventually reduce the tear resistance. It is better to mention that keep reducing volumetric throughput above 10% of loading will decreasing fiber diameter, so there are high possibility of large particle size related defects or agglomeration embedded within fibers. Stress is likely to propagate across those weak fibers and brittle bonding regions, and crack around rigid filler particles. These all result into low toughness to resistant to tearing force in a quick motion. However, such deterioration by chain breaking may contribution to easy-to-tear fashion of spunbond products.
Figure 5-21: Varying of filler loading concentration on tongue tear strength of 100 gsm fabrics (a). Optimum tear strength compare at two basis weight (b).
Figure 5-22: Bonding region morphology of spunbond fabrics with 2.5%~30% GCC fillers bonded at 140°C. (a) PP crystalline regions; (b) 10% partial softened fibers beneath fabric; (c) 2.5% form compacted fiber recrystallized upon heating; (d) 20% show roughness on bondings.
5.4. CONCLUSIONS AND SUMMARY

The function of CaCO\textsubscript{3} filler particles reflects in the reinforcement of spunbond nonwoven bonded by thermal point bonding. In this chapter, we characterize fabric mechanical property of spunbond fabric from tensile and tear motion to understand the bonding effect with dispersed particulate fillers. Fabric bonding mechanism is a synthesized function of temperature, which combines the single fibers strength with bonding connections. First of all, the weakening in single fiber strength does not significantly result into fabric strength deterioration, indicating thermal point bonding by heat conduction and radiation will help to enhance the bonding toughness. Breaking mechanism of spunbond at optimum bonding temperature can deform the patterned bonds, and redistribute the orientation of fibers. Next, hindering from web entanglement through bridge fibers will be functioning as stress transferring bridge. Although early disintegration of bonding region may result failure of stress transferring by pull the bridge fibers out of bonding pads, however, increase loading of CaCO\textsubscript{3} fillers enhance form a tacky and densely fused fibers beneath the embossed region. Increase of loading concentration reduces the optimum bonding temperature from 150°C to 140°C. While lower tensile strength occurred as filling with 30% in 100 gsm fabric, or even lower at 20% of loading in 50 gsm fabrics. Raise up loading concentration may reduce the bonding window temperature of spunbond fabric. As to 50 gsm fabric, increase bonding temperature may cause overheating that result into brittleness at bonding region, also the weakness interface around bonding perimeter will lower strain at breaking. It is optimum bonding effect at the lower temperature around 135°C for filler loaded up to 20~30 wt. % (Table 5-2).
Inorganic filler phase will conduct heat outwards which may expand bonding area and fuse bridge fibers at the perimeter, as shown in Figure 5-9 (c, d). Thermal transferring rate in the vertical direction influence amount of fibers are melt in the mid-plane. Increasing CaCO$_3$ fillers into fiber spinning lower the heat capacity of polypropylene as follow the rule of mixture at concentration level above 10% in Figure 5-11. Therefore, it takes less amount of energy to increases up polymer temperature to the melting point, so that the heat diffuses around and penetrates through the web in faster rate. At optimum bonding temperature, stretching force concentrate on the bonding regions by load transferring throughout fabrics. Optimized breaking condition is by rupturing bonding region where the stress can be maximized by concentrate on the bonds. Tear strength yield at higher filler loading (from 10%), indicating there are more fibers are fused with plastic bonding pads. Fabric thickness is reduced with more filler weight fraction, and both produce a thinner fashioned spunbond both for 50 gsm and 100 gsm. Rupture of fabrics at peak load is substantially enhanced since more fibers participated into the synthetized resistance to shearing, rotating, stretching and breaking deformation. Our main conclusion is polymer bonding structure is reinforced by inorganic fillers loaded between 2.5wt. % and 10wt. %. Above 10wt. %, tensile strength is maintained but tear strength is compromised, and there are a decreased in thickness and weakened structure around the perimeter at interface from bonds to fibers.
REFERENCES


CHAPTER 6 Sheath/Core Polymeric Structure and Tensile Property of PP Bicomponent Fibers added with Inorganic Particulate Fillers

ABSTRACT

Polymer melt spinning containing with inorganic fillers bring a changed thermal conductivity that influence the heat transfer rate in quenching, associated with mechanical properties developed in spin draw formation. To improve fiber spinnability and modify fiber forming structure and properties, we produced bicomponent fibers with sheath-core configuration loading with inorganic fillers. The fiber tensile properties were found to be closely related to the sheath/core loaded fraction and loading configuration. Needle-shape Precipitated Calcium Carbonate (PCC) incline to accompany with polymer orientation in sheath component with more particle alignment with the flow jet. Ground Calcium Carbonate (GCC) fillers existed in sheath component tends to roughen the fiber surface which imposes hand softness to fiber products. While loading fillers in core will not generate such rough surface but generate a relative smooth surface of fibers. Fiber cross-section and morphological of bicomponent configuration are investigated with optical microscope and scanning electronic microscopy (SEM), indicating there is good dispersion with particles in loading components. However, a different fiber cross-sectional dimension was found to be closely related with filler loading position. Fiber melt spinning cooling and solidification influence fiber forming structure and the filler loading influence heat transfer of polymer with ambient air. The main contribution that loading fillers in core is that fabric tensile strength is well maintained because of a longer
period of time in fiber quenching and crystallization resulted into larger crystal size. Our main result on GCC bicomponent fibers at 10~30% of loading is that keeping in core develop higher single fiber tensile strength but lower fiber modulus.

**Key Words:** Bicomponent Fibers, Calcium Carbonate, Shear Induced Crystallization, Skin-Core Structure, Tensile Properties

### 6.1. INTRODUCTION

Nonwoven spunbond processing is time efficient and cost saving by a series of procedures from fiber spinning, web processing and web bonding. The fast processing speed lower down the production cost; meanwhile, those production lines applied for disposable markets are consistently seeking for lower raw material cost and a renewable resource to replace part of polymer resin. Calcium carbonate filler (CaCO$_3$), as the most widely applied additives used in plastics [1], paints [2] and films [3], is arising as one of the most popular additives in polymer extruding. Previous literatures has less attempt to step into the nonwoven spunmelt and fibers spinning using such inorganic fillers, more attention during last few decades covered plastic molding [4-5] and paper in-situ precipitation [6, 7]. Strategy of loading CaCO$_3$ into melt spinning comes with all kinds of challenge in that fiber fine structure but the relative difficult compatibility within polymer. Particle size distribution, which is regarded as the most important index for mineral fillers, should be tailored precisely to anchor inside of small
fibers. If the CaCO$_3$ fillers can be spun into fibers and nonwoven into fabrics, those potential values may come from those white calcium carbonate which may influence the whiteness and opacity of a fabric like in the previous arts of wet-laid papers $[8]$. At same time, those particulate factors affect fiber structure, bring properties changes in their fibrous assembly incorporated with CaCO$_3$. Traditional nonwoven raw materials have been greatly developed to optimize staple fibers structure and processability in carding and air-laid. However, it is uncertain about the potential of mineral fillers in fiber forming by melt spinning, especially in fiber structure-properties which can vary from the traditional nonwoven raw material. No mention about spunbond processing that the function of CaCO$_3$ is not only for a changing attenuation rate, but also may give any impact on the structure of web bonding.

We caring about use inorganic fillers in bicomponent fiber technology is because for partial modification of fibers with CaCO$_3$ we may acquire similar property improvement with less dependent on loading concentration. The previous results have indicated tensile properties of mono-component fiber deteriorate significantly with concentration, because amount of loading directly induce structural defects in fibers. However, high loading could reduce fiber diameter and make particulate fillers bumpy out of fiber surface. DeLucia and Hudson brought up the idea of using CaCO$_3$ fillers in melt spun and spunbond nonwovens to change the plastic feel of relevant products, such as generating a cloth-like softness improve the hand pleasant $[9]$. McAmish et al. investigated the mono-filaments filled with one ground calcium carbonate and claimed top cut > 10$\mu$m account for more than 5% in total will cause severe fiber surface unevenness $[10]$. According to Peng et al., certain sheath-core bicomponent fiber
ratio is tailored for specific type of calcium carbonate particles, since stick-out effect of larger particle size is related with the thickness of sheath component \[^{[11]}\]. These particles can be incorporated specifically in fiber sheath using bicomponent technique by blending compounded masterbatch with polymer resin and sending into one of screw extruder \[^{[5,9-10]}\]. Either the sheath added with polypropylene plus CaCO\(_3\), or the core stuffed with such mixture, may result into crystalline structure change and influence fiber strength and modulus.

Nonwoven market scope in for example baby diapers, wipes, medical gowns and masks all cherish a common value in comfortable contacting and touching by skin. Therefore, those changed in topography of fiber may bring a different tactile feeling to skin, since by adding more protruded nubs between fabric and finger tips in a motion like rubbing, sense may be improved from physiological functions. As it is defined by DeLucia and Hudson, an uncomfortable gloss and slipping surface are always exhibited by using synthetic fibers. Potential value associated with calcium carbonate filler particles will contribute to cloth-like feeling on a great amount of products \[^{[9]}\]. In bicomponent nonwovens using two polymers which has a higher and a lower melt point, such as PP/PE, PET/Co-PET, can also be used to improve fabric soft hand during web bonding \[^{[12]}\]. Sheath/Core fibers in thermal bonding nonwovens tend to keep softness during thermal bonding by partially melting polymers (usually sheath) to form molten polymer interfusing under compression, while the other polymer is still intact to keep the strength integrity. Using bicomponent with a different sheath/core ratio, for example, 25:75, 50:50 and 75:25 usually relate CaCO\(_3\) loading
concentration with its bi-component structures \cite{11, 13}. Core of Polypropylene bicomponent fibers filled with 10-25% of CaCO$_3$ fillers is accordingly increase fabric strength at 150°C \cite{13}. Hisakatsu et al. reported production and properties of bicomponent spunbond nonwoven containing fillers. This bicomponent fiber contains fillers in polymer blend of low melt point LDPE added with a copolymer of ethylene-vinyl acetate. The resin blend ratio is from 95/5 to 60/40, and filler particles concentration varying from 1000~35000 ppm. Combined with high melt point polypropylene located either in core or side by side, such structure will enhance adhesiveness in spunbond web bonding \cite{14}.

Although some research focusing on polymer composite show material mechanical properties varying with filler volume fraction, higher loading concentration increase stiffness and modulus, decrease strength and impact strength and hinder polymer ductile deformation \cite{1, 15}. However, there is few evidence shows calcium carbonate fillers will change fiber tensile properties in an analogous models as polymer composites, because of unique characteristic of the fibers. We will expect a varied structure in bicomponent sheath/core configuration if loaded into each component may further change fiber tensile properties. Obviously in the subsequent spunbond process, bonding structure can be formed by using sheath/core bico fibers. Fiber structure formation in addition to particulate filler has great impact on maintaining the certain structure and properties of spunbond fabrics. This involves stable extrusion of filled-polymer through the capillary to the outside of spinpack where the dispersion or agglomeration determines a continuous supplement of polymer jet \cite{16}. In another words, the key for a good spunbond structure as well as for desired functionality
depend on how to contribute each fibers into a whole fabric, by loading inorganic particulate fillers stably, soundly and strongly in high speed of fiber spinning. Our objective in this paper is to investigate the effect of calcium carbonate on structure formation in bicomponent melt spinning, and evaluate sheath/core loading configuration profiles on fiber structure-properties relationship.

6.2. METHODOLOGY

6.2.1. Materials

The calcium carbonate masterbatch is provided by Imerys Groups (GA), which contains FiberLink 201S® ground calcium carbonate specially designed for nonwoven use. Compounded ratio between PP and CaCO$_3$ is 20/80. The particle size distribution is plotted in Figure 1. Polymer is i-PP (CH360H) supplied by Sunoco Chemicals (PA). It has melt flow index (MFI) of 35 g/10min. Average molecular weight is 180,000g/mol, and the polydispersity is 3.3. Three types of calcium carbonate fillers were produced by bico melt spinning melt extrusion unit. The ground calcium carbonate FiberLink (Imerys Inc.) is pre-compounded with PP in 80/20 with stearic acid treated with an average particle size of 2.28μm. Other two types are precipitated calcium carbonate (PCC) fillers (Specialty Minerals Inc.), the EMforce are aragonite form of calcium carbonate in needle-shape, with aspect ratio of 5.4, two dimensions are main and minor axis are 1μm, and 0.25μm, respectively. Superpflex and FiberLink both have calcite crystals, but Superpflex is of finer particle size 0.38μm and a narrower size distribution compared to ground calcium carbonate (GCC).
6.2.2. Bicomponent Fibers Melt Spinning

Bicomponent PP/CaCO$_3$ fibers were produced using Tri-co Melt Extrusion Spinning unit in Textile, Engineering, Chemical and Science (TECS) spinning lab of College of Textiles (North Carolina State University, Raleigh). Ground CaCO$_3$ (GCC) is pre-compounding with Polypropylene in 80/20 weight ratio. PCC is compounded with Polypropylene in 50/50 ratio. Raw polymer pallets blended with CaCO$_3$ masterbatch were extruded, melted and mixed with two screw extruder in our facility. As shown in Figure 6-2, two of three extruders are working to send GCC masterbatch in 10 wt. %, 20 wt. % and 30 wt. % into the spinpack, which channels through into sheath/core two different components. Fiber samples with only core filled with 10~30% of CaCO$_3$ or sheath filled with 10~30% of CaCO$_3$ are produced.
under intension, meantime, we produced mono-component fiber containing with 5, 10, 15, 20, 30% of GCC using this extrusion unit, to conduct a comparative study in the design of experiment. Samples ID listed in Table 6-1 gives us information on how fillers has been loaded into fibers and the weight fraction it is contained within that specific component. In the following bicomponent trial, other types of calcium carbonate fillers (PCC EMforce and Superpflex) were focusing on, also with varying of concentration combining with sheath/core loading configuration. The concentration level is varying from 2.5% to 30% varyingly, included in Table 6-2, with more flexibility to stop at certain concentration level when further loading cause spinning instability. The spinning performance is highly dependent on the loading configuration, especially at higher concentration. When spinning speed at 2000 meters per minute (mpm) did not drawing fibers without breaking, the spinning speed is lowered down to 1600mpm, as include in APPENDIX I- Table 6-5. Sheath roughness can result in rejection of spin finish during fiber drawing on high running spin godet, for example, Superpflex PCC contain up to 10% in sheath, and 15% in mono-component. So it allows add up to a higher concentration for incorporating into the core of fibers with 20~30% of Superpflex. To find more spinning performance, readers are encouraged to refer APPENDIX I for spinline conditions during the spinning trials.
Pumping each extruder A and C at a controlled rate, raw material of PP and PP with 10, 20, 30% of calcium carbonate were conveyed into the spin-pack at same volume rate so that two components of sheath/core have a volume ratio of 50 to 50. Temperature in extruder were set at four increasing levels: zone one 190°C, zone two 210°C, zone three 215°C and zone four 230°C. Volumetric throughput is controlled at 0.782cc/hole/min and 36 holes in the spinneret. 0.782cc/hole/min volumetric throughput is equivalent of 0.6ghm for 100% polypropylene. All the melt spinning parameters are included in Table 6-3.
Table 6-1: Sample ID of Bicomponent PP/CaCO$_3$ fibers:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Material (wt%) in Sheath</th>
<th>Material (wt%) in Core</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td>Bico-Ca10-core</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Bico-Ca20-core</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Bico-Ca30-core</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Bico-Ca10-sheath</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>Bico-Ca20-sheath</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>Bico-Ca30-sheath</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>PP-control</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Homo-Ca5</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>Homo-Ca10</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>Homo-Ca15</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>Homo-Ca20</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>Homo-Ca30</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 6-2: Melt Spinning Unit Parameters Setting:

<table>
<thead>
<tr>
<th>Extruder and Spin-pack</th>
<th>Extruder A (sheath)</th>
<th>Zone 1</th>
<th>Zone 2</th>
<th>Zone 3</th>
<th>Melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td>199</td>
<td>226</td>
<td>230</td>
<td>245</td>
</tr>
<tr>
<td>Extruder C (core)</td>
<td>Zone 1</td>
<td>190</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zone 2</td>
<td>210</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zone 3</td>
<td>225</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zone 4</td>
<td>230</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Melt</td>
<td>241</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spin Head</td>
<td>230</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quench Air</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rolls</td>
<td>DR1: 30, DR2: 35, DR3A: 45, DR3B: 45</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Through put

| Extruder A: 0.6cc/rev Pump Speed: 23 RPM 13.8 cc/min |
| Extruder C: 1.8cc/rev Pump Speed: 8 RPM 14.34 cc/min |

26.14cc/min, 0.782cc/hole/min

Draw ratio

<table>
<thead>
<tr>
<th>Spinning Speed (M/M)</th>
<th>1:2 Draw Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed 945</td>
<td>DR1 950</td>
</tr>
<tr>
<td>1:2 Draw Ratio</td>
<td>DR2 1900</td>
</tr>
<tr>
<td>Relax 1950</td>
<td>2000</td>
</tr>
</tbody>
</table>

Spin Finish

Lurol PP 912 (Level varies 35%–80% depends spinning condition)
6.2.3. Properties Characterizations

Fiber Diameter

Fiber structure is studied using optical microscope (Zeiss) to evaluate filler distribution inside of fiber. The microscope is connected to a Nikon camera (DS-Fil), by which pictures were captured with high definition of morphology of filler dispersion inside of filament. 40x magnification is applied for fiber structure observation, this include particle distribution inside of mono-component fibers since the mineral particles impose a higher light scattering when it transmitting through polypropylene fibers. There are at least 20 readings of fiber diameters are read from optical microscopy images, and the average diameter of each samples as well as CV (%) are recorded.

Scanning Electronic Microscope (SEM)

Fiber surface and fiber cross-section are observed using Hitachi S-3200N SEM at the Analytical Instrumentation Facility of NCSU. Fiber samples coat with gold for 15 minutes. For preparing fiber cross-section, cutting comes right after immersing in liquid nitrogen for a few seconds.

Single Fiber Tensile Test

Fiber mechanical property is being studied using fiber tensile test, using equipment of MTS Q-Test with a 50gram load cell. Gage length is 1 inch (2.54cm), and elongation rate is 60mm/min. At least 10 specimen of each sample were tested. Linear density of each fiber specimen is measured using Vibromat for exact size (denier) to put into the Q-test software. Fiber peak load, tenacity, secant modulus at 5% strain, yield strength and strain at breaking
are being evaluated normalized with fiber cross-section area. The stress-strain curves are well manipulated using the MTS software.

**Fiber Shrinkage**

We randomly pick up five fibers with initial length $l_0$ (around 10 cm), marking at the end with a pin, for a better measuring later on since the pin put on a pre-tension on that fiber. Next boil a breaker of deionized water on a heater plate, containing a thermometer for consistency at 100 °C after fibers were put inside of the water. Fibers are immersed in boiling water to fully relax its polymer chains until 10 minutes later, the second reading is recorded as $l$. Then the shrinkage of fiber samples is calculated according to equation below (Eq. 2):

$$Fiber\ shrinkage = \frac{l-l_0}{l_0} \times 100\%$$  \hspace{1cm} (1)

**Fiber Birefringence**

To characterize fiber refractive index in parallel direction and crosswise direction, we apply the indexed immersion oil with known refractive index and observe the interface of polymer and oil medium and use this refractive index to estimate polymer refractive index. Indirect method refers to finding fiber refractive index from its surround medium, this is because theoretically when light transverse through the interphase light refraction is replaced by light direct transmission for equal refractive index of polymer and oil phases. Therefore, the interphase dark line will disappear with exact matching refractive index and light propagation velocity. Fiber refractive index is measured by polarized microscopy (College of Textile). To approach to the same refractive index, accuracy to the third position right after decimal (0.001) was read. Fiber has birefringence phenomenon, rotating circular rotating stage to the
same alignment of fiber specimen to horizontal position or to vertical position. The parallel refractive is recorded respectively, denoted as \( n\parallel \) and \( n\perp \). Then birefringence is calculated based on Eq.2 as follows:

\[
\Delta n = n\parallel - n\perp
\]

\((2)\)

**DSC**

Thermal property of polymeric material is evaluated using DSC. Differential Scanning Calorimeter (DSC), from TA Instrument, gives a circle of melting and cooling of material under heating rate of 20ºC/min from 25 ºC to 190 ºC, then cooling from 190 ºC to 25 at 10 ºC/min. Endothermic and exothermic peaks are analyzed using software Trios Version 3.3, so that we will get on-set melting temperature (\( T_m \): ºC), peak melting temperature (\( T_{m\ \text{peak}} \): ºC), crystallinity (%), peak width at half height (PWHH: ºC) and also the crystallization on-set temperature (\( T_{c\ -\ \text{onset}} \)) and peak crystallization temperature (\( T_{c\ -\ \text{peak}} \)). Crystallinity is calculated based on equation:

\[
\chi_c(\% \text{ crystallinity}) = \frac{\Delta H_m}{\Delta H_m^0}\omega \times 100\%
\]

\((3)\)

Where \( \Delta H_m^0 \) is the heat of fusion (165 J/g) for 100% iPP; \( \Delta H_m \) is the heat fusion per unit gram of fiber sample; \( \omega \) is mass fraction of PP in the fiber composite. Sample used in DSC is fibers of weight around 5 mg.

**Modulated DSC**

The measurable physical quantity of heat energy required to change the temperature of an object by a given amount is defined as heat capacity.
\[
\text{Rev } C_p = \frac{\text{Heat Flow Amplitude}}{\text{Heating Rate Amplitude}} \times KC_p \text{Rev} \tag{4}
\]

Where \( KC_p \text{Rev} \) = Calibration Constant for Reversing \( C_p \), Rev Heat Flow = Rev \( C_p \) \( \times \) Average Heating Rate; Calibration of MDSC used sapphire on TA Discovery DSC instrument. Fiber samples weighing of 10~15mg was prepared using aluminum pan. Modulation method based on ASTM E2716, setting heat rate at 2°C/min, 100s modulation period, \( \pm 1^\circ \)C amplitude, and ramping from 25°C to 230°C. Then record the normalized modulated heat flow curve and using derivative of modulated temperature curve, thus we have the amplitude of heat flow (W/g) and amplitude of heat rate (°C/min).

Heat capacity of PP fibers is measure as control, and calcium carbonate raw powder was measure as 100% of filler, and PP with different amount of calcium carbonate filler (5~30%) was measured and compared with the values calculated based on the Rule of Mixture:

\[
C_{p-k\%} = C_{p-PP} \times (100 - k) + C_{p-CaCO_3} \times k \tag{5}
\]

Where \( C_{p-k\%} \) is the specific heat capacity of PP containing with k% of wt.% of calcium carbonate filler. \( C_{p-PP} \) is the specific heat capacity of PP fiber, and \( C_{p-CaCO_3} \) is the heat capacity of calcium carbonate powder.
6.3. RESULTS

6.3.1. Bicomponent Fiber Structures

In tri-co melt extrusion two material form into the bicomponent fiber. Sheath core volume ratio is 50:50 in whole fibers with clear interphase boundary as shown in Figure 6-3. Packing of 10% GCC fillers inside of fiber include some discontinuous voids in the core. In the Figure 6-3.b specifically incorporated 10% filler in sheath scatter back all light beam transmit through the fiber. Keep increasing sheath loading fraction, as shown in Figure 6-5 filler distribute in sheath compactly and scatter light intensely. By observing free fall filaments, the filler dispersion condition is revealed as involved in Figure 6-4. The diameter of filament reflects a deformation spinneret capillary down to the position by elongational deformation. As we discussed in previous chapters, it was found fiber diameter for mono-component fibers spun at 500 mpm and 1250 mpm show an increasing CV(%) with higher loading concentration of CaCO₃ fillers, but at 2000 mpm the CV(%) normally keeps constantly no matter filled with CaCO₃ or not. From Table 6-3, the standard deviation σ of draw fibers were not significantly influenced by filler loading concentration, however, we find that when loading in sheath component the σ slightly decrease with concentration increase from 10% to 30%. Although the draw fiber as shown in Figure 6-5 did not show as clear sheath/core interface as free fall filaments, it is mainly because of fibers diameter is much finer with 21~23μm so that CaCO₃ with particle size larger than 5μm may have a high probability to protrude out of sheath boundary. From the free fall fiber cross-section, particles are dispersed uniformly within certain components, so that it allowed the drawn fiber can maintain fillers in position. But as fiber cross-section area is apparently decreased, the dimension of fiber
sheath and core narrowed apparently (Table 6-3), therefore make the particles protrude inward to core and outward on the fiber surface. Such transfer across boundary is mainly due to the large particle size but not related with polymer diffusion. Such denser fiber coated with GCC particulate fillers also influence fiber surface roughness, higher concentration resulted into closer packing of particles and make the light scatter intensely as shown in optical microscopy and SEM picture in Fig. 6-7.

Figure 6-3: Single bicomponent fibers filled with 10% of fillers in core component (a) and sheath component (b).
Figure 6-4: Cross-section of free fall filaments with 20% of additive in core (Bico-Ca20-core) and 30% of filler in sheath (Bico-Ca30-Sheath).

Figure 6-5: Fiber cross-section vary from 10% to 30% of FiberLink CaCO3 filler loaded in the sheath component of fibers.
Table 6-3: Diameter of Bicomponent Fibers and Dimension of Core Component in Fibers:

<table>
<thead>
<tr>
<th>Bico Fiber Sample ID</th>
<th>Fiber Diameter (μm)</th>
<th>Core Diameter (μm)</th>
<th>Sheath Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP control</td>
<td>20.8 (σ =1.6)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bico-Ca10-Core</td>
<td>21.9 (σ = 1.7)</td>
<td>15.8 (σ = 1.4)</td>
<td>3.1</td>
</tr>
<tr>
<td>Bico-Ca10-Sheath</td>
<td>22.9 (σ = 2.5)</td>
<td>14.5 (σ = 1.7)</td>
<td>4.2</td>
</tr>
<tr>
<td>Homo-Ca5%</td>
<td>20.6 (σ = 1.4)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bico-Ca20-Core</td>
<td>22.4 (σ = 1.1)</td>
<td>15.8 (σ = 0.7)</td>
<td>3.3</td>
</tr>
<tr>
<td>Bico-Ca20-Sheath</td>
<td>21.4 (σ = 1.7)</td>
<td>15.1 (σ = 1.2)</td>
<td>3.2</td>
</tr>
<tr>
<td>Homo-Ca10%</td>
<td>21.2 (σ = 0.8)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bico-Ca30-Core</td>
<td>23.0 (σ = 1.4)</td>
<td>15.8 (σ = 1.1)</td>
<td>3.6</td>
</tr>
<tr>
<td>Bico-Ca30-Sheath</td>
<td>21.0 (σ = 0.8)</td>
<td>15.3 (σ = 1.1)</td>
<td>2.8</td>
</tr>
<tr>
<td>Homo-Ca15%</td>
<td>22.9 (σ = 0.7)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Homo-Ca 20%</td>
<td>21.8 (σ = 0.9)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Homo-Ca 30%</td>
<td>22.9 (σ = 1.3)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

From Table 6-3, diameter of bicomponent fibers is larger than PP control fibers, also correlated with filler loading concentration and the configuration. If load particles in core, increase of concentration resulted into continuously increasing in fiber diameter; adversely, loading particle in sheath has a negative correlation with loading concentration. Fiber diameter should be constant at same volumetric throughput and be drawn under the same draw ratio. As we specifically loading one of bicomponent with particulate fillers, the thermal property of the material will affect the real volume in the component. Increases in fiber diameter with calcium carbonate fillers reveal that it may actually affect spin-draw process if part of fibers is modified with inorganic fillers. One possible influence is on the friction coefficient between fiber and godet rolls that the slippery on the draw rollers
decreases the actual drawing speed and resulted into larger fiber diameter level. As increase from 10% to 30%, filler loading in the sheath component changed fiber surface condition, as illustrated in SEM surface morphology in Figure 6-6. With such surface condition it will change dynamic friction of multi-filaments to spin godet, adjusted with spin-draw ratio to be approximately get close to the theoretical value (950/1900/1950/2000 mpm).

6.3.1.1 Fiber Surface Roughness
Increasing concentration in fiber core, expectedly that fiber surface is smooth with covering of pure polypropylene, which one hand avoid abruptly transferring to expose onto the surface, one other hand maintain the lustering as polypropylene fiber does. Remove from sheath into core component is supposed to hide that unevenness on surface which make the spin finish likely to be applicable during fiber drawing process. In fiber formation, polymers apart from center withstand a large shear stress and earlier row nuclei developed in the surface layer. Agglomeration of fillers may affect the unexpected transferring from core component to fiber perimeter, as shown in Figure 6-6a. With loading concentration increase above 15~20%, voids at filler particle interface appear in the fiber. From Figure 6-3a the distribution of fillers shows us unevenness formed from clusters of GCC particles within the fiber core. It was surprising to find that in the fiber loaded with 10% in core, the cooling of fibers may not form a uniform shell on fibers, there seems to be local protruded particles on the sheath rather than wrapping beneath the polypropylene. This is also coincidence as sheath thickness at this case is rather smaller compared to 20% and 30% of loading (Table 6-3).
With filler concentration increase up to 30%, fiber morphology reveal fiber surface unevenness is apparently covered under a thick polymer sheath, beneath which inorganic fillers mix up with polymer in core component. We think the probable mechanism to change surface smoothness is from the consistency in decreasing the diameter of the core that polypropylene shell will have sufficient volume to wrap around the core. Shown in Figure 6-6a and 6-6b there were some wrinkled area come up there on the surface which could be a result of inner hot melt that crush the top layer of the fiber. The smooth surface help with stabilize melt spinning process especially at higher filler loading concentration, as roughness on fiber surface cause difficult in taking up spin finish. As surface are roughened with filler particles, contact surface bear friction and may influence the yarn quality when winding tension is high because of large friction force \cite{29}. Incorporate filler inside of core is meaningful in controlling spin finish adhesion onto fiber surface and keep a hydrodynamic lubricant boundary at winding godet. While filler in sheath not always make the case worse, as shown in Fig. 6-6d that replacing GCC with the high aspect ratio EMforce fiber surface become less rough since all long axis tend to align in parallel with polymer jet direction.
Figure 6-6: Fiber surface morphology at varying of loading from 10~30% with FiberLink in core (a~c) and EMforce with 10% in sheath compare to FL with 20% in sheath.

6.3.1.2 Skin-Core Crystalline Structure

Fibers melt spun at high spinning velocity will form distinctive skin and core birefringence. The skin-core effect represents temperature-dependent and shear stress induced crystalline structure where the birefringence of sheath value is above the core. This is because polymer jet has higher sheath temperature than core at the extrusion spinneret, while quenching first cool down the polymer at the outskirt on sheath then gradually solidify the core polymer
since center has relatively higher temperature. Polypropylene molecules oriented sooner outside the capillary which contribute to great amount of row nuclei in sheath, grow of crystallites are triggered when skin cool down and developed twisted lamellae crystals. Further crystalline orientation by higher shear stress at sheath structure will stretch twisted lamellae as shown in Figure 6-8, whereas polymers keep less oriented in the core. In the bicomponent fiber birefringence the reduced birefringence is most significant at mono-component fibers (Figure 6-7). Loading in sheath, the birefringence value from Figure 6-7 has apparently leveled up with concentration from 5% to 20%, in contrast orientation also decline for same amount of filler loaded in core configuration. In a word, fillers existence restrict polymer orientation no matter the loading concentration, the heterogeneous molten polymer has yielded its flexibility to rigidity around the fillers. However, using the larger aspect ratio filler particles (PCC-EM) help assist sheath orientation as much as how fast the elongational deformation can orient those needle-shaped particles with the flow jet (Fig. 6-6d).

As to sheath loading, increasing loading concentration from 10 wt.% to above, chain orientation align more with high shear stress, but higher birefringence is mainly come from amorphous orientation because its fiber shrinkage at 30% is dramatically increased (Figure 6-9). When load into core left the sheath with PP, the birefringence is constantly decreased from 5% to 20%, because the heterogeneous nucleus in core retard untwisting of lamellae of polymer molecules in this case which may affect the lamellae orientation on pure PP sheath. Thereafter, chain fold as twisted lamellae in the core by growing in a longer period of
crystallization time, and hinder the amorphous orientation at higher loading concentration. As a reverse, core structure may form with larger crystalline phase but with less orientation. Except at 5%, fiber behaves with reduced heat shrinkage, clearly indicate more crystallized orientation in fibers with higher crystalline birefringence (Fig. 6-9). More amorphous region alignment indicated larger fiber shrinkage could be related with higher fiber modulus as shown in Figure 6-15. Keeping increasing loading in the core, crystalline orientation into fiber structure imposes more heat stability with lower fiber modulus. However, even if loading in the core result into higher shrinkage below 10 wt. %, keep increasing fillers concentration to 20 wt.% and 30 wt.% inside of core assist to achieve the property improvement.

As shear stress in fiber radius direction orient polymer molecules into its own characteristics, filler particulate which are interacted with polymer shear flow must find a dominant alignment angle and exhibit the internal network of fillers. In previous study, we mainly investigate the filler particle with needle-shape with aspect ratio=5:1, and spherical shape, and found that the orientation of large aspect ratio particles is with a small orientational angle with polymer jet along z-direction. In the contrary, particles isotropy character such as PCC-Superpflex does not have featured alignment. Previous work by Fujiyama et al. flake like talc and mica or strand like glass fillers will cause stress concentration or melt orientation in polymer flow [28]. In that case, skin-core structure was noticed for injection molding, talc fillers aligned parallel to the mold wall because of higher shear stress, when the (0 4 0) planes of polypropylene pile epitaxial on the cleavage plane of talc [28, 31], acting as nucleating sites which promote crystallization along the thickness direction (b*-axis). In a
shish-kebab crystalline model of fibers, the folded planes grow perpendicular to the long fibril nuclei in shish. The heterogeneous filler particles distributed radially from fiber core to sheath may affect the folded chain compaction on the lamellae plane. As we find the GCC-FiberLink has increased melting temperature ($T_{m-on-set}$) of fibers compare to PP control by 1~2°C, where core loaded with GCC has higher temperature than sheath component, which means lamellae plane dimension is smaller for sheath loaded with fillers. It may indicate with higher particle alignment with polymer, the folded chains may grows tightly by epitaxial growth perpendicular to the GCC plane, which reduce the lamellae plane thickness.

**Birefringence of Fibers**

![Birefringence of Fibers](image)

Figure 6-7: CaCO$_3$ (PCC) loading configuration and filler concentration effect on bicomponent fiber birefringence
Figure 6-8: Theoretical model of polyester fiber skin-core lamellae structure developed in high speed spinning [22].

Figure 6-9: Compare bico fibers to the same total weight fraction in mono component fibers, total weight loading are 5, 10, 15 wt.% in the fibers.
PCC particles tend to form a closely packing geometry in narrow fiber volume because of its unique fine particle shape. Compare with EM, SF stands out in its isotropic property, apparently the sphere-like particles keep equilibrium shear component in stress tensor and bear normal stress. While from the different spinning performance that SF loaded in core works relatively better than loaded in sheath configuration (Appendix F), from practical experience, sheath contained with SF fillers withstand high spinline tension. Since frequent breaking occurs until spinline speed reached to 2000 mpm, we must reduce the winder speed to 1600 mpm. SF fillers disperse in polymer flow from steric repulsion force generated by 2% stearic acid coverage on particle surface, absorb polymer molecules and form an interlayer adhesion at alkyl chains. Existing at large shear strain of polymer, periphery intermolecular force takes the spherical fillers to move with the flow jet out of the spinneret and reduce melt fracture with enhanced deformability \[32\]. It was realized that the interfacial molecule clusters control the relative movement of fillers particles, and it also impact the mechanical properties of injection molded material \[33\]. Generally, surface coverage of fatty acid determine composite tensile strength and deformability \[34\]. That strength decreases because of immobilized interfacial braches form small crystallites and induce fiber brittleness. As shown in Figure 6-10, there are internal agglomerations due to bad adhesion of polypropylene molecules during spinning. The primary effect of filler loading varies in the volume fraction occupied by inorganic particles which may segregate into aggregations and agglomerations. The existence of apparent large cluster retard the long PP chain compacted into crystalline form but only partially set down into amorphous orientation. This is due to the more filler dispersion in the sheath and less segregation which restrict the crystalline
orientation. From an amorphous orientation structure, fiber sheath loaded with SF particles directly influence the crystal size. Based on our WAXD result, crystal size at (0 4 0) α – iPP crystalline increases dramatically from 63Å to 117Å comparing loading 10% PCC in sheath to 10% in core. This elucidate at larger shear rate on fiber skin, such finer spherical particles may hinder the large crystal growing, while incorporated inside of core contribute to a longer period of crystallization growth.

Lamellae plane chain folding related with the ease of decreasing free energy. As shown from \( T_{c-on-set} \) in Table 6-5, inorganic particulate changed rate of polymer crystallization. Obviously, lower small amount of PCC fillers improve the crystallization temperature indicating there is a substantial nucleating effect from EM particles. These fine particles act as nucleating sites and lower the system free energy by interacting with polymer molecules. Possible crystallization folding format may have epitaxial growth along the major axis of needle-particles. However, the nucleating effect is not consistently occurring at more loading concentration, because the stearic acid branches around filler particles actually restrict chain flexibility of polypropylene. Upon cooling, the density of polypropylene embryos must reach to certain limit where the kinetic energy may trigger on-set crystallization. From the Table 6-5, the on-set melting time comes much later when incorporate two PCC up to 20% within bico core structure, which is not competing with 0.55 minute earlier in the initialization time for GCC. As all the DSC testing procedure follows the exactly same time sequence in the testing, so the early initiating time indicate GCC-FiberLink is related with relatively looser lamellae crystalline density.
Figure 6-10: Fiber cross-section containing with 30% of SF (a) and 20% of EM (b) in bicomponent core component; compare with 20% of EM in sheath component (c).

Table 6-4: Index in Melting Behavior of Bicomponent Fibers:

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$-onset (°C)</th>
<th>Melt Peak Height (mW/g)</th>
<th>$T_m$-peak melting (°C)</th>
<th>Enthalpy $\Delta H$ (J/g)</th>
<th>$\chi_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>153.9</td>
<td>7.26</td>
<td>169.9</td>
<td>94.14</td>
<td>57.0</td>
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<td>Homo-Ca5</td>
<td>155.1</td>
<td>6.45</td>
<td>169.2</td>
<td>74.22</td>
<td><strong>47.0</strong></td>
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<td>6.77</td>
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</tr>
<tr>
<td>Bico-Ca10-sheath</td>
<td>154.7</td>
<td>5.14</td>
<td>168.5</td>
<td>87.52</td>
<td><strong>55.8</strong></td>
</tr>
<tr>
<td>Homo-Ca10</td>
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<td>5.61</td>
<td>169.3</td>
<td>81.98</td>
<td><strong>55.2</strong></td>
</tr>
<tr>
<td>Bico-Ca20-core</td>
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<td>5.29</td>
<td>168.8</td>
<td>81.04</td>
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<td>Bico-Ca20-sheath</td>
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<td>6.33</td>
<td>168.7</td>
<td>81.21</td>
<td><strong>54.7</strong></td>
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<td>168.8</td>
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<td>4.81</td>
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Table 6-5: Melting and Cooling Behavior of Bicomponent Melt Spun Fibers Filled with Different Types of Fillers:

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<tr>
<th></th>
<th>T\text{m-On-set (°C)}</th>
<th>On-set Time (min)</th>
<th>T\text{m-Peak (°C)}</th>
<th>Peak Width at Half Height (°C)</th>
<th>ΔH (J/g)</th>
<th>X\text{c (%)}</th>
<th>T\text{c-on-set (°C)}</th>
<th>Exothermic Peak Height (W/g)</th>
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<tr>
<td>PP control</td>
<td>154.2</td>
<td>13.58</td>
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<td>55.0</td>
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<td>EM5-Sheath</td>
<td>154.5</td>
<td>13.61</td>
<td>169.2</td>
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<td>91.7</td>
<td>56.1</td>
<td>125.78</td>
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<td>126.32</td>
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<td>13.562</td>
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<td>92.2</td>
<td>58.8</td>
<td>122.32</td>
<td>2.37</td>
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<td>81.9</td>
<td>54.7</td>
<td>121.20</td>
<td>2.63</td>
</tr>
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<td>169.2</td>
<td>15.6</td>
<td>91.0</td>
<td>55.7</td>
<td>122.14</td>
<td>2.73</td>
</tr>
<tr>
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<td>83.6</td>
<td>55.3</td>
<td>121.00</td>
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<td>SF30-Core</td>
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<td>13.694</td>
<td>168.4</td>
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<td>80.9</td>
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<td>53.5</td>
<td>122.40</td>
<td>2.24</td>
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6.3.1.3 Fiber Crystallinity

![Graph showing different loading configuration effect on fiber crystallinity](image)

Figure 6-11: Fiber crystallinity forming by bicomponent fiber spinning incorporated with 10~30% of fillers in sheath/core component vs. mono-component.

When compare fiber crystallinity at two different bicomponent configurations, sheath composing with filler result into lower crystallinity than loading in the core. The latter one keep constant fiber crystallinity in 20~30 wt.% of loading. This indicates that crystallization in a fiber spinning process varies with amount of loading fraction as well as the distance from loaded component from center to the skin. When fiber sheath contain with fillers, fiber tends to form distinct skin-core structure. While incorporating filler in core form a viscous polymer fluid extruded out of capillary, this increases the elongation stress within the core, decreases the rate in polymer crystallization. When polymer jet
goes across the necking point, the temperature gradient is almost equal in fiber radius, then crystallization rate accelerated by higher extensional stress onto fibers. So that a pure polypropylene skin will have a fast response with spinnal stress to form a row nucleated crystal transformation, as shown in Figure 6-8. Dees and Spruiell described radial crystalline structure developing in fiber spinning, which ribbon-like crystals are nucleated and grow in epitaxial on fibril nuclei under the shear-induced crystallization \cite{26, 27}. By the oriented melt forming c-axis orientation, the lamellae go twisted outwards from inner core to outside skin (in two directions along a-axis and b-axis). At high tension mainly winded at higher velocity, the twisted lamellae do not exist but preferring to untwist the lamellae crystals perpendicular to the fibril nuclei, at the same time the orientation in z-axis is significantly improved \cite{27}. As results in Figure 6-11 shows, containing with more than 10% CaCO₃ fiber crystallinity is related with the integral inorganic distribution. Over 20% of local distribution of filler particles could result into the lamellae a-axis and b-axis crystallization undergoes irreversible loosely packing, especially for the untwisted lamellae developed on fiber skin. For example, 30 wt. % in fiber sheath result into fiber crystallinity drops more substantially than incorporating in fiber core. This means that the heat transfer of fiber skin with ambient cooling air will greatly reduce the time window for crystalline phase to grow in the spinline. High polymer orientation from birefringence curve may indicate the aligned polymer chains under fast cooling, but it may result into fiber stiffness (high modulus) and less strain at breaking.
6.3.2. Single Fiber Tensile Properties

Skin temperature cools faster by incorporate with calcium carbonate fillers, leaving the core temperature keeping high to hinder the row nucleated lamellae untwisted. Skin distributed filler particles make an alignment under shear flow in fiber spinning, in this way to orient polypropylene chains from skin to core by untwisted lamellae chain segments. Because loading filler in sheath result in strain at breaking lowered but fiber tenacity improved as shown in Figure 6-12, especially at high concentration 10% and 20%. For example, 10% sheath loading generously contributed to higher tenacity at 4.418 gf/denier, while loading 5% in mono-component shoot at 4.213 gf/denier therefore decrease 4.64% comparing with the former one. Even worse, comparing with 10% loaded in core, the strength level drops to 3.994 gf/denier. The better performance at loading filler in sheath indicate spinning in this condition well overcome structural defects in spinning, and help polymer molecular chain orient to higher order.
Figure 6-12: Bicomponent fibers containing with PCC-EMorce in sheath/core configuration at certain loading concentration

Figure 6-13: Fiber strength for varying loading concentration of GCC-FiberLink in mono-component and bico configuration
Fiber tensile behavior has a dependence on filler concentration that higher loading resulted in lower tenacity and lower strain at breaking. As discussed in previous chapter, structure defects form at weak interface bonding between fillers and polymer matrix. Last chapter we have conducted fiber tenacity which is unified in gf/denier, which taken account of fiber specific strength to the linear density of fiber material. As shown in Figure 6-13, we plotted fiber strength data with 5~30% of loading concentration in mono-component and bicomponent fibers, unified with the fiber cross-sectional area ($\mu m^2$) based on the assumption that they have round shape with diameter known. We found that using bicomponent fibers may perform higher strength at the same component blending ratio; that especially control one component loading fraction without sacrificing total loading concentration work better in toughening the fibers. For 20-30% of loading in bicomponent fiber, the total loading in fiber equal to 10% and 15%, while fiber strength is also equal to or supreme than the mono-component fibers. While bicomponent with filler in sheath increase concentration from 10% to 30%, it peaks at 20% of loading, at which level it is even higher than the core filled. While at 10% and 30%, loading filler in core perform higher fiber strength than the reverse.

Fiber strain at breaking represents the extent of polymer chains to be extended in a tensile behavior that amorphous molecules pulled apart followed by crystalline region inter-platelet distance increased. The relative larger strain at breaking indicated a less oriented
in the fiber formation, so that polymer chains can be stretched and tightened into a great extent. As we can see from Figure 6-14, mono-component fibers containing with 5% has equally total amount of loading of 10% in bicomponent fillers. But the former one apparently perform less strain at breaking, the 5~10% loaded mono-component fibers are brittle than bicomponent fibers with 10% in sheath/core structure. That the distinctive low specific heat shown in Figure 6-19 pointed out that the lower than theoretical (Rule of Mixture) value at 2.5~5% CaCO₃ resulted high spinline tension due to fast cooling rate, which cause much amorphous orientation of polymer but also hinder the strain of single fibers. Up to 10% in mono-component, fibers keep behaving with lower strain at breaking compare to 10% in sheath/core bico configuration. The extent in fiber tensile stretching give us an idea of molecular orientation along the fiber main axis, without filler loading in polypropylene fiber, the polymer flow is very flexible in the melt condition which gives a much extension conformation under spinning tension. While increasing filler concentration reduces such chain flexibility in fiber, before fiber formed from filaments under solidification, some of polypropylene chains are still not fully oriented into a highly crystallized region. Then those relatively coil polymer chain molecules are pulled out from the loose packed lamellae phases that resulted into higher strain at breaking. We have used Wide Angle X-ray (WAXD) to calculate the crystal plane spacing d (Å), find that spacing distance is increase with filler concentration, so that thickened lamellae phase is a direct reason for increasing the strain of chain molecules if neglecting the
structural defects within fibers. However, when loading concentration reach to or above 20%, the probability of fibers encounter with structural defects is apparently increases, so there is still chance that fiber breaks without fully unravel the crystalline lamellae, but by breaking at the weak interfacial linkage.

![Filler Blend Ratio in Loading Component Influence on Fiber Strain at Breaking](image)

Figure 6-14: Fiber strain at breaking for filler contained structures in bicomponent sheath/core configuration.

Melt spun fibers perform initial deformation potential from its elastic region in tensile stress-strain behavior. Secant modulus at 5% strain is mainly compared in Figure 6-15, at varying of filler loading concentration from 5% to 30% we can see the modulus decreases in mono-component fibers. There are two sharp transitions in modulus of mono-filaments, one occurs when just loading 2.5% of GCC into PP fibers, the modulus reduce at least by 400 MPa. The other drop is occurring when loading concentration is above 20
wt. %, and then there is a dramatic reduction of 300 MPa. Compare bicomponent fibers with mono-component, the variation in modulus also represent the molecular orientation level as shown in previous birefringence. For example, to get a higher modulus, load 10~15% in mono-filament cannot compete with sheath loaded with higher fraction. As we can see, loading in sheath component has an improvement on modulus when concentration is above 10%. While for same loading amount, incorporated in core or in mono-component fibers will almost keep at the same modulus level. Even though the local fraction of CaCO$_3$ increases, but the larger spinline shear force support to form more amorphous orientation, which significantly improve fiber stiffness in the melt spinning formation.

As shown in Figure 6-15, fiber yield strength is compromised with filler concentration increases from 5% to 30 wt. %. When synthesize of both bicomponent yield strength as well as secant modulus as shown in Figure 6-11, we have found that filling GCC (FiberLink) at 10% to fiber sheath could result into less yield strength and lower modulus. Polymer stress-strain curve behave yielding point as strain as total release the elastic energy in the initial deformation. The fiber crystalline structure is continuously deformed in the plastic region. Reversely, increase to 20% to sheath component has greatly improve the fiber yield strength.
Figure 6-15: Fiber secant modulus at 5% for varying loading concentration of GCC.

Figure 6-16: Yield strength of melt spinning mono-component and bicomponent fibers.
Previous with a maximum loading of 30%, increasing up loading in sheath using GCC has reduce the fiber strength and yield stress even though keeping at higher modulus, it elucidated only by amorphous orientation in polypropylene chains could be offset the deterioration in weakened fiber strength because of structural defects become apparent. Fu et al. gave us mathematical modeling work on fillers incorporated polymer composite, where yield strength is one of properties studied. They argued that small loading of BaSO$_4$ (<16 wt. %) in polypropylene did not sacrifice in yield strength, but more than 16 wt. % the composite polymer yield at lower strength \cite{25}. From fiber tensile behavior, obviously it resulted lower yield strength, because fiber structure which highly dependent on polymer orientation. However, relative better yield strength is hit at 20% in sheath.

### 6.3.2.1 Stress-Strain Curves

![Stress-Strain Curves](image-url)
Figure 6-17: Stress-strain curves of single fibers containing with 10%~30% of GCC filler loaded in the sheath of bicomponent fibers (a); and structure effect for 30% of GCC filler loading in sheath/core compare to 15% mono fiber (b).

From stress strain behavior of single fibers, we are able to figure out the fiber spun forming structure containing with GCC and PCC-EMforce under same spinning conditions, which tensile performance comes from the shear flow-induced fiber orientation and structural development during spinning. There is high possibility of fibers reduce its tenacity if there is severe chain segment defects either stay in amorphous or within less perfect semi-crystalline region. While longer strain at breaking is likely to represent the less orientation fiber possess with during the spinning process, as indicated in Bico-Ca10-Sheath in Figure 6-17 (a), which could due to fast cooling rate that hinder the polymer chain orientation. When determine loading filler in sheath or core will works better, as shown in Figure 6-17 (b), it has been found that loading 30% in sheath resulted
into poor tensile strength than loading same amount in core component or as a homogeneous component. However, fiber stress dropped significantly from original stress-strain curve of PP control fiber, which means the dominate factor deteriorate fiber tensile properties control by structural defects. What has been found from the other PCC type of CaCO₃ is that its toughening effect on fiber stress-strain curves compared with PP fiber with 10% filled EMforce as shown in Figure 6-18 (a) and (b). It is unexpectedly that 10% EMforce incorporation in sheath can have even better yield strength than PP fibers. This represent its toughening effect in fiber formation that there is a highly efficient alignment with polymer flow direction, causing less severe defects in PP fibers compare with GCC fillers. When the stress pulls on the fibers, it can be transferred through the oriented polymer chains with those particles in alignment with the orientation. Meanwhile, we found for PCC-EMforce, 20% loading works efficiently when they are incorporated with the sheath component, shown in Figure 6-18 (b). It is not only reflected from higher tensile stress during the deformation of fibers, but also behaves with higher yield stress and lower strain at breaking. With such needle-shape fillers, the matrix/filler interaction enhances such a tie friction in tensile behavior, the large specific surface area provide a generous amount of stearic acid branches which laterally harness the lamellae disintegration. Afterwards, a new question is brought up on how the differentiations in radius temperature affect polymer crystallization in spinning formation.
Figure 6-18: Stress strain behavior for melt spun bicomponent fibers filled with PCC-EMforce in sheath/core bicomponent fiber at 10 % (a) and 20 wt. % (b).
Fiber strength shows an improvement for both 20% in sheath and 20% in core, compared to lower concentration at 10% and higher loading concentration 30% (Fig. 6-13). However, until concentration reach to the level when thermal conductive pathway form by interconnecting filler particles in fibers, will not it have significant improvement in improving the cooling rate of fiber. This gives the fibers a less likely to freeze polymer chains in fibers within too fast time period, which may result into less crystallized orientation in fibers. It most likely occurs when specific heat of fibers is significantly lowered, for example at 5% of loading (Fig. 6-19), at which point fiber crystallinity reduced indicating crystal growth is compromised due to large quenching rate of polymer. Replacing 5% in mono-component with a 50/50 sheath/core bicomponent fiber configuration help overcome such crystalline structure defects caused by over relaxation in a high heat transfer medium. 10% loading in the fibers, although still lower down the heat capacity compare to PP control fibers, the relaxation of polymer chain in the fiber spinline is also limited by a more densely compacted fibers. So that fiber crystallinity of bicomponent fibers recover back from 47% to 55%, as shown in Figure 6-11.

6.4. DISCUSSIONS

In this paper, the bicomponent fiber structure-properties relationship has been addressed for varying of loading concentrations in sheath/core configuration. Single fiber tensile strength, elongation, modulus and yield stress are characterized to gives reasonable explanation on fiber morphology change associated with polymeric orientation.
Comparing with previous mono-component fiber spinning, using bicomponent structure can change fiber partial filler loading fraction from 10% to 30% but varied in total amount of loading from 5~15%. So for spunbond fabric properties related with fiber surface roughness, opacity, for example, combing CaCO₃ fillers with sheath component of spunbond fibers will improve fabric performance with less filler loading. On the other side, for less breakage in fiber spinning, incorporating fillers in core structure will benefit for spinnability improvement that spin finish may be easier to be taken up by kiss-roll applicator. More importantly, since a pure polypropylene material wrap around the inner core which filled with impurities, that by increasing the amount of loading inside we may reduce the cost of raw material but also perform rather smooth surface which is required for fiber entanglement in nonwovens. It was found that surface unevenness comes from calcium carbonate particles that protrude outside of sheath layer as the average size d₅₀ falls in same scale level as fiber sheath thickness, furthermore, amount of loading in sheath control space in packing therefore impact fiber surface roughness [17]. The particle size distribution of CaCO₃ as loaded with different bicomponent configuration will have an impact on how much fillers are protruded or submerged under the fiber boundary. Although some others types of bicomponent incorporating different polymers into side-by-side, segment pie or island-in-the-sea fibers, and improve fabric softness by reduce fiber diameter, or by add another low melting point polymer into bicomponent, such as using propylene/ethylene copolymer into polyolefin [18]. In our example, fabric softness is
mainly targeted by generated such surface irregular or partial regular packing of fillers, and influence the hand softness and comfort in hand rubbing with the fabric surface.

In a specific investigation in polymer material heat capacity with varying concentration levels, we reveal that increase the concentration specific heat (J/K·g) is correspondingly reduce which meet with the rule of mixture model above 10% included in Figure 6-19. Heat conductance based on fiber center in a radius to surround air temperature, particulate fillers existing layer determine how fast heat diffused through fiber sheath layer. Apparent, if sheath is made of pure polypropylene, the thermal conductivity from center to outside is not comparable to inorganic filler contained within the sheath layer. This is because of lower heat capacity of fiber sheath will lower down the amount of thermal energy it requires to diffuse heat between crystalline lattice which is based on phonon movement which cause dissipation of heat by polymer bonds vibration. Therefore, we would expect a fast time consumed in fiber quenching when sheath component is especially filled with particulate calcium carbonate. If in the opposite, when fiber cooling time is hindered by extending the heat diffusion efficiency, fiber would have less orientation in the following spin-draw process. From higher strain at breaking as well as lower fiber secant modulus, we all expect filler loading in sheath will improve fiber crystalline orientation because of this thermal conductivity differences.
6.4.1. Heat Transfer

From previous study (Chapter V) it has been revealed that calcium carbonate fillers promote polymer thermal point bonding by reducing polymer specific heat, and the apparently higher thermal conductivity assist fast melting and crystallization rate of polymer. We used MDSC to characterize fiber heat capacity at varying of CaCO₃ filler loading level, and it was found $C_p$ decreases with loading concentration of inorganic fillers. Stand on the point of fiber formation, different rate of heat transfer coefficient will also cool down polymers in a distinctive different rate. If heat transfer improves in fiber solidification, then it could move up the frost line and increase the spinline tension. Fiber polymer is driven by drawing polymer chains in the lamellae folded chains and form into highly oriented crystallization. In this process, the heat release from inner to skin which, presumably generate a gradient of fiber crystalline structure, according to Ziabicki in Figure 6-8. The skin of fibers during spinning imposes higher shear stress due to lower surface temperature so that untwisted lamellae appear sooner in outer layer. Bicomponent fiber structure build specific loading compartments for inorganic fillers (CaCO₃) so that one component of fibers is exposed to quenched air first, either sheath layer or inner core. Our intention is incorporating CaCO₃ fillers in a specific component for improve fiber orientation, crystallinity as well as fiber crystal size. However, it is difficult to get higher orientation at the same time to grow crystal size to a larger phase. Because the highly orientation usually comes at high spinline velocity which impose quick cooling rate,
crystallization for lamellae plane grows to a larger crystal size only when cooling rate is relatively slow and there is moderate spinline tension to induced the larger crystallites. Either for crystallization of fibers during quenching or for the bonding formation at calendar roll is aiming for a better tensile behavior of nonwoven products. Therefore smaller crystal size with more $f_a$ may assist the bonding formation, while high orientation especially $f_c$ will hinder the reptation across fiber boundary.

Heat capacity of polymeric material is about its intrinsic thermal property respond temperature variation to systematic energy change. The inorganic particulate fillers, substantially, will connect within the intermolecular polypropylene interstice and functionalize with a conductive passage. Plastic processing technique has potentially apply all kinds of inorganic fillers to blend with thermoplastics, and achieve higher thermal conductivity in processing such as injection molding to control the heat and cooling circle time, in the meantime assist de-molding of plastic articles $^{17, 18}$. Calcium carbonate is with thermal conductivity ($\kappa$) 2.7 W/(m·K), compare to polypropylene 0.5 W/(m·K) the inorganic phase carry on at least five times more enthalpy from higher temperature area to lower region. In macromolecules state, the degree of freedom at temperature $T$ defines the specific heat of polypropylene, which could be enhanced by varying filler particles loading from the aspect of Brownian motion. Enthalpy transfer at filler/polymer matrix interface in regardless of cavity around fill particles can form rather
efficient heat transfer pathway at higher filler loading concentration. Decreasing in fiber birefringence for loading in core may reflect a less heat conductance path through the polypropylene skin layer because the heat entrapped in filled core compartment may cause chain relaxation at skin layer.

In case of fiber spinning, the thermal energy release gradient is interpreted as temperature reduction in the direction from fiber core to the surface. The formation of fiber structure in crystalline orientation, crystallinity and amorphous defects during the spinning process is a complex way because of the rheological response of polymer under different temperature and velocity, even the nonisothermal effects resulting from heat transfer with ambient temperature \(^{[27]}\). The rate in thermal diffusivity is represented as

\[
\alpha = \frac{\kappa}{\rho C_p}
\]  \(\text{(6)}\)

Where \(\kappa\) is thermal conductivity, \(\rho\) is fiber density (kg/m\(^3\)), and \(C_p\) is specific heat capacity (\(J/(kg \cdot K)\)). So with thermal conductivity increases with loading fraction, it is accompanied by reduction in the specific heat, so the diffusion rate goes faster. This represents in fiber spinning as heat transfer with quenching air that temperature of the melt cool down with solidification as frost line moves up. Previous work by Kase and Matsuo have argued temperature gradient in polypropylene fibers is dependent on quenching rate along the spinline, where cooling rate (m/min) represent in the velocity of air blowing to the filaments. They also pointed out fiber cross-section area deform sharply
and solidification distance is shortened from spinneret to the frostline \cite{23}. The diffusion direction in fiber transverse direction is regarded as from core to its skin, as pointed in Figure 6-20, theoretically the polymer temperature at one point with distance of $x$ apart from center should be symmetric for a cylindrical filament. This distribution curve, based on the schematic graph of heat flux diffusion in the quenching (Figure 6-20 (b)), reveal the true function of radial distribution temperature in fiber transverse direction. Heat flux $Q$ is following $Q = -k \frac{dT}{dx}$ that the wave transfer rate in the temperature gradient is related with material thermal conductivity, so that the inorganic filler particle loading configuration should be respectively discussed in this case.

$$Q = -(k_c \frac{T_c - T_{12}}{r} + k_s \frac{T_{12} - T_a}{R-r})$$  \hspace{1cm} (7)$$

where $k$ is thermal conductivity of fiber material, $c_1$ and $c_2$ are denoted as core component and sheath component, respectively. $T_c$ is the center temperature of polymer melt flow, which is quenched by cool ambient air with temperature $T_a$. Since CaCO$_3$ may fill out either component 1 or 2, then we use $T_{12}$ as the interphase temperature. To involve the fiber radius temperature, Kase and Matsuo has conducted temperature differential between filament surface and filament core, and concluded with the differential between core and surface is less than 10% of that between filament surface with ambient air \cite{24}. And the temperature profile in fiber spinline is a function of distance from the spinneret, time and also the exothermic energy diffused in polymer crystallizing.

$$d\bar{T}/dx + 2\pi a^* R (\bar{T} - T_\infty)/WC_p - \kappa_c \frac{\theta_c}{V} C_p = 0$$  \hspace{1cm} (8)$$

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$\bar{T}$ is the average spinline temperature from spinneret position at $x = 0$ where temperature of melt is set at the spinpack temperature profile. $T_\infty$ is the temperature of ambient air. $\alpha^*$ is the surface coefficient of heat transfer. $R$ is fiber diameter, $W$ is the mass outflow (g/sec) or mass throughput out of the spinneret capillary. $C_p$ is the heat capacity of polymer, which should be reduced if adding in inorganic filler particles. $\kappa_c$ is the latent heat of crystallization. $\dot{\theta}_c$ is the degree of crystallinity. $\bar{V}$ is the speed in spinline accelerating from polymer extruded out of capillary where $\bar{V} = 0$ to the same speed as the take-up winder.

$$\left( \frac{\partial T}{\partial r} \right)_{r=R(x)} = -[T(x, R) - T_\infty] \frac{\alpha^*}{\lambda} \quad (9)$$

$\lambda$ is thermal conductivity of polymer, $T(x, R)$ is the temperature at fiber surface down from a distance $x$ to the spinneret. Then the partial derivative of temperature to fiber radius is positively correlated with heat transfer coefficient $\alpha^*$.

There are two possible interpretations of heat transfer coefficient that associate with where is the heat source from and how the heat diffusion direction towards to. The first mechanism is in the spinning process, where fiber core is possess with higher temperature thus diffusivity also always balance the temperature gradient from core to the ambient air.

In the sheath/core configuration, when sheath is filled with calcium carbonate particles, then thermal conductivity of sheath layer should be higher than the core where polypropylene occupies the center. As shown in Figure 6-20 (a) curve 1, in temperature
distribution curve 1 sheath cooling rate is substantially higher than the core, then the fiber skin temperature will be quenched quickly and increase the temperature gradient from core to the skin. In this way, when the larger temperature gradient dominate polymer melt in the beginning of quenching, it will enhance the \( \frac{\partial T}{\partial r} \) as shown in equation (9), and cooling completed faster. According to this mechanism, polymer amorphous orientation can be significantly increases, proven from loading fillers in sheath with 10% and 20% of EM fillers (Figure 6-7), the promotion of fiber quenching rate increases the birefringence, therefore fiber strength improves and strain decreases (Figure 6-12). In the second mechanism, the heat transfer direction may from skin to the core when spunbond fabrics are thermal point bonded. While when fibers under calendar embossed pattern accepted heat from ambient pores and surface contact with calendar surface, heat transfer coefficient from sheath inward to the center will also be through the layer containing with CaCO\(_3\) initially, and then soften inner core polymer lamellae fraction. Also from Figure 6-20a, at same fiber surface temperature, loading filler in core configuration is hardly to increase the core temperature to as much as the temperature level when sheath is added. Because the filler contained layer connected between ambient air with center of polymer conduct heat more quickly. In this way amount partial of fiber orientation is kept within the core, which contribute to maintain fabric structure integrity during subsequently cooling. While with polypropylene sheath layers are melted to be tacky diffuse around adjacent fibers, in this way to form reptation of polymer chains effectively.
It is considered state of amorphous constructed around crystalline structure will not different affect the on-set melting time, however, if the GCC particles already cause unavoidable structural defects in the component, then heat transfer can involve radiation more to the voided inner structure. Therefore, the heat treatment impose relaxation and flow property of the polymer around the void interphase, in combination with radiation as an addition format of heat transfer through the spunbond webs. In this way, the fabric mechanical properties containing with up to 20% of GCC is maintained as discussed in previous Chapter V.

Figure 6-19: Heat capacity of FL GCC contained fibers at 50°C (■), 100°C (●), 150°C (▲), and 190°C (◆). Linear is a theoretical results from the Rule of Mixture in equation (3)
Figure 6-20: The schematic graph of fiber cross-sectional thermal conductance from fiber core to the skin, and the temperature diffusion gradient as in bicomponent sheath/core structure for CaCO$_3$ filled in the sheath (1) and CaCO$_3$ filled in the core (2).

\[ \rho C_p \nu(z) \frac{d\theta}{dz} = -\frac{2h}{R(z)} (\theta(z) - \theta_a) + (\sigma_{zz} - \sigma_{rr}) \frac{d\nu}{dz} \]  

(10)

$\theta(z)$ is the polymer temperature along the spinline, $z$ is the position down from leaving the spinneret exit ($z=0$) to the vertical position, $\theta_a$ is the temperature of ambient cool air, $h$ is heat transfer coefficient, $C_p$ is the heat capacity of polymer, $R(z)$ is the diameter of filament at position $z$, $\rho$ is the density of filled-polymer material. With polymer jet accelerates from $\nu = 0$ extruded outside of spinneret to speed of $\nu(z)$ the stress increasingly reach to a maximum level that when it is higher than the intrinsic strength of fibers, then spinning may encounter with breakage. But with fillers increase heat transfer coefficient, the polymer viscosity may increase at same spinline position $z$, because the temperature gradient as fiber cooling may be varied.
Dragging in the high velocity air comes along with attenuation of filament into highly oriented polymers by aspirator in the aforementioned spunbond. With contractions in radial direction the coiled polymer chains extended significantly in longitudinal direction. It is possible due to the radial temperature gradient in polyester fibers that resulted into skin-core structure, shown in Figure 6-8. The larger the filaments cross-section dimension, and lower the take-up speed, the more distinction between crystalline structures through fiber radius. If loading in the core, especially when filler weight fraction become more, polymer chains tend to be relaxed in the core because of heat entrapment to the center of fibers. Ziabicki and Spruiell estimated such skin-core differences could disappear when spinning speed is above 5000 meter/min for polyester yarns [22, 26]. For polypropylene with CaCO₃ filled in whole fibers or partially filled, the reasonable explanation on varied tensile properties is from polymer chains orientation together with crystalline phase defects after filled with particles. Inner filaments with higher temperature and large entropy value undergo conformation compaction later on, therefore sufficient time allow the polymer chains to sufficient adhere to filler particle surface. It may also bring needle-like particle rotating at the inner core that minimize the benefit of particle alignment with the high shear rate. However, when the core contains fillers, heat entrapped under the polypropylene sheath may hinder an overall heat transfer rate, resulting in a decrease in drawn fiber crystallinity, but increase the polymer chains orientation. From bicomponent fiber diameter listed in Table 6-3 and Figure 6-7, fiber
diameter are larger at 10% and 20% of fillers loaded in core comparing with same levels loading inside of sheath.

6.4.2. Bicomponent Fibers in Thermal Bonding

In thermal processing of nonwoven webs, the importance of using bicomponent fibers is for purpose of improving fabric softness, achieved by partially deformation of fiber component with low melting point and form bonding at relative low temperature. As long as fibers are kept at optimum bonding window, the strength will be kept at the largest strength. Although lower down bonding temperature may help overcome the plastic like rigidity in the fabrics, it also deteriorates fabric strength. Bonding agent in some case is supplied to enhance lamination bonding between nonwoven with the other film layer [19].

Inorganic fillers may be incorporated into a film like such to impart an internal microvoids structure, and thus improving the breathability in relevant application [3]. For example, layered structure in baby diaper requires the comfort fibrous thermal bonded layer to be laminated with a topsheet which guide liquid to penetrate through and absorb by liquid collecting layer beneath. By the good adhesiveness from bonding agent, two layers of material can be effectively laminated meanwhile not destroy the integrity of each layer [19]. Furthermore the improved surface roughness of fibers can avoid over adhesion between two layers so that leave an extra interlaminate space which help to guide liquid horizontally. As mentioned for hygiene and surgical nonwoven fabrics, those particles fillers exposed outside of bicomponent fibers change a physiological hand
feeling, which remove cold and plastic characteristic of polyolefin $^{[10,11]}$, in replacement of a smooth and softness. To make consistent quality in roll goods, bicomponent fibers can respond with temperature when it reaches the melting point of one of the multi-component, by partially flow this component around fiber assembly to achieve the bonding of the webs. The time requires to cool down the bonded web must be close up before wounded into rolls because if any fibers are still molten they will be attached to the adjacent layer. The advantage by adding inorganic fillers is that they improve the thermal conductivity speed, and assist for fast cooling of fiber web. Similarly, rolling up those nonwoven fabrics or laminated goods is better to avoid polymer sticky effect at softened spots throughout the webs.

Incorporation inside of fiber core is for considering of fiber strength integrity especially at higher filler loading concentration. This is from the economic aspect that increases up the loading but still keep the fiber strength, which means that filler impurities are hided back under a shell of pure polyolefin. Ground calcium carbonate either produced from dry grinding or wet milling influence its particle size distribution and functions $^{[20]}$. Ultrafine particles may add up the cost for the calcium carbonate, also bring high melt viscosity when load exceed certain fraction of loading in the polymer melt $^{[1]}$. In fiber spinning process when both cost saving and extrusion stability are desired, using bicomponent fibers to embed filler particles inside of core works for this purpose. Such as mentioned in
bicomponent fiber inventions, the inert particulate fillers are incorporated into core made of polypropylene and then co-melted with polyamide sheath into multi-lobal fibers [21]. Because of polypropylene dominate in our spunbond fiber structure, wrap around the core component which include filler particle do not create a distinct interface at sheath/core transfer boundary as shown in Figure 6-4 and 6-5. Also because of the reptation across this boundary, polypropylene chains could involve some filler particles to transfer from one side to the other. However, generally the fiber surface is lack of bumpy roughness in this case that is another benefit in considering of fiber spin-draw stability. The reverse effect of only incorporating fillers in sheath is just generate a surface unevenness, but since the PCC-EM fillers has high aspect ratio which can easily align along the shear flow direction, so these fillers cause less problem in surface roughness. Therefore, loading the high aspect ratio of PCC in sheath can still maintain relatively good strength and fiber orientation at higher loading level.

6.5. CONCLUSION AND SUMMARY

Bicomponent configuration contributes to fluent and sound spinning on drawing godet. We have conducted a comparison evaluation on sheath/core loaded with calcium carbonate fillers on fiber surface condition, and observe using microscopy of filler dispersion in targeted component with 10~30% of GCC-FiberLink. A uniform distribution is necessary for different levels of concentration study in 50:50 S/C, which refers to two calculation methods in blend ratio for that component and in total of fibers.
This method in bicomponent production has two-way consideration – loading filler in sheath to change fiber stiffness and surface unevenness, and loading filler in core to hide fillers from exposing to surface roughness. Previous results on mono-component spinning have indicated calcium carbonate significant change polyolefin surface smoothness that particles anchor on fiber surface tend to protrude out. So as to bico fibers the surface bumpy feature is more likely to achieve only when loading in sheath component. It also shows secant modulus of those bico fibers when containing with 20% and 30% in sheath will be much larger than in mono component fibers filled with 10%-20%. Furthermore, % strain at breaking is also reduced for sheath filled with both FiberLink and EMforce, importance of the sheath layer on fiber crystallization rely on a thermal conductive pathway which speed up crystal growing and make fibers chains turns rigid with higher secant modulus.

In some spinning application, we also want to avoid spinline instability on the stand point of surface smoothness. It is necessary to hide inorganic fillers beneath the sheath, because a hydrodynamic water film will form in between fibers and godet rolls, which stabilize the spinning performance. Most surprising is loading filler in core component at 50% of volume ratio will change the actual volume of core/total volume of fiber. Increase the amount of CaCO₃ loading, the core volume ratio in the total fiber volume is decreasing as loading concentration varies from 10% to 30%. As heat capacity decreases, the core
component respond to a short period of chain relaxation before it solidified. Compare to a finer core wrapping around by pure polypropylene, there is less likely to expose big particles outside of fibers because the shell is thick and well covered over the stuffing minerals. Very important on single fiber tensile performance about keep the fiber spinnability as well as sustain a good mechanical performance for spunbond fabrics, it is suggested when loading more than 20%, incorporating fillers inside of core will function as better spining condition. We also found that slight amount of filler around 5~10%, incorporating in core also works better than in sheath. With higher fiber strength (Fig. 6-9) we would expect such fiber structure should have a more perfect crystalline structure. Also the polymer orientation of EMforce filled fibers indicate 5% of loading in core construct the polymer fiber with higher birefringence, which also induced larger secant modulus at 5% and yield strength of fiber (Fig. 6-15).
REFERENCES


CHAPTER 7 
Effect of Sheath/Core Loading Configurations on Bicomponent Spunbond Web Structure and Thermal Bonding Related Fiber Melting and Crystallization on Mechanical Property

ABSTRACT

Two different polymers extrude through bicomponent spinpack and spun into sheath/core bicomponent. The potential values adding inorganic fillers with bicomponent in PP fibers is that exposing CaCO$_3$ to surface with same roughness effect but in less total fraction. Based on last chapter, we have found the different particle shape may produce fiber with different tensile property with special skin-core chain oriented structure. Compare to ground CaCO$_3$ (GCC), precipitated CaCO$_3$ (PCC) is with finer particle size 0.25-1μm and larger specific surface area (10 m$^2$/g), imposing enhanced the interfacial adhesion with PP fibers. This paper discussed the mechanical property of nonwoven structure, in both considering fiber structure and bonding structure that both contribute to fabric entanglement of fibers by calendaring. So we have been achieved at more profound understand on using bicomponent configuration of loading calcium carbonate fillers that related to structure-properties of fabrics. This chapter continues on discussing crystallization of fiber polymers by a second melting and cooling, and mainly differentiates the particulate shape effect on embedded particles interaction with compressed polymers. The relevant inorganic specific heat and the polymer matrix
perform a changed heat transfer rate after commingled with the inorganic phase, which helps to explain the crystallinity changed in fibers, bonds and whole 2-dimensional fiber mat.

Key Words: Calcium Carbonate, Bicomponent Spunbond, Crystallinity, Filler Reinforcement, Tensile Strength

7.1. INTRODUCTION

Mineral resources of calcium carbonate in mining industry originate from limestone, chalk and marble \(^{[1]}\). The rock transforms into fine calcium carbonate particles by a series of process: crushing in mills, grinding, classifying and sorting \(^{[1,2]}\). Chemical precipitation of calcium hydroxide with carbon dioxide gas can form under controlled processing temperature and pressure to aragonite metastable polymorph, with needle-like or spherical particle shape \(^{[3,5]}\). Ground CaCO\(_3\) with a wider particle size distribution than precipitated ones, are in stable calcite crystal form with lattice unit as rhombohedral and scalenohedral \(^{[3]}\). Market available GCC fillers are seldom free of any impurities, such as MgCO\(_3\), dolomite CaMg(CO\(_3\))\(_2\) are existed in CaCO\(_3\) because existence of magnesium and slightly silica occasionally \(^{[4]}\). A large proportion of calcium carbonate is applied paper coated pigments which improve the ink acceptability papers, therefore improve its printability as well as a smooth and gloss surface appearance \(^{[1,3]}\). Other than papers, plastics manufacturing such as injection molding, blow molding also need a great amount
of fillers added into polymer flow to aid the thermal conductivity of materials and can enhance impact resistance, flexural rigidity, and improve heat distortion temperature and fast heat-cool-heat circle \[6, 17\]. Not only calcium carbonate fillers, but also other mineral fillers such as titanium dioxide, kaolin, mica, talc, magnesium carbonate, and silicate have been applied in molding articles used for automobile and furniture \[2\]. Due to the specific gravity of calcium carbonate (2.7g/cm\(^3\)) is higher than pure polymer (\(\rho = 0.9g/cm^3\)), adding filler into polymer resin can increase material density. For PP there is lower melt density (\(\rho_m = 0.74g/cm^3\)), meaning that volume of PP will expand significantly after heated up above melting point \[6\]. Comparing with PP the volume of mineral fillers expands slightly, giving polymer composite good dimension stability upon heating and cooling circle in molding.

Previous research has stepped in the field of fiber structure containing with inorganic fillers, the pioneer work from Idemitsu Kosan Inc. was conducted by Ookawa in 1970 \[7\], that interfacial separation generate microvoids around fillers inside of polyester fiber. Mineral supplier Imerys Inc. has been focused on a series of ground calcium carbonate fillers that applied to melt spinning fibers and their relevant performance in tensile strength with concentration up to 20 wt. % \[8\]. DeLucia and Hudson claim the improvement of softness thermoplastic fabrics by using CaCO\(_3\) fillers in form of nonwovens produced by meltblown or spunbond, with loading concentration limited
below 4 wt.%\textsuperscript{[10]} Development in spunbond technology contributes to a diverse area of products that combine bicomponent fibers with varying of thermoplastic polymers. PP and PE share a large portion of raw polymers in nonwoven manufacturing because of lower cost and performance in mechanical and thermal stability, but also available in grades of melt viscosity that can fit for specific techniques. Bicomponent spun filaments after being cut and crimped into staple fibers, they may fit application into high bulkiness\textsuperscript{[16]}. Thermal bonding of one component with lower melting temperature in sheath-core and side-by-side bico fibers allow the fiber webs to bond without compromise its bulky and softness.

Due to small diameter of fiber cross-section area, it is a big challenge to allow the incorporation of mineral filler into polymeric fibers without fiber breakage and spinneret blockage during the extrusion process. In choosing mineral filler, not only particle size should be taken into consideration, but also particle size distribution. Precipitate calcium carbonate (PCC) has higher purity with finer particle size around 0.7 to 2 μm, while GCC have particle size classified into two size grades in 3-7 μm and ultrafine size down to 1 μm\textsuperscript{[2]}. Particle size and size distribution influence filler incorporation with the finer size of fibers, as well as the dimension in specific component. Bornemann and Haberer used particulate fillers (D_{50}<6μm) to fill into Reicofil bicomponent spunbond machine by using 75/25, 50/50 and 25/75 sheath/core ratio\textsuperscript{[9]}, but only using constant calendar temperature
on bicomponent structure consolidation. Jayasinghe et al. illustrated a laminated fabric invention composited with at least one spunbond layer which contains multi-component fibers that incorporate inorganic fillers in the core component, but no further investigation reveal the mechanism of fillers in sheath component will resulted in thermal bonded spunbond and laminated structure \cite{12}. Although in a relevant work it was shown the efficiency of improvement of air barrier of the spunbond by reducing fiber diameter of spunbond made from pure polyolefin \cite{11}, but in the CaCO$_3$ contained web the results illustrated no relation between loading concentration and bicomponent configuration of CaCO$_3$ with the permeability and water column \cite{9}. Apparently there is few literatures mention on the calcium carbonate particle shape effect on web structure bonding and subsequently thermal bonding in the spunbond process. Based on our previous Chapter VI, we noticed the different spinline structure formation added with GCC particles (FiberLink) from the other two PCC which has needle-shape particles (EMforce) and another spherical finer particle (Superpflex). Due to the variability of CaCO$_3$ in the geometry dimensions, there will be different fiber crystalline structure and polymer orientation during fiber spinning and subsequent thermal point bonding. In a word, smaller the particle size, larger the aspect ratio of the particle shape, the distinct specific surface area particulate filler will get, which must enhance the probability of forming agglomeration, but it may also enhance interaction between polymer shear flows with the fillers in spinning.
This paper intends to construct fibers structural-properties relationship based on the bicomponent spunbond containing with calcium carbonate fillers. From types of CaCO₃ particle embedded into melt spun fibers, it is required to reveal the necessity of loading fillers in bico sheath/core fibers rather than mono-component spunbond in some circumstances. Structure related properties especially on mechanical property is our objective to reveal the incorporating inorganic particulate fillers on the sheath/core bico configurations and its influence on web bonding mechanism. The ultimate goal should complete the optimum loading configuration to compatible with spunbond processing threshold, keeping in balance with lower cost polymer raw material.

7.2. EXPERIMENTAL

7.2.1. Materials
Pure polypropylene resin carries with three different types of calcium carbonate. These additives come from mineral suppliers such as Specialty Minerals Inc. who sells a bunch of species of calcium carbonate tailored for different applications. Polymer is isotactic-Polypropylene (PP) CH360H (Braskem, Brazil). Melt flow index = 35. Molecular weight = 180,000 and the polydispersity = 3.3. Calcium carbonate is pre-compounded with PP in certain weight fraction with surface treatment of stearic acid. Information is included in Table 7-1.
Table 7-1: Calcium Carbonate Fillers Types GCC vs. PCC:

<table>
<thead>
<tr>
<th>Filler Brand Name</th>
<th>Supplier</th>
<th>Masterbatch Ratio</th>
<th>Specific surface (m²/g)</th>
<th>Average Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FiberLink201S</td>
<td>Imerys (GA)</td>
<td>80/20</td>
<td>4.8</td>
<td>2.24</td>
</tr>
<tr>
<td>EMforce</td>
<td>Specialty Minerals (PA)</td>
<td>50/50</td>
<td>10.3</td>
<td>1.0/0.25</td>
</tr>
<tr>
<td>Superpflex</td>
<td></td>
<td></td>
<td>5.2</td>
<td>0.38</td>
</tr>
</tbody>
</table>

7.2.2. Bicomponent Spunbond

Web forming is produced by 0.5 Meter Bicomponent Spunbond Line (Hills - Nordson) in the pilot plant of the Nonwovens Institute. Two extruders convey polymer material into spinneret, where core component of filaments come from primary extruder, and sheath come from secondary extruder. Three screens filters of 250 mesh size are located on the spinpack channels as shown in Appendix 9-3, 9-4. Spinneret has 1162 holes, polymer melting containing blend ratio of filler particles first being filter out any impurities, second pump out in a constant throughput, then coming down to spinneret, finally being quenched in cooling air. Technical index include speed and temperature profiles, as well as pressure of calendar can be found in Table 7-2. Calendar connected with web forming belt catch webs and bonding under five temperature levels: 130°C, 135°C, 140°C, 145°C and 150°C. Smooth surface and an emboss surface on each of the calendar.

Fabric samples made are mainly based on four different parameters. Calcium carbonate filler were selected from three types: FiberLink (FC), EMforce (EM) and Superpflex
Filler weight concentration design from 2.5% to 30%, covering several levels 5%, 10%, 15%, 20%, 25%, 30%. But for certain filler type only part of these concentration levels were selected. Web bonding takes place at five calendar temperature 130~150°C. Fabric basis weight has 50 gsm and 100 gsm.

![Schematic graph of bico spunbond processing line](image)

**Figure 7-1:** Schematic graph of bico spunbond processing line [12]

| Table 7-2: Temperature and Speed Profiles of Spunbond and Calendar Bonding: |
|-------------------------|-------------------|-------------------|
|                         | Primary core      | Secondary sheath  |
| Temperature (°F)        |                   |                   |
| Extruder                | Zone 1-Zone 6     | Zone 1-Zone 5     |
| Spinhead                | 465               |                   |
| Quench air              | 40%               |                   |
| Speed                   |                    |                   |
| Thoughput               | 0.3 ghm           | 0.3 ghm           |
| Quench air              | 25%, 1055 RPM     |                   |
| Aspirator Fan           | 45%, 1619 RPM     |                   |
| Calendar pressure       | 750 psi           |                   |
7.2.3. **Nonwoven Web Consolidation on the Spunbond Webs**

7.2.3.1. **Thermal point bonding**
Polypropylene spunbond web consolidate under calendar point bonding. Embossed calendar roll imposed an 18% of oval pattern coverage onto spunbond web, with another side compressed with a smooth calendar roll. During spunbond production for FiberLink in mono-component fabrics, the calendar surface temperature is adjusted at exactly 130°C, 135°C, 140°C, 145°C and 150°C. Since 130°C is apparent under bonded for most of filler concentration (except 30 wt.%), we delete this bonding temperature for the EMforce filler (precipitated calcium carbonate) in the following spunbond production. 155°C is also applied for PP control fabrics and EMforce at 2.5%, but not consistently apply to higher concentration. In the last thermal bonding experiment using Superpflex, we have to give up the temperature levels from 140 to 150°C because pump pressure issue had already been occurring for the initial processing at 135°C. We will talk about this part in results and discussion section.

7.2.3.2. **Thermal bonding with Double Smooth Calendars**
This experiment is designed for learning fiber recrystallization in the embossed bonding region. Being compressed in two smooth rolls, previously unbounded webs are bonded in the whole region contacting with calendars. Such treatment is keeping at constant calendar pressure at 750 psi and same running speed. We mainly study temperature at 135°C and 145°C. The sets of unbounded nonwoven were previously collected when
producing precipitated calcium carbonate – Superpflex. Since pump pressure issue, we have to stop running Superpflex 200x for rest of spunbond samples. The only fabrics being bonded are at 135 °C with two concentration 5% and 10%, and three filler loading configuration in fibers which are sheath, core or mono-component. So using calendar roll with embossed roll as well as with two smooth rolls gives us a better understanding of the semi-crystallization inside of nonwoven fabrics.

7.2.4. Properties Characterization

Scanning Electronic Microscope (SEM)

Fiber spunbond structures are imaged using Phenon SEM from the Nonwovens Institute physical testing lab. From platinum coated fibrous samples, images generate from which able we are able to measure fiber diameter and bonding structure, and the breaking spot of those tensile test fabric samples. From varying of magnified from 400x to 20,000x, our view perspective covers from a general fiber orientation to particulate fillers hanging on fiber surface. On web bonding morphology, one interesting part is the cross-section to view the web mid-plane under embossed region. So by using liquid nitrogen, fabric samples are cut in transverse direction across several patterned bonds.

FIB Dual Beam Scanning Electronic Microscope

Fiber cross-section sample is prepared using ion beam enhanced etching, on focused ion beam (FIB) DualBeam instrument, the FEI Quanta 3D FEG from Analytical
Instrumentation Facility. It takes about 30 seconds to sputter coat gold and platinum (Au+Pd) onto fiber samples. The average accelerating voltage is less than 30 kW, with a resolution of 1.2 nm at 30 kV in high vacuum. This instrument is equipped with an Omniprobe micro manipulator for a 360 rotation of sample etching edges, cross-section and even fiber surface. The ion beam moves forward for a distance of 13μm, generating a dynamic view of cross-sectional PP added with CaCO₃ at different location.

**Single Fiber Tensile Property**

The single-fiber tensile properties of the PP/CaCO₃ fibers were evaluated according to ASTM 3822-10 with an Instron MTS instrument with 50-g load cell (Canton, MA). The gauge length was 2.54 cm, and the rate of extension was 15mm/min. The tenacity, toughness, and strain at break were calculated from the tensile stress-strain curve. Secant Modulus was the slope of stress-strain curve at 5% of strain. The average of 10 samples is reported.

**Differential Scanning Calorimeter (DSC)**

The melting and crystallization behavior of the filaments samples were analyzed by Discovery TA Instrument Differential Scanning Calorimetry (DSC). All samples were first heated at 10°C or 20°C/min from 25°C to 195°C, followed by cooling at 10°C/min rate. Thermograms were obtained from DSC analyzed with the Trios software.
Crystallinity is calculated from endothermic peak, which reveal fiber crystallinity developed in spinning. Crystallinity is calculated based on equation:

\[ \chi_c (\% \text{ crystallinity}) = \frac{\Delta H_m}{\Delta H_m^0} \omega \times 100\% \quad (1) \]

Where \( \Delta H_m^0 \) is the heat of fusion (165 J/g) for 100% iPP; \( \Delta H_m \) is the heat fusion per unit gram of fiber sample; \( \omega \) is mass fraction of PP in the fiber composite.

**WAXD**

The scattering patterns were scanned using Omni Instrumental X-ray diffractometer (Biloxi, MS). Bragg angle \( \theta \), plane distance \( d \), crystal size of the sample were measured from diffraction pattern. The diffractometer was equipped with Be-filtered Cu Ka radiation with a wavelength of 1.54 Å and generated at 35 KV and 25 mA. The fiber samples were wound around the sample holder and locate at the same horizontal level with holder front surface. Then the sample holder was placed inside the chamber of the sample holder. The samples were scanned in the 20 range 5° to 40° with an increment of 0.05°. Plane spacing \( d \) of crystal unit was calculated using Bragg's equations:

\[ \lambda = 2dsin\theta_B \quad (2) \]

where \( \lambda \) is wavelength of X-ray (1.54 Å), \( d \) is interplanar spacing (Å) and \( \theta_B \) is Bragg angle.
Nonwoven Grab Tensile Test

Five MD samples and five CD samples were tested using the United Tester (the Nonwovens Institute Physical Testing Lab), based on standard ASTM D5034. Testing used the type of CRE operating at speed of 300mm/min and tester records the breaking strength as well elongation at breaking for each sample. After each test, the fabric secant modulus is analyzed from exported stress-strain curves. At the same time, SEM is being used to observing the fracture morphology at tensile breakage spots.

Tongue Tear Test

Tongue tear strength is also tested on United Tester with an 8 inch gape length. The testing method is according to ASTM D 5737. Samples were measured on MD and CD two directions in 8 by 3 inch. At least five samples were tested and record the tear strength.

7.3. RESULTS AND DISCUSSIONS

7.3.1. Crystalline Phase Transformation

7.3.1.1. Bicomponent Spunbond Crystalline Structure

The polymer melting and crystallization behaviors are influenced by the loading configurations, and it is caused shear force induced crystallization kinetics that influence lamellae crystallites. Heat transfer starts from hot melt in the center to the ambient air as to spinning process, whereas calendar bonding melt fibers from sheath to the core of
fibers (Table 7-5). Web bond at 135°C in two cases, for engraved calendar with 20% point coverage, those fibers under bonded will result into similar recrystallized condition as calendared with double smooth (Table 7-5 (b-c)). Fabric crystallinity for point bonded fabrics is increased compared with drawn fibers except for loading in sheath configuration, which hardly change the crystallinity level at 54% which is the same level as PP drawn fibers (Table 7-3). On the contrary, core filling not only increase the drawn fiber crystallinity to 55.6% but also improve point bonded fabric crystallinity by 5%. While for the other PCC particle-EMforce (Table 7-4), the core comprise with 20% of such fillers decrease result into peak temperature decreases, but $X_c(\%)$ of fiber forming crystallites apparently reduced by 3~4%. Therefore, the particle shape may result into different crystallization kinetics of in correlation of loading configuration in bico fibers and density of filler packing within the component. It is also noticed that crystallization temperature keeps constant at same bonding condition, but the crystallization peak height shows correlation with the bicomponent configuration for loading the fillers. Theoretical energy in exothermic peak must be associated with weight fraction of inorganic fillers, that total amount of concentration affect specific heat and the kinetics in the polymer crystallization.
Table 7-3: Spunbond Drawn Fibers Melting and Cooling Behavior Filled with EMforce (PCC) from 2.5% to 20%:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$T_{m On-set}$ (°C)</th>
<th>On-set Time (min)</th>
<th>$T_{m Peak}$ (°C)</th>
<th>Peak Width at Half Height (°C)</th>
<th>$ΔH$ (J/g)</th>
<th>$X_e$ (%)</th>
<th>$T_{c On-set}$ (°C)</th>
<th>Crystallization Peak Height (W/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>158.3</td>
<td>6.82</td>
<td>170.0</td>
<td>15.6</td>
<td>89.7</td>
<td>54.4</td>
<td>127.2</td>
<td>2.16</td>
</tr>
<tr>
<td>2.5%</td>
<td>158.4</td>
<td>6.82</td>
<td>167.1</td>
<td>13.7</td>
<td>91.4</td>
<td>56.8</td>
<td>126.4</td>
<td>2.63</td>
</tr>
<tr>
<td>5%</td>
<td>157.6</td>
<td>6.78</td>
<td>168.3</td>
<td>14.4</td>
<td>87.1</td>
<td>55.6</td>
<td>126.2</td>
<td>2.19</td>
</tr>
<tr>
<td>10%</td>
<td>157.3</td>
<td>6.77</td>
<td>169.1</td>
<td>14.8</td>
<td>82.9</td>
<td>55.8</td>
<td>124.2</td>
<td>2.23</td>
</tr>
<tr>
<td>20%</td>
<td>156.4</td>
<td>6.72</td>
<td>166.9</td>
<td>13.7</td>
<td>72.8</td>
<td>55.2</td>
<td>123.7</td>
<td>2.18</td>
</tr>
</tbody>
</table>

Table 7-4: Melting Behavior of Bicomponent Fibers Containing with GCC-FL and PCC-EM:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$T_{m on-set}$ (°C)</th>
<th>$T_{m peak}$ (°C)</th>
<th>Peak Width at Half Height (°C)</th>
<th>Enthalpy (J/g)</th>
<th>$X_e$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FL10-Sheath Fibers</td>
<td>157.9</td>
<td>168.3</td>
<td>15.0</td>
<td>86.0</td>
<td>54.9</td>
</tr>
<tr>
<td>FL10-Core Fibers</td>
<td>158.2</td>
<td>170.8</td>
<td>15.1</td>
<td>81.2</td>
<td>51.8</td>
</tr>
<tr>
<td>FL20-Sheath Fibers</td>
<td>158.2</td>
<td>168.3</td>
<td>14.0</td>
<td>76.1</td>
<td>51.2</td>
</tr>
<tr>
<td>FL20-Core Fibers</td>
<td>157.5</td>
<td>167.2</td>
<td>14.3</td>
<td>79.7</td>
<td>53.4</td>
</tr>
<tr>
<td>EM20-Sheath-Fibers</td>
<td>157.6</td>
<td>169.9</td>
<td>14.8</td>
<td>81.7</td>
<td>55.0</td>
</tr>
<tr>
<td>EM20-Core-Fibers</td>
<td>157.3</td>
<td>163.6</td>
<td>15.4</td>
<td>76.6</td>
<td>51.6</td>
</tr>
</tbody>
</table>
The energy releases from polymer should equal to the decrease in free energy during polymer recrystallization \[^{13}\]. This means PCC-Superpflex in core configuration assist larger crystals forming by either thickening the lamellae plane. It has been found spunbond with core loaded with PCC-Superpflex could greatly increase the fabric crystallinity from 53.78 to 59.25%. The possible higher crystallinity could possibly come from more perfect fiber crystalline structure when loaded SF fillers in core, as drawn fibers already perform higher fiber crystallinity before thermal point bonded. However when specific investigate those point bonds by bonding the spunbond with double smooth rolls. This indicate the sheath/core bicomponent loaded with inorganic fillers in one of two components mainly represent in the recrystallization effect of unbonded fibers, because the loading configuration in single fibers affect the heat transfer pace in either sheath or core layer mainly determine the bicomponent fiber crystallization rate in the subsequent cooling. If loading in sheath, heat will be transferred from hot air to the fiber core faster. But if fillers are incorporated in the core, heat reach to the polymer in core will help with the packing of lamellae crystalline to form into more compacted spaces and larger crystallites. Meantime, during the subsequent cooling, fibers which are partially melting must crystallize by release the heat to the ambient cooling air. At this time, the sheath loaded with CaCO\(_3\) fillers will convey the energy in a sprint way because those particles in the sheath work as heat transfer carrier. In the opposite, as to the fibers which composed of pure polypropylene sheath or the polypropylene pure fibers has to undergo a
longer period of crystallization in a quiescent condition. In this way, it helps the fabric to
develop higher polymer crystallinity, as well as to thickening the lamellae crystalline
plane.

Figure 7-2: WAXD of spunbond fabrics comparing to drawn fibers, both contain with 5% of EMforce fillers
Table 7-5: Melting and Cooling Behavior of Spunbond Drawn Fibers, Thermal Point Bonded Fabric and Double Smooth Roll Bonded Fabric:

### a. Spunbond Attenuated Fibers (before forming into web)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$T_{m\text{-On-set}}$ (°C)</th>
<th>On-set Time (min)</th>
<th>$T_m$-Peak (°C)</th>
<th>Peak Width at Half Height (°C)</th>
<th>$X_c$ (%)</th>
<th>Crystal Size (Å) at (130)</th>
<th>d-spacing (Å) of (130)</th>
<th>$T_{c\text{-on-set}}$ (°C)</th>
<th>Crystallization Peak Height (W/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF10-Core</td>
<td>157.1</td>
<td>7.02</td>
<td>168.6</td>
<td>14.9</td>
<td>55.6</td>
<td>70.2</td>
<td>4.6</td>
<td>125.2</td>
<td>2.45</td>
</tr>
<tr>
<td>SF10-Sheath</td>
<td>157.7</td>
<td>7.04</td>
<td>167.3</td>
<td>14.2</td>
<td>54.8</td>
<td>125.9</td>
<td>4.5</td>
<td>124.5</td>
<td>2.22</td>
</tr>
<tr>
<td>SF10-Mono</td>
<td>157.8</td>
<td>6.79</td>
<td>170.0</td>
<td>14.8</td>
<td>53.9</td>
<td></td>
<td>-</td>
<td>125.3</td>
<td>2.54</td>
</tr>
</tbody>
</table>

### b. Spunbond Fabrics bonded (Emboss Roll + Smooth Roll) at 135°C

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$T_{m\text{-On-set}}$ (°C)</th>
<th>On-set Time (min)</th>
<th>$T_m$-Peak (°C)</th>
<th>Peak Width at Half Height (°C)</th>
<th>$X_c$ (%)</th>
<th>Crystal Size (Å) at (130)</th>
<th>d-spacing (Å) of (130)</th>
<th>$T_{c\text{-on-set}}$ (°C)</th>
<th>Crystallization Peak Height (W/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF10-Core</td>
<td>157.3</td>
<td>7.02</td>
<td>170.6</td>
<td>14.3</td>
<td>59.2</td>
<td>132.2</td>
<td>4.6</td>
<td>122.6</td>
<td>2.87</td>
</tr>
<tr>
<td>SF10-Sheath</td>
<td>156.6</td>
<td>6.98</td>
<td>170.7</td>
<td>17.0</td>
<td>53.8</td>
<td>137.7</td>
<td>4.6</td>
<td>122.0</td>
<td>2.24</td>
</tr>
<tr>
<td>SF10-Mono</td>
<td>156.8</td>
<td>7.00</td>
<td>169.4</td>
<td>13.1</td>
<td>56.2</td>
<td></td>
<td>-</td>
<td>122.8</td>
<td>2.99</td>
</tr>
</tbody>
</table>

### c. Spunbond Fabric bonded (Double Smooth Roll) at 135°C

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$T_{m\text{-On-set}}$ (°C)</th>
<th>On-set Time (min)</th>
<th>$T_m$-Peak (°C)</th>
<th>Peak Width at Half Height (°C)</th>
<th>$X_c$ (%)</th>
<th>Crystal Size (Å) at (130)</th>
<th>d-spacing (Å) of (130)</th>
<th>$T_{c\text{-on-set}}$ (°C)</th>
<th>Crystallization Peak Height (W/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF10-Core</td>
<td>156.4</td>
<td>6.98</td>
<td>168.2</td>
<td>13.9</td>
<td>53.6</td>
<td></td>
<td>-</td>
<td>122.8</td>
<td>2.65</td>
</tr>
<tr>
<td>SF10-Sheath</td>
<td>156.8</td>
<td>7.01</td>
<td>169.7</td>
<td>15.6</td>
<td>54.9</td>
<td>98.4</td>
<td>4.56</td>
<td>122.4</td>
<td>2.18</td>
</tr>
<tr>
<td>SF10-Mono</td>
<td>156.8</td>
<td>7.00</td>
<td>169.4</td>
<td>13.0</td>
<td>54.0</td>
<td></td>
<td>-</td>
<td>122.8</td>
<td>2.99</td>
</tr>
</tbody>
</table>
Table 7-6: Melting and Crystallization of Spunbond Fabrics at 135~150°C Bonding Temperatures:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$T_{\text{melt _set}}$ (°C)</th>
<th>$T_{\text{m _peak}}$ (°C)</th>
<th>Peak Width at Half Height (°C)</th>
<th>Enthalpy (J/g)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-control-140°C</td>
<td>158.2</td>
<td>168.5</td>
<td>14.2</td>
<td>90.7</td>
<td>55.0</td>
</tr>
<tr>
<td>FL20-Sheath -140°C</td>
<td>157.2</td>
<td>167.3</td>
<td>14.3</td>
<td>80.0</td>
<td>53.9</td>
</tr>
<tr>
<td>FL20-Core -140°C</td>
<td>156.4</td>
<td>169.6</td>
<td>15.6</td>
<td>78.1</td>
<td>52.6</td>
</tr>
<tr>
<td>PP-control-145°C</td>
<td>156.9</td>
<td>171.9</td>
<td>14.4</td>
<td>91.8</td>
<td>55.6</td>
</tr>
<tr>
<td>FL5-Mono-145°C</td>
<td>156.7</td>
<td>169.1</td>
<td>15.4</td>
<td>84.8</td>
<td>54.1</td>
</tr>
<tr>
<td>FL20-Sheath-145°C</td>
<td>156.3</td>
<td>172.8</td>
<td>17.0</td>
<td>82.01</td>
<td>55.22</td>
</tr>
<tr>
<td>FL20-Core-145°C</td>
<td>156.1</td>
<td>170.8</td>
<td>13.8</td>
<td>78.5</td>
<td>52.9</td>
</tr>
<tr>
<td>FL15-Mono-145°C</td>
<td>156.6</td>
<td>172.6</td>
<td>15.3</td>
<td>74.6</td>
<td>53.2</td>
</tr>
<tr>
<td>FL20-Sheath-150°C</td>
<td>156.6</td>
<td>169.7</td>
<td>12.7</td>
<td>82.8</td>
<td>55.7</td>
</tr>
<tr>
<td>FL20-Core-150°C</td>
<td>155.9</td>
<td>170.7</td>
<td>14.1</td>
<td>79.8</td>
<td>53.7</td>
</tr>
<tr>
<td>EM20-Sheath-140°C</td>
<td>157.2</td>
<td>167.5</td>
<td>15.6</td>
<td>79.4</td>
<td>53.5</td>
</tr>
<tr>
<td>EM20-Core-140°C</td>
<td>157.4</td>
<td>168.8</td>
<td>16.4</td>
<td>77.8</td>
<td>52.4</td>
</tr>
<tr>
<td>EM10-Mono-145°C</td>
<td>156.7</td>
<td>169.2</td>
<td>15.6</td>
<td>85.0</td>
<td>57.2</td>
</tr>
<tr>
<td>EM20-Sheath-145°C</td>
<td>157.1</td>
<td>169.2</td>
<td>14.6</td>
<td>85.5</td>
<td>57.6</td>
</tr>
<tr>
<td>EM20-Core-145°C</td>
<td>156.8</td>
<td>170.7</td>
<td>13.9</td>
<td>76.3</td>
<td>51.4</td>
</tr>
<tr>
<td>EM20-Sheath-150°C</td>
<td>157.7</td>
<td>171.8</td>
<td>15.4</td>
<td>79.2</td>
<td>53.3</td>
</tr>
<tr>
<td>EM20-Core-150°C</td>
<td>156.6</td>
<td>167.3</td>
<td>16.0</td>
<td>84.7</td>
<td>57.0</td>
</tr>
</tbody>
</table>
Table 7-7: Polymer/Fillers Relative Configuration and Structures of Spunbond Fibers after being Drawn by Aspirators:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Filler Loading Configuration</th>
<th>( n_\parallel )</th>
<th>( n_\perp )</th>
<th>Birefringence ( \Delta n = n_\parallel - n_\perp )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-control</td>
<td>Mono-component</td>
<td>1.520</td>
<td>1.492</td>
<td>0.028</td>
</tr>
<tr>
<td>EM5-Sheath</td>
<td>Bico-sheath</td>
<td>1.516</td>
<td>1.492</td>
<td>0.024</td>
</tr>
<tr>
<td>EM5-Core</td>
<td>Bico-core</td>
<td>1.516</td>
<td>1.492</td>
<td>0.024</td>
</tr>
<tr>
<td>EM5-Mono</td>
<td>Mono-component</td>
<td>1.520</td>
<td>1.494</td>
<td>0.026</td>
</tr>
<tr>
<td>EM10-Mono</td>
<td>Mono-component</td>
<td>1.520</td>
<td>1.495</td>
<td>0.025</td>
</tr>
<tr>
<td>EM10-Sheath</td>
<td>Bico-sheath</td>
<td>1.518</td>
<td>1.494</td>
<td>0.024</td>
</tr>
<tr>
<td>EM10-Core</td>
<td>Bico-core</td>
<td>1.518</td>
<td>1.492</td>
<td>0.026</td>
</tr>
<tr>
<td>EM20-Mono</td>
<td>Mono-component</td>
<td>1.520</td>
<td>1.500</td>
<td>0.020</td>
</tr>
<tr>
<td>EM20-Sheath</td>
<td>Bico-sheath</td>
<td>1.520</td>
<td>1.496</td>
<td>0.024</td>
</tr>
<tr>
<td>EM20-Core</td>
<td>Bico-core</td>
<td>1.518</td>
<td>1.496</td>
<td>0.022</td>
</tr>
<tr>
<td>FC10-Sheath</td>
<td>Bico-sheath</td>
<td>1.519</td>
<td>1.494</td>
<td>0.025</td>
</tr>
<tr>
<td>FC10-Core</td>
<td>Bico-core</td>
<td>1.518</td>
<td>1.494</td>
<td>0.024</td>
</tr>
<tr>
<td>FC20(25:75)-Sheath</td>
<td>Sheath (25%)</td>
<td>1.517</td>
<td>1.494</td>
<td>0.023</td>
</tr>
<tr>
<td>FC20(25:75)-Core</td>
<td>Core (25%)</td>
<td>1.518</td>
<td>1.494</td>
<td>0.024</td>
</tr>
<tr>
<td>SF5-Mono</td>
<td>Mono-component</td>
<td>1.518</td>
<td>1.494</td>
<td>0.024</td>
</tr>
<tr>
<td>SF10-Sheath</td>
<td>Bico-sheath</td>
<td>1.518</td>
<td>1.492</td>
<td>0.026</td>
</tr>
<tr>
<td>SF10-Core</td>
<td>Bico-core</td>
<td>1.518</td>
<td>1.493</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Table 7-8: Crystallography Phase Information on Polypropylene Diffraction on (1 1 0), (0 4 0), (1 3 0) and (1 1 1) and the Peak Related to CaCO\(_3\) Fillers within the PP denoted as (1 1 1):

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Peak Position</th>
<th>( d ) (Å)</th>
<th>Crystal Size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-140</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1 1 0)</td>
<td>5.9</td>
<td>164.8</td>
</tr>
<tr>
<td></td>
<td>(0 4 0)</td>
<td>5.0</td>
<td>131.2</td>
</tr>
<tr>
<td></td>
<td>(1 3 0)</td>
<td>4.6</td>
<td>140.7</td>
</tr>
<tr>
<td></td>
<td>(1 1 1)</td>
<td>4.0</td>
<td>65.7</td>
</tr>
</tbody>
</table>
Table 7-8 Continued

<table>
<thead>
<tr>
<th></th>
<th>EM5%-Mono-140C</th>
<th></th>
<th>PP Attenuated fibers</th>
<th></th>
<th>EM5%-Mono-Attenuated fibers</th>
<th></th>
<th>SF10%-Core Attenuated fibers</th>
<th></th>
<th>SF10%-Sheath Attenuated Fibers</th>
<th></th>
<th>FL20%-Core Attenuated Fibers</th>
</tr>
</thead>
<tbody>
<tr>
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7.3.1.2. Fabric Recrystallization under Bonding

Polymer chains melting and cooling after web consolidating by thermal calendaring is different from shear induced crystallization by attenuation. Under thermal bonding, the small lamellae crystal in fibers melted, then let chains go relaxation and forming the bond by heat transfer. It is more likely to form larger crystals after polymer recrystallization. By investigating drawn fiber crystalline structure as well as of bonding region, fiber recrystallization has been found develop higher fabric crystallinity as loading filler in sheath. Specifically, drawn fibers crystalline morphology represent effect of inorganic fillers in fiber.
formation, while the bonding region melting and cooling behavior represent polymer recrystallize in quiescent cooling. By using double smooth calendar rolls, we are able to look at the morphology of crystalline. Calendaring fibers assists the small lamellae crystalline phase to be thickened by a longer period of time under heat treatment, not like in aspirator gun, molten polymers undergo a sufficient time in recrystallization. As shown in Table 7-4, we find that peak melting temperature raise up by 2-3°C for calendared fabrics, but did not change much after being calendared by double smooth rolls. It elucidate the crystallinity might be changed, but most likely occurred to fibers is their crystallinity is reduced and increase the size of crystal.

From melting and cooling behavior of drawn fibers and bonded fabrics at 140°C, loading GCC in core component of fibers influenced the on-set melting temperature decreasing by at least 0.5°C. Drawn fibers for FC20-sheath formed more volume fraction of crystalline structure as indicated in Figure 7-4, which also proved from intensity of diffraction peak of FC20-Sheath-140C is sharper than FC20-Core-140C, which demonstrates the crystal perfection vary with bicomponent sheath/core structure. That loading filler in sheath will improve integral perfectness of crystalline phase due to a fast heat conducting mechanism. However by Scherer’s equation, we also noticed that the crystal size is larger for 20% in core component (Figure 7-3). This may refer to a longer time in polymer crystallization when heat is entrapped within the bicomponent core layer, which extend the crystallization period of time in the subsequent cooling after thermal calendar bonding. When we just incorporate pure polypropylene in fiber sheath, then the temperature gradient from inner core to outside
is not equal to the case of sheath loading and mono-component fibers where inorganic fillers densely packed in between core with ambient air. As we know, a fast cooling mechanism should involve such a medium with high thermal diffusion coefficient as described in previous chapter VI, sheath component filled with calcium carbonate accelerate the heat transfer rate. Then from fabric crystallinity as included in Table 7-5 (b), it was noticed bicomponent spunbond containing with fibers which has sheath added with fillers will develop higher crystallinity no matter for FiberLink (GCC) or EMforce (PCC), compared to the other way of incorporating in core. Especially PCC-EMforce incorporated in core component induced apparently low crystallization rate as well as low fabric crystallinity from 140°C to 145°C, accompanied with a significant higher melting temperature both on-set temperature and PWHH range. This phenomenon has also been noticed for FiberLink filled at 20% in the sheath component, only except at its crystallinity is not compromised at sheath loading.

Additional finding based on diffraction patterns of fibers shows that inter-planar spacing keeps at constant value for GCC filled fabrics no matter in sheath or core loading (Fig. 7-3). However, fibers filled with PCC-EM filler in core or in sheath resulted into significant different crystalline structure. The (1 1 0) (0 4 0), (1 3 0) and (1 1 1) peak move to a larger Bragg angle, which induced a higher compacted inter-lamellae spacing in the bonded fabrics. As claimed in previous work, aragonite form of CaCO₃ tends to form nucleus which help to reduce the inter-particle spacing in polypropylene [20]. So the nucleating ability for loading filler in sheath could be triggered after rearranging of polymer orientation by packing particles in parallel or almost uniform packing into a fine volume in fiber structure. Under the
high shear stress at skin layer, the needle-like particles tend to align with shear flow which even intensify shear flow rate, so that we believe the higher crystallinity comes from an acceleration of crystal growing. As fabric leaves outside of nip region, bonding formed by cooling down polymer and renewing the package in lamellae crystallites. Therefore, higher crystallization kinetic with loading filler particle in sheath component promotes the inter-lamellae packing during the subsequent cooling process, and enhance the bonding formation.

Figure 7-3: WXAD diffraction pattern compare two spunbond fabrics bonded at 140°C.
7.3.2. Bicomponent Spunbond Fabric Structure

Thermal calendar bonding provide heat treatment by compressing freely jointed fiber web to a perfect large crystalline padding. Web consolidate after leaving calendars mainly behave like squeezed thickness and crushed fluffy geometry. Based on previous results, it has been realized fiber diameter first increase with higher loading to 10% and then decrease when loaded more than 10%. As shown in Figure 7-4 (a), 10% loading of GCC particles in mono-component spunbond has thickness curves decreasing with temperature, then leveling off above 140˚C, meaning the extent of bonding has less effect on web thickness as temperature is above optimum temperature. Efficient bonding over embossed area contributes to thickness reduction, as bonds compress deep into the mid-plane to melt the fibers throughout the webs. Next, the thickness plot demonstrates bicomponent configuration also affect web bonding thickness. shown in Figure 7-4 (b), the trend in PCC-EMforce differ from GCC-FiberLink as well as PCC-Superpflex, where for the needle-shape CaCO₃ loading in sheath or core will not generate much variation in fabric thickness. Adversely, incorporating SF and FL mainly reduce fabric thickness as loading fillers in the core structure. The smooth surface of fibers is the key to getting enhanced fiber web package with reduced thickness but increased solid volume fraction (Table 7-9). While on-sheath with those bumpy features it is difficult to form a sufficient fiber adhesion, but more steric repulsion will make porous geometry even distinct. Among the steric repulsion, the static charged onto filled coated fiber surface may evoke the freedom during fiber web laid down movement, which generate bulkiness to the fabric structure. As to various types of CaCO₃, difference in sheath/core structure on fabric thickness and solid volume fraction (SVF) become more significant for
FL and SF as included in Table 7-9. This is apparently related to fiber surface evenness forming from fiber spinning that EM tend to align with elongation stress, as previously mentioned forming inter-lamellae packing efficiently during crystallization. Comparing with EM, GCC fillers roughen fiber surface obviously that resulted larger thickness and bulk fashion.

Fabric thickness not only reflects the fiber packing in web lay down formation, but also influenced by fiber density and web running velocity to keep at constant basis weight at 100 gsm. As shown in Figure 7-4 (b) and Table 7-9, PCC-SF loaded up to 10% greatly thicken the spunbond, which may because of fiber density decreases that the fiber laid down into lighter web in unit time onto the moving belt. So to keep at constant basis weight, velocity of belt slow down to collect an extra amount of fibers. Meanwhile, with 10% PCC loaded in core configuration decreases the SVF even more from 0.18 to 0.17 for EM, and from 0.176 to 0.154 for SF, both are comparatively bulkier than PP fabrics. This because as SVF is calculated from SVF = \( \frac{\rho_{\text{bulk}}}{\rho_{\text{fiber}}} = \frac{\text{BSW}}{\text{Thickness} \cdot \rho_{\text{fiber}}} \), so the fiber density increases for SF and EM filled fibers resulted in SVF decreases. Comparatively, loaded CaCO\(_3\) into core component is regarded as an effective in reducing fabric thickness and relative enhance the bonding in spunbond web laying.
Fabric Thickness (μm)

Bonding Temperature (˚C)

Thickness of Fabrics Filled with GCC-FiberLink

- PP
- Ca 10%-Mono
- Ca 20%-Sheath
- Ca 20%-Core

100 gsm

Fabric Thickness (μm) vs. Bonding Temperature (˚C)
Figure 7-4: Fabric thickness with different loading configurations in bicomponent fibers filled with 10 wt. % of GCC (a). Filler types on bicomponent fabric thickness (b) and loading configuration on fabric SVF (c).
As fabric containing with calcium carbonate fillers in fibers increase its diameter, voids may generate around at those particles surface especially when lack of sufficient wetting by polymer melt. It was noticed from SEM picture of fiber cross-sectional area that two types of PCC fillers may result into different core loading effect. As shown in Figure 7-5 (a) and (d), the interface between sphere filler form (SF) and polypropylene show partial wetted with tightly polymer diffusion around the particles, but also existed local micro-voids less than 0.5~1μm. In previous application of calcium carbonate in film blow casting, microvoids were also form after being drawn from biaxial stretching force; and the voids are forming within the film matrix, especially around particular fillers \[^{3(\text{old})}\]. Although there is local

Table 7-9: Fabric Structure Relationship with Fiber Diameter, Fabric Thickness and Solid Volume Fraction (Bonded at 135°C):

<table>
<thead>
<tr>
<th>Bico Fiber Sample ID</th>
<th>Fiber Diameter (μm)</th>
<th>Solid Volume Fraction (%)</th>
<th>Fabric Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP Control</td>
<td>14.91 (0.75)</td>
<td>0.198</td>
<td>0.528</td>
</tr>
<tr>
<td>FL10%-Core</td>
<td>16.03 (0.35)</td>
<td>0.171</td>
<td>0.531</td>
</tr>
<tr>
<td>FL10%-Sheath</td>
<td>17.08 (1.10)</td>
<td>0.163</td>
<td>0.584</td>
</tr>
<tr>
<td>FL10%-Mono</td>
<td>16.44 (1.05)</td>
<td>0.182</td>
<td>0.554</td>
</tr>
<tr>
<td>FL20%-Mono</td>
<td>15.38 (0.80)</td>
<td>0.154</td>
<td>0.492</td>
</tr>
<tr>
<td>EM5%-Mono</td>
<td>17.46 (0.84)</td>
<td>0.180</td>
<td>0.540</td>
</tr>
<tr>
<td>EM10%-Core</td>
<td>16.92 (0.33)</td>
<td>0.180</td>
<td>0.534</td>
</tr>
<tr>
<td>EM10%-Sheath</td>
<td>16.67 (0.61)</td>
<td>0.180</td>
<td>0.531</td>
</tr>
<tr>
<td>EM10%-Mono</td>
<td>17.70 (1.36)</td>
<td>0.169</td>
<td>0.509</td>
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<tr>
<td>SF5%-Mono</td>
<td>16.74 (0.86)</td>
<td>0.176</td>
<td>0.536</td>
</tr>
<tr>
<td>SF10%-Core</td>
<td>16.51 (0.91)</td>
<td>0.183</td>
<td>0.525</td>
</tr>
<tr>
<td>SF10%-Sheath</td>
<td>16.54 (0.84)</td>
<td>0.173</td>
<td>0.571</td>
</tr>
<tr>
<td>SF10%-Mono</td>
<td>16.17 (0.94)</td>
<td>0.154</td>
<td>0.560</td>
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agglomeration of Superpflex as shown in Fig. 7-6 (a), we do not expect severe inner core structure deterioration even filled up to 30 wt.%. While adding needle-shape PCC also have a close packed interface with polypropylene matrix as shown in Figure 7-5 (b), however, the cut down cross-sectional unravel a lot of irregular mixed crystalline phases. Unexpectedly, the sheath/core interphase shows fault at the interface where pure polypropylene start being pulled out from EM filler contained phase. The reason for this occurrence of irregular internal morphology could be investigated from fiber crystallinity. It has been demonstrated that PCC-EMforce resulted into fiber crystallinity decreases with loading in core component, which is in opposite way as GCC and PCC-Superpflex. The particulate fillers possess with calcite crystalline form but an isotropic cubic or spherical feature. This form is different from aragonite calcium carbonate EM from interfacial interaction with polypropylene in bicomponent fibers, that isotropic fillers existed in high shear rate layer (sheath component) may interrupt the large viscoelasticity movement of oriented molecules, especially when the immobilized interphase at spherical perimeter by absorbing polypropylene molecules will hinder the shear mobility. For calcite form GCC with cleavage planes, the interface lamellae grow may adhere to plane vertically in an epitaxial growing, where may hinder the twisted lamellae to be untwisted during shear stress \[^{25}\]. Although epitaxial has been found for aragonite particle rod as well \[^{15, 24}\], since anisotropic characteristic of PCC will align with the shear flow and assist the polymer orientation to the ultimate extent.
30% Superpflex in Core

25% PCC-EMforce in Core
Figure 7-5: Fiber cross-section with PCC particles filled in sheath/core bicomponent fibers. Where 30% Superpflex in core structure (a); 20% of EMforce with core loading in fibers (b); FIB fibers cut image contain with 25% of EMforce in mono-component (c); Cross-sectional of 25% Superpflex containing within PP (d) and its magnified image show local details of filler-polymer interaction (e).

A separation from fillers to matrix is noticed for two types of PCC by characterizing using Dualbeam SEM in the FIB cut fiber cross-section (Figure 7-5c, d). Fibers FIB SEM graphs demonstrate with PCC-SF could sustain relatively good dispersion, but in some cases, cluster involving a cavity around small cluster existed. Some cavities with different morphology was also noticed for GCC fiber in Chapter III (Fig. 3-18), the distinctive difference reveal that craze around GCC larger particle phase is caused insufficient adhesion of polymer. When we
specifically looks the interphase around PCC-SF perimeter, a high brighten perimeter feature appear at PCC spherical area (Fig. 7-5 e), which demonstrated lack of uniformity in ion around particulate regions. Such phenomenon reveal that as polypropylene are absorbed by stearic acid layer, there form the interphase that affect the crystalline density, there are mainly small crystalline grow at the interface impact the lamellae index and birefringence. In Fig. 7-5 c it shows relatively denser interfacial layer surround EM fillers, with focus ion beam microtome samples by continuously moving forward but only leave a limited number of voids. Cause the needle shaped inserted vertically to the microtome cross, so those voids leaving behind must have left empty after cutting polymer material. Some particles are dispersed uniformly with a good interface adhesion as shown in Fig. 7-5d. Spherical particles tend to separate from polymer matrix so continuous leaving behind some voids randomly, gives traces left behind by those incubation sites of SF fillers. The result is consistent with our previous finding on fiber diameter that dramatically increased after incorporated with PCC spherical particles. Based on the micromechanics of polymer flow deformation, the strain induced shear yielding could explain dilatant effect of particle filled fiber materials [18]. As we explained before, a good wetting of polymer require a similar surface polarity between inorganic filler and organic matrix. For a group of moving particles moving in polymer flow jet, even though there is interfacial adhesion that alkyl fatty acid molecules adsorb the polypropylene molecules, polymer shell lower the surface tension of inorganic particles, surface crystals are immobilized from stearic acid chain hindering. So synchronous movement of inorganic fillers in shear flow with polymer is an ideal extrusion condition, if possible that will keep steady phase dispersion in polymer jet. Overall the surface coating
help dispersion, but the immobilized layer of polymer molecules hides potential craze weakness at the small crystallite phases \[18\]. Even more, as polymers jet elongate fast with a large poisson deformation, the depletion of polymer from the inter-particle spacing will cause them aggregate into larger clusters. We can see the Figure 7-5b reveal the enormous particulate orient its minor axis (250 nm) vertically to the cross-section view of fibers, where even some cluster formed but the possible cause of such agglomerate is because of less alignment along polymer shear flow. While most of fillers are dispersed with their tip hanging at the cross-sectional view, some voids are also generating throughout the polypropylene material.

### 7.3.3. Mechanical Properties of Bicomponent Spunbond

Tensile strength of spunbond fabrics is influenced by filler loading configuration in sheath or core component. In traditional bicomponent usually the component with lower melting temperature can behave like a binder that bond the whole fiber structure \[17, 25, 26\]. This is by partially melting the sheath of the bicomponent fibers, still keep the core intact after exposure to heat. In this way, product softness is maintained meanwhile using the bonding to keep the mechanical strength under deformation. In the PP fiber, varying filler loading concentration into sheath/core configuration change morphology of heterogeneous crystalline and such skin/core structure contribute to bonding forms. Based on previous analysis on melting and crystallization behavior, we find that loading higher amount of PCC fillers in core increase fiber crystallinity and narrow of crystal size population. Conversely, although cubic shaped calcite (GCC and PCC-Superpflex) loaded in core cause the perfection of crystalline is
compromised due to the heat may be entrapped for longer periods of time within the fibers, we find that crystal size is increased significantly meaning time for crystal growing is sufficient.

7.3.3.1. PCC vs. GCC Comparison Study on Tensile Properties

Bonding phase transformation upon thermal bonding will generate more reinforcement by using higher bonding temperature, more than the difference coming from sheath/core configurations as shown in Figure 7-6. Filler loaded in sheath can increase fabric strength in average level, responded with less structural weakened as shown in minimum strength in the error bar. Polypropylene fibers can be reinforced prominently from interface reptation by fiber to fiber contacting, if contain with EM filler the chain molecules free ends reach out of melted phase and generate cross-fiber linkage. From Figure 4-16e such bonding reinforcement had occurred for small loading of EM, which is speculated from the isotactic polypropylene fibrils are stretched out from block crystalline. The bonding become more efficient for polypropylene fiber has less oriented molecule ($\Delta n = 0.024$) on its sheath when EM force is loaded in sheath comparing to $\Delta n = 0.026$ when loading filler in core. The lower polymer orientation at skin layer will respond to calendar heating with fast softening and reptating across the fiber boundary, which enhance the bonding formation. Varied in sheath/core loading configuration not only affect the fabric consolidation, but also spun the drawn fibers with more toughness. As shown in Figure 7-8, fiber tenacity of attenuated fibers for 10% and 20% of EM and FL pointed out the contribution of loading in sheath structure to a higher tenacity. Since incorporated fillers in core may decreases the rate in crystallization, so the attenuation caused the soften fibers to keep stretching into finer fiber size (Fig. 7-8a).
The strength at a continuous stress-strain curve represents the whole orientation movement of fibers. Fabric strength is somehow related to single fiber tensile strength, especially when stress has separate bond apart by tightening the bridge fibers, then the stronger fibers withstand stretching force to the ultimate extent.

Figure 7-6: Fabric tensile strength influenced by bicomponent Sheath/Core structure
Figure 7-7: Stress-Strain curves of spunbond containing with 10% of EMforce (EM) in two different bicomponent loading configurations. The solid line: MD, dash line: CD.

Bridge fibers connect as main structural component in spunbond, which are intertwining bonding pads and control the stress distribution network in fabric. With a thermally bonded structure, the fiber crystalline structure is reformed after crystallization with larger crystal size appear with higher temperature and longer bonded time. Sheath incorporated with EMforce has significantly enhance the lamellae folded chain packing, as indicated in Figure 7-3, the d-spacing decreases when fiber sheath are filled out with 20% of fillers. The stronger bonding region will efficiently reorient fibers without stress concentration effect onto the weakened fiber structure. Adding particles may also improve surface friction coefficient in bundles of fibers, therefore, mainly contribute to overcome fabric deformation. It also has been noticed that in replace of mono-component, adding in sheath/core configuration intensify the fiber stiffness and induce less strain at breaking and lower fiber toughness.
Figure 7-8: Bico fiber linear density (a) from spunbond attenuation and the tenacity.
Figure 7-9: Average MD and CD tensile strength of fabrics made with mono-component and bicomponent at varying levels of loading of GCC-FiberLink fillers in 100 gsm spunbond.

The different behaviors are reflected from the bicomponent structure reinforcement between two filler particle types. While needle-shaped PCC fills tend to perform a higher bonding effect for sheath loaded fabrics, when we further investigate GCC-FiberLink in core loading, the result is opposite which means GCC loaded in core contribute to enhance bonding effect, shown in Figure 7-9. Attached fibers under embossed bonds reinforce the porous fiber mediums which allow the contribution of each fiber elements reach to its optimum when bonding temperature melt the fibers sufficiently below the embossed regions. The improvement in both 10% and 20% loaded in core support a competent bonding effect more than sheath or mono-component filled with 5% and 10%. Although at 10~20 wt. % with mono-component spunbond with calcium carbonate shows improved strength, the advantage
does not exceed the core configuration. In previous chapter, we discussed core loaded of GCC particles may retard crystallization time which forms twisted lamellae crystals with larger crystal size. Core incorporated with GCC fillers, especially at higher loading concentration (>10%), resolve the issue of high stiffness low strength. This feature contributes to fabric tensile strength with more fiber strength contribution. More significantly, fabric crystallinity formed with spunbond fabrics indicated filling GCC particle in sheath can formed higher crystallinity but small crystal size at 133Å compare to 154Å (Table 7-5, Figure 7-3). We have found spunbond drawn fibers shows a higher $X_c$ (%) when core is incorporated with fillers that in post fiber web recrystallization, extending the time in softening crystallites inside of fiber material, so that keep the fabric strength better than in mono-component fabrics. While from higher fabrics $X_c$ (%) but lower fabric strength elucidate there is not directly relationship between fabric crystallinity and the strength. Polymer orientation in bridge fibers after recrystallization and the transition from bridge fibers to the bonding region dominate on strength development over crystallinity part.

Bicomponent fabric improves in the modulus from the MD deformation, especially when incorporating CaCO$_3$ particle in core of fibers. As we discussed previously, GCC incorporated in core may affect the recrystallization rate. Within a sufficient longer time for recrystallization, fabrics form more rigid and stronger point bonds. This is why fabrics perform higher modulus when loaded in the core structure. At the same time as 20% within 50:50 core/sheath structures, the modulus reach to a higher peak than 10% in mono-component based on the discussion ahead. Therefore, when a 20% of fiber surface roughness
is targeted at the same time maintain fabric secant modulus at 5%, we can using bicomponent to replace mono-component fibers.

![ GCC Filler Concentration Effect on Fabric Secant Modulus (140°C) ]

Figure 7-10: Secant modulus bicomponent spunbond fabrics filled with GCC FiberLink

7.3.3.2. Temperature on Bicomponent Bonding Effect

Apparently, temperature is a variable that affect the fabric mechanical properties, however, at same calendar temperature of 140°C, 145°C or 150°C, GCC-FiberLink loading in core or sheath configuration with same amount of loading only correlate the bonding formation during recrystallization to form into different brittleness around bonding patterns.

\[
\text{Strength Change Ratio} = \frac{(\sigma_x - \sigma_{pp})}{\sigma_{pp}} \times 100\%
\]  

(3)
When fabric forms with embossed pattern, the recrystallized polymers restrict the stretching from both MD and CD direction that fibers redistributed under tension must transfer the load from bridge fibers connecting to those bonds. Because when bonds are sufficiently strong to withstand tensile stress, the tension will be well spread out the webs. Within bonding region, heat penetrates through the web structure to rise up to the melting point of polymer as much as polymers are impacted, from center to outside, or from surface layer to the mid-plane of the web.

Figure 7-11: Relative changes in fabric tensile strength with loading fillers to PP fabrics at different bonding temperature.
In a sufficient amount of polymer chains soften and recrystallize, the strength of fabric is improved by increase up the temperature, especially for those composed of pure PP and slight amount of fillers. Because as filler concentration increases, the optimum bonding temperature lower down by 5~10°C, but further heat up will cause overbonding that fabrics breakage initialize at the structural defects around polymer bonds. As increase temperature from 140°C to 150°C, CaCO₃ contained in 5% and 10% total within the fabrics, falling below the PP fabric. From previous study in Chapter V, we have proved PP spunbond does not reach to the optimum bonding effect until 150~155°C, but CaCO₃ filled up to 10~20% within 100 gsm fabric can reduce this temperature by 5~10°C, where at 10% of CaCO₃ loaded with fabrics the strength achieve maximum at 140°C. As shown in the Figure 7-11, apparent increase in fabric tensile strength hit around 10~20% of CaCO₃ at 140°C, however, when keep heating up the advantage of higher strength by using inorganic particles added in fibers not long show any more advantage compared to PP fabrics. Since weak perimeter may form around bonding points, so the continuously lowering with loading concentration is the trend in fabric consolidation.

However, the evidence from fabric strength has consistent improvement with loading configuration in core component of fibers at 20%, and show a broad bonding window from 140°C to 150°C (Fig. 7-11). We also compare the bicomponent fibers with 50:50 sheath/core with the mono-component with 5% which do not has comparable strength level as 10% loaded in core and sheath, the former cases also induce strength reduction and close the optimum bonding temperature to 145°C. Previous results show that filler incorporated in
sheath resulted into increasing amorphous birefringence in fibers, that upon calendaring these partially orientation chains retract back corresponded to larger heat relaxation. This indicates a faster heat transferring rate can induce larger crystallization rate, but also reduce the time period for PP crystal growth in core of fibers.

It was found that both 10% and 20% loaded in core component support strength improvement. Especially at 20%, loading fillers in core component works even better than 10% and 20% of GCC loaded in mono-component (Fig. 7-11). For 10% in mono-component the total loading is equal to 20% in core but the bonding window for optimum strength is narrow and less efficient. For 20% in mono-component even though the total amount is higher than 20% in core configuration, the former one caused over-bonding above 140°C. From SEM image of fabric rupture above peak load (Fig.7-11 SEM), core loaded with 20% in core can keep the integrity of bonds that stress will force them to reshape with stress line, therefore maximize the elongation to the breaking. But for the opposite sheath loaded with 20% GCC at 145°C (Fig. 7-11 SEM), some stress will be concentrated on those bonding regions which resulted into a few breakings. Then the elongation at breaking, shown in Figure 7-12, is able to incline up to 20% of loading in core as expected because of more restriction from bonding region.
Figure 7-12: Fabric elongation at breaking of fabrics at varying of temperature

Either loading in sheath with 10~20% or mono-component loaded 5~10% result into fabric brittleness. At early breaking, some regions in the bonds may rupture or generate pin holes, while most likely those periphery region where fibers are partially loss the orientation but still not form into the bonds. From fabric crystalline structure, it has been consistently proven from our results in Figure 7-3 that crystalline phases form into larger crystal size when core is loaded with GCC fillers. It was also noticed that in melting behavior of spunbond containing with GCC in bicomponent structure, the on-set melting temperature lowers and
peak melting temperature increase when core configuration is incorporated with fillers, which means population of crystallites rather expand as fillers contained in core will prolong recrystallization period and induce larger crystal size as well (Table 7-5). It was also important to find that the peak width at half height (PWHH) may also represent the lamellae plane size distribution formed during thermal bonding. In the relatively longer time period, there are new formed nucleation sites in the partial softened polypropylene, which will be growing into a wider range of lamellae plane dimensions. However, the filler particles incorporated on fiber sheath may increase the heat transfer rate in web crystallization, when may cause fabric brittleness at those emboss periphery. That causes the 10% and 20% in sheath component tend to sacrifice their tensile strength at higher bonding temperature at 150˚C.

7.4. SUMMARY & CONCLUSIONS

The outcome of research on structure-process-properties relationship on spunbond filled with calcium carbonate meet with the objectives on finding the key parameters of fillers influence on nonwoven process. From spinning process we summarized the actual loading in fibers is dependent on specific surface area, larger the surface area, more agglomerating tendency in spinpack. We also find top cut in size distribution determine the maximum strength level in single fibers. On particle shapes effect on fiber and fabric strength, improving filler aspect ratio can reinforce fibers at small amount and also improve spunbond tensile strength significantly. Fabric optimum strength can be achieved at lower bonding temperature from calendaring which also indicate heat transfer coefficient is closely related with loading amount.
On bicomponent nonwoven structure, the loading configuration in fibers influence the spinning condition of fibers especially from on-godet drawing, where fiber crystalline kinetic is significantly increased by highly orientated polypropylene chains. Loading filler in fiber core component improve spinnability at high speed, especially for smaller particle size. For example, loading Superpflex 200 in core structure can significantly improve efficiency in taking up spin finish and overcoming fiber fanning out problem on draw rolls. Another finding on fiber tensile property is fiber modulus formed during spinning is related with bico loading configuration, especially in sheath layer. After fabrics finish calendar bonding and leave the bonding zone, those particles also improve the bico fiber crystallization rate because of higher heat conductivity.

Bonding crystallization after web leaving out of calendar rolls impose a sufficient amount of polymer melting and cross boundary chain reptation. With bonding consolidation reinforce the free fibers, it hinder the fibers from pulling out and increase the elongation at breaking during tensile behavior. From 10% to 20% of loading concentration, we find that loading in core may contribute to more polymer long chain molecules diffusing around beneath the embossed area. This conclusion again prove that loading in fiber core component has great energy to reinforce the recrystallized structure in the bonding regions, therefore can fuse more floating fibers to adhere to the sticky bonding pads.
REFERENCES


CHAPTER 8  Fabric Whiteness and Opacity Influenced by Loading of Particulate Calcium Carbonate – Focusing on Bicomponent Spunbond Nonwovens

ABSTRACT

Whitening effect from inorganic fillers adds on aesthetic value to a variety of products applied to fibers and nonwovens. To optimize the visual appearance, the calcium carbonate (CaCO$_3$) with different particle characteristics are selected as inorganic additive to blend with thermoplastic melt, for modifying amount of light reflection and transmission through such fibrous medium. CIE (L*, a*, b*) color space is applied for characterizing the whiteness and opacity of nonwoven fibers and spunbond fabrics. Melt spinning transforms the polymer into fiber in width of 22μm containing with particles uniformly dispersed within fibers. Three types of CaCO$_3$ fillers added spunbond fabrics with fibers attenuated into even smaller size at 16μm. CIE whiteness index (CIE-WI) of fibers has significantly improved to which extent depends on the filler types and loading fraction on sheath component of fibers. Not only the roughness on fiber surface impact the light reflectance, those point bonding on fabric surface are also influenced by loading configuration and concentration of CaCO$_3$ fillers. Optical microscopy and scanning electrical microscopy (SEM) have been applied to characterize the surface morphology of fibers and geometrical characteristics of spunbond fabrics. It has been shown Ground CaCO$_3$ (GCC) keep increasing fabric whiteness up to 20 wt. %. Contrast ratio of spunbond filled with GCC increases with the loading concentration in the sheath as well. Comparatively PCC fillers induce yellowish CIE white as increasing loading to 10 wt. %, but
from the lightness and contrast ratio of PCC filled fabrics showing light scattering is greatly enhanced. In addition to CaCO$_3$ particle loading concentration, geometrical structures including basis weight and fiber diameter are considered as auxiliary factors contributing to fabric light reflectance.

**Key Words:** Bicomponent Fibers, Calcium Carbonate Fillers, Whiteness, Light Scattering, Contrast Ratio

8.1. **INTRODUCTION**

White pigments, such as titanium dioxide imposes gloss, texture and smoothness to thermoplastic material. Mineral additives, regarded as inorganic fillers constituent of earth metal oxide, carbonate and hydroxide from micro to nano scale in filler form adding with polymer. Calcium carbonate is the most widely applied mineral filler because of its advantages in cost, non-toxic, and a variety of particle size range to meet with different applications. Most inorganic particulate fillers are produced by molding $^{[1]}$, extruding $^{[2]}$, papermaking $^{[3]}$ or laminating $^{[4]}$ into plastics, that surface unevenness caused by different physical characteristic of fillers with resin matrix brings substantial transformation on optical property $^{[3, 5]}$. Driven by the fluctuating prices in raw petroleum and its derivatives products, the applications of calcium carbonate fillers will emerge in new field of applications, such as spunmelt nonwovens $^{[6-9]}$. Due to processing challenges, a fast output and scale-up production rely on a stable dispersion of calcium carbonate in polymers. Higher requirements on filler particle size distribution should be met with to minimizing filler clogging in
capillary extrusion and subsequent polymer spinning \cite{3, 10-12}. However, there has not been any extensional research on fiber forming spunbond properties, especially optical-related effects based on a structure-properties mechanism study on calcium carbonate fillers.

Optical whitening effect bringing from calcium carbonate (CaCO$_3$) makes it a substitute of titanium dioxide (TiO$_2$) as whitening coating agent. For example in papermaking, applying precipitated calcium carbonate (PCC) can impart opacity to fine pulp fibrous structure \cite{13, 15} by filling into the small compartment of cellulose fibers in subsequent procedures of deposition. Comparing to melt spun fibers, paper fibers are in L/d ratio $\leq$ 4, apparently lack of entanglement of long fibers with L/d ratio $\geq$ 10. Furthermore, polymer melt spinning impose high shear force onto jet flow which force fillers to move along with the melt, and phase separation from solidified fibers may result into microvoids forming in fibers \cite{14}. Surface texture of bicomponent fibers as claimed by Peng et al. has brought up the concept of inter-particle spacing for filler packing density on sheath component \cite{21}. However, barely do they evaluate such structure feature on optical properties. We suspect that the packing fraction in fiber surface could possibly influence light scattering of polymer, such scattering effect as claimed by Delucia and McAmish is improve the softness of spunbond nonwovens \cite{6-8}. There is similarity as paper coated with CaCO$_3$, but more important is the structure of spunbond medium which spontaneously interact with light. It is also realized that incorporated calcium carbonate by in-situ precipitation method combine the fined aggregates with core lumen of cellulose fibers, which improve the optical property but decreases the mechanical property \cite{13}. But different from wet processing where fillers are washed by
water, in melt processing CaCO$_3$ are taking by the running polymer flow. These fillers tend to be anchored into specific internal voids as filament crystallizes $^{[16]}$. The structure features combine the mineral particles characteristics with polymer crystalline phase, additionally, will influence the visual perception of light reflected.

Color, a phenomenon of light reflectance, behaves in systematic chromic coordinates RGB; L, $x_n$, $y_n$; or CIE (L*, a*, b*) chromatic spaces. White surface is with strong light reflectance value (>50%) through whole visible spectrum $^{[18]}$. Fabric whiteness improvement will impose a visual pleasant for some applications in hygiene and wipes. In some circumstance, fluorescent additives are added into textiles to improve the white discussed by Lin et al. $^{[22]}$. Fluorescent brightening agent or optical brighter usually are added to papers and relevant goods $^{[23]}$. Numerous whiteness formulae have been constructed on applications in woven fabrics $^{[19]}$, papers $^{[23]}$ and dental restoration material $^{[30, 36]}$. CIELAB L* a* b* color space has been proved to continuously reflect the sample whiteness if measured at same illuminants, corresponding to a visual ranking according to Katayama and Fairchild $^{[25]}$. Uchida et al. also constructed arbitrary whiteness formula which expanded the applicable range of CIE whiteness. Based on fabrics whiteness under different formulae, Jafari and Amirshahi involved a comparison evaluation on CIE and Uchida whiteness index $^{[26]}$. In paper coating, PCC yield a bulky and good light scattering effect, therefore improve paper gloss and print gloss $^{[27]}$. But there has not been any relevant study based on inorganic fillers particles loaded in nonwoven fabrics using standard whiteness index, such as CIE whiteness or Tappi whiteness.
Web structures are composed with CaCO$_3$ appears in long fibers bonded to spunbond and meltblown fabrics or transform into carded and air-laid as bulky structure, either way is emerging as a new contribute to applicable nonwoven products. Light scattering at fiber surface, especially modified with CaCO$_3$ fillers area applied to modify fabric softness, whiteness and some other aesthetic value for product development. In this chapter, the primary goal is to find the effect of fillers on light reflectance of spunbond fabrics, including using bicomponent sheath/core structure for loading with CaCO$_3$. It is expected to have a fundamental understanding from the light interacting with fiber geometry as well as filler particles influencing on fabric whiteness and opacity. The second question need to be solved is how to combine bicomponent sheath/core structure with CaCO$_3$ fillers, from the light scattering mechanism to understand the phenomenon related with opacity of fabric medium, in order to achieve improvement on certain optical property.

8.2. EXPERIMENTS

8.2.1. Material Preparation
Three Types of Calcium Carbonate fillers are pre-compounded with spunbond grade polypropylene (MFI=35).
Table 8-1: Calcium Carbonate Fillers and Compounded Masterbatch Information:

<table>
<thead>
<tr>
<th>Filler Brand Name</th>
<th>Supplier</th>
<th>Filler Types</th>
<th>Masterbatch Compounding Ratio</th>
<th>Particle Size (Ave.) μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>FiberLink201S</td>
<td>Imerys (GA)</td>
<td>Ground CaCO₃</td>
<td>80/20</td>
<td>2.24</td>
</tr>
<tr>
<td>EMforce</td>
<td>Specialty Minerals (PA)</td>
<td>Precipitated CaCO₃</td>
<td>50/50</td>
<td>Major: 1, Minor: 0.25</td>
</tr>
<tr>
<td>Superflex</td>
<td>Specialty Minerals (PA)</td>
<td>Precipitated CaCO₃</td>
<td>50/50</td>
<td>0.38</td>
</tr>
</tbody>
</table>

8.2.2. Spunbond Fabric Producing

Web forming is produced by 0.5 Meter Bicomponent Spunbond Line (Hills - Nordson) in the pilot plant in the Nonwovens Institute. Two extruders convey polymer material into spinneret, which has 1162 holes. Polymer melting in blend ratio of CaCO₃ was first filtered out of any impurity, and followed by pumping out in a constant throughput, then coming down to spinneret. Fibers are quenched and drawn by high velocity air through the aspirator slot. Technical index include speed and temperature profiles, as well as pressure of calendar can be found in Table 6-2 and Table 7-2. Calendar connected with web forming belt catch webs and bonding under five temperature levels: 135°C, 140°C, 145°C and 150°C. Smooth surface and an emboss surface on each of the calendar.
8.2.3. Fabric Structure Characterization

Particle Size Distribution

We analysis size of calcium carbonate particles using a particle size analyzer (Beckman Coulter) in Department of Natural Resources in NCSU. The FiberLink 201S was first using acetone as a suspension liquid and measure the differential volume of coated one. Then both GCC and PCC fillers were ashing in high temperature (800˚F) furnace for 8 hours to remove their surface coating off. Then those fillers were respectively suspended in water, using clean pipette carefully collect the top layer of suspension and put several drops into analyzer entrance.

Whiteness

Whiteness is measured using X-rite spectrophotometer, under CIE L, a*, b* coordinator spaces, conducted on calibrated spectrophotometer using D65 at 10°. Eight measurements were taken from four specimens, with each specimen read from the machine based on average of 2 readings. To avoid sample texture influence on light reflectance, reverse the sample by 90° rotation at the second reading. The instrument is calibrated using 6mm aperture. Light reflectance value is characterized based on the whole visible light spectrum from 360 nm to 750nm. Whiteness index and CIE (L*, a*, b*) chromaticity coordinators are accordingly recorded from the spectrophotometer.

Sample preparation involved powder and single filament in a specific sample holder used for spectrophotometer. We put 1 gram of raw filler particles on glass slide, slightly meshed those granule calcium carbonate powders into thin flat sheet form. If the field is sufficiently
covered by such powder, light transmitting is prohibited by such layer of particles on the glass slide. Put a cover slid taped by the four edges to adhere parallel with the top of powder layer. Then blows off the residual powder on that glass slide using canned air duster, which provide a clean contact onto the aperture of spectrophotometer.

Single fibers from melt spinning experiment were applied onto a sample holder for further evaluation. Samples are prepared by wrapping fibers around onto a 1 inch wide rectangular black sample hold. A close and tightly wrapping is recommended and no leaking of background black color proves the validation of reading. The wrapping coverage should be at least 10 mm wide to sufficiently cover the 6mm aperture.

**Optical Microscopy**

A Zeiss optical microscope with an objective of 25× and 40× was used and images were captured with a Nikon high-definition color camera DS-Fi1 mounted on the microscope. Using optical microscope helps us to characterize the filler particle dispersion fiber sample. Fiber diameter is also measured from the optical microscope image by taking average 20 measurements on ten fiber samples. We mainly observe fibers in between two bonding points where fiber diameter seldom disturbed by heat conduction. Phenom SEM is conducted for obtain images, which is analyzed by Image J software on fiber diameter.

**Scanning Electronic Microscope (SEM)**

Fiber sample is observed using Phenom SEM in Physical Testing Lab of the Nonwovens Institute, NCSU. Surface roughness and cross-section of single fibers were observed. Fiber or
fabric samples are sputter coated with platinum and to impose the smooth electrical conductive metal onto polymer fiber surface.

**Fabric Opacity**

Standard testing method use light reflectance contrast ratio to compare opacity of pile of paper sheet. Based on ASTM D 589-97 (2002), paper backing has 89% reflectance and a black backing with zero reflectance is measuring reflectance contrast ratio $C_{0.89}$.

$$C_{0.89} = 100 \frac{R_0}{R_{0.89}}$$  \hspace{1cm} (1)

Where $R_0$ is reflectance of fabric back of a cavity lined with black velvet material which causes the reflectance of the cavity is 0.5 % or less. $R_{0.89}$ is reflectance of a white background with absolute reflectance equal to 0.89. Instead of 89% reflectance backing, using a pile of same sample is also applicable in spectrophotometer. Color Touch2 (Model ISO) is set up with D65 with 10° observation angle. Firstly we placed the specimen backed by a pile of the same fabrics, then place specimen back by the black cup, record up to 10 readings of each sample. Results output include $100R_0/R_{\infty}$, where $R_{\infty}$ is the reflectivity. At the same time, ISO opacity, scattering power and absorption power are calculated.

### 8.3. RESULTS AND DISCUSSION

#### 8.3.1. CaCO$_3$ Fillers

Reflectance value characterizes percentage of light reflected to the total amount of light accepted by the object. When incident light beam goes into a dense medium refraction
changes the direction of wavelength, and keep refracting at air-polymer interface if there are pores. After inorganic fillers are incorporated, light propagation direction is even randomized because the scattering at the polymer-filler interface. Among three types of calcium carbonate particles, rod-shaped PCC filler with 0.25μm by 1μm shows a supreme light reflectance value than PCC-Superpflex which has 0.38μm in size (Table 8-1). In the whole spectrum, SF keep leveling up the reflectance from 400nm to 600nm, while for EM and FL (GCC) starting from lower 430nm the reflectance approaches to an equilibrium level. It was speculated the EMforce (EM) particles overlay into a powder layer more uniformly that enhances the maximum reflection of light at the contacting surface. Fine SF particle has the feature in the dry brightness as well as the reddish (a*=-0.2) and yellowish tint (b*=1.46) compare to the other two types of fillers. When we compare chromaticity coordinates of these different types of CaCO₃ (Table 8-2), is that L* for both PCC fillers (EM and SF) hit at higher lightness level, and chromaticity coefficient b* (b* range from -1 to +1 represent from blue to yellow) indicate PCC fillers possess with higher yellowness (positive in b* axis) than GCC. While the difference in a* is less distinct which means the coefficient in red to green coordinate is close (a* range from -1 to +1 represent from green to red).

Fillers packing characteristics will be related to particle size distribution, as shown in Figure 8-2. GCC powder is with wide particle size distribution from 0.1μm to 12μm. SF particle distribution moves down to smaller size range falls within 0.2 μm to 2μm. GCC with an average particle size 2.24μm, shows less amount of particles below 1μm, with d₅₀/d₂₅ =1.92. SF comprises with ≥10% of fillers distributed less than 1μm, in d₅₀/d₂₅≈ 2.11, the larger ratio
indicate \( d_{25} \) of SF falls into a smaller size range. This explains the higher light reflectance of PCC in Figure 8-1 may cause more scattering at finer PCC particle-air interface. Santos and Velho pointed out as an alternative pigment type, GCC is hardly to have as bulky as PCC fillers that have been applied as a coating onto papers, but GCC can maintain small pore volume inside of coating that is also contributed to light reflectance value \(^{[27]}\). Such bimodal size distribution would allow the small particles less than 0.5\( \mu \)m, shown in Figure 8-4, to fill into large pores generated by those with larger than average \((d_{50})\) as 2.2\( \mu \)m GCC fillers dispersed with surface coating. The largest portion of PCC-Superpflex may fall in the same size as the 2.9\( \mu \)m plotted in Figure 8-4 (b), a larger portion forms in the Gaussian distribution average at 1.3\( \mu \)m. This indicates that majority pore within PCC powder stacks will be much smaller. However, for GCC powder form particles they have the ability to distribute in a polymer flow by combining finer particles with relatively larger pore size, which are open and allow polymer molecules to take some finer particles to flow through without clogging the open pores. Similar results were reported by Kemperl and Macek that the precipitated calcium carbonate fillers with coarser particle size obtain lower yellowness than finer particles \(^{[20]}\). From the maximum absorbing band in the whole visible light spectrum, included in Figure 8-1, SF powder form particles stands out at 650 nm which is close to red reflective band. EM powder particles reflected light at 540 nm which impose a yellowish white to the filler particles.
Figure 8-1: Light Reflectance of Powder Form of Calcium Carbonate Fillers with FiberLink (FL), EMforce (EM) and Superpflex (SF) in Different Behavior in Whole Spectrum of Light.

Table 8-2: Powder Form Calcium Carbonate CIE-Whiteness, L*, a*, b* and Brightness

<table>
<thead>
<tr>
<th>Sample</th>
<th>CIE-Whiteness</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>Dry Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td>FiberLink</td>
<td>86.26 (0.50)</td>
<td>95.10 (0.23)</td>
<td>-0.03 (0.028)</td>
<td>0.35 (0.092)</td>
<td>-</td>
</tr>
<tr>
<td>EMforce</td>
<td>90.52 (0.24)</td>
<td>97.35 (0.30)</td>
<td>-0.13 (0.076)</td>
<td>0.63 (0.222)</td>
<td>&gt;94</td>
</tr>
<tr>
<td>Superpflex</td>
<td>84.04 (0.50)</td>
<td>96.24 (0.16)</td>
<td>0.2 (0.067)</td>
<td>1.46 (0.059)</td>
<td>97</td>
</tr>
</tbody>
</table>
Figure 8-2: Particle Size Distribution of Precipitated Calcium Carbonate (SF) — , comparing to Ground Calcium Carbonate (FL) — .
Figure 8-3: Particle morphology of calcium carbonate of aragonite crystal forms of PCC – EMforce (a); GCC calcite form FiberLink (b) and cubic PCC fillers Superpflex (c).
Figure 8-4: Bimodal phenomenon in particle size distribution of GCC with 1~2% stearic acid surface coated (a) and PCC-Superpflex after burning out coating (b).

8.3.2. Fiber Whiteness
From characterization of fibers form by melt spinning containing with different CaCO₃, it points out that even slight amount of loading at 2.5% can correspondingly improve the light
reflectance of fibers (Fig. 8-5). From visual perception, the lustering of light from fibers is removed, replacing with smooth white, such matte and gloss appearance must be associated with the CaCO$_3$ fillers. Mono-component fibers surface is roughened by particulate fillers, which can remove luster effect on synthetic fibers. The fillers also increase the CIE-whiteness (Fig. 8-5) of polypropylene fibers, resulting in the extent of modification depends on loading the concentration in fibers. At small amount of loading (2.5%) both PCC types (EM and SF) have higher CIE-whiteness value than GCC-FL, indicating uniform size and particle shape of CaCO$_3$ particles whitening the fibers more efficiently. Especially for SF in the light reflectance value is supreme than others. While raise up loading to 10% in mono-component fibers, the light reflectance from fiber added with FiberLink increases, so that CIE-whiteness of FL reach to above the level of SF, which is due to a yellowish shade from Superpflex fillers.

Using bicomponent has substantial benefits over mono-component by providing rougher and higher filler coverage to scatter the light at fiber surface. Incident light beams meet with inorganic solid which forms in one component of fibers, while the other component is polypropylene which is not as competent as CaCO$_3$ fillers in reflectance. The intensity of reflectance is sensitive to the filler loading fraction in the sheath layer, so 2.5%~5% of total amount of fillers can be specially loaded into the sheath as for FL, which has higher CIE-whiteness at 10% than PCC-SF. We first load PCC fillers into 50:50 sheath/core component in fibers because if higher filler amount of PCC on sheath of fibers, then the b* value reflecting the yellowness can be influenced by the packing fraction on fiber sheath. On the
contrary, the whiteness value of PCC filled in core component of fibers, as shown in Figure 8-6, scatter light that transmit through without imposing any shades on the skin layer.

Figure 8-5: Fiber CIE-Whiteness and light reflectance value of mono-component Fibers (Hills Melt Spinning Unit) filled with 2.5% and 10% of EMforce (EM), FiberLink (FL) and Superpflex (SF). The whiteness is characterized by spectrophotometer X-rite.
Figure 8-6: Fiber morphology under optical microscope of fiber sample with (a) 20% of Superpflex in the core, (b) 20% of EMforce in core; (c) polypropylene loaded with 10% of FiberLink in sheath and (d) 10% loaded only in core-component.

Optical microscope images shown in Figure 8-6 reveal that when light transmit through fibers containing with PCC filler in core, a denser packing comes at finer particle SF with 0.38μm that impose intense light scatter effect with 20% loading in the core. While needle-shape particles tend to orient along the shear stress in fiber extrusion, which may cause more
light transmission through the gaps between the parallel aligned needle particles. Comparing
to PCC, the GCC fillers form a network of particle skeleton within the core. The light
transmission through the fibers diffracted at the inorganic particle interfaces in the matrix.
This indicates that an intermediate phase of air is formed around such filler particles, as
during fiber drawing some micro voids formed by phase separation between polymer melt
and GCC filler particles. This result has been recorded by Ookawa in 1970 that higher draw
ratio over polyester fibers can form a flat long microvoid around fillers [32]. It can be
observed that a large amount of voids formed when GCC loaded up to 10% in sheath of the
fibers.

To estimate whitening effect of PCC fillers on bicomponent fibers, CIE chromaticity
coefficient including L*, a*, b* and WI-CIE and yellowness index are characterized, as listed
in Table 8-3, we find SF particle improve the whiteness index of PP fibers, while with more
than 2.5% in sheath it is hardly to have substantial influence on WI-CIE, only induce a higher
yellowness value accordingly. If loading 5% SF in core component, the lightness L* reduce
from 85% to 83%, but the yellowness index also decreased since exposure of particles with
yellowish tint to incident light beams is hided. If SF is mixed with an additional 5% of GCC
fillers in the sheath, we see a higher WI-CIE and a decreased b* value. It is found for PCC-
EM fillers that 2.5% in mono component fibers resulted in same level of reflectance,
lightness and whiteness as fibers incorporated within the core at 5 wt. %, indicating packing
fraction of EM fillers may have less effect on surface scattering. This should be related with
the needle-like particle shape of EM that tends to align its long axis with polymer flow
direction. The anisotropic filler particles tend to align with polymer orientation during melt spinning. From Steen and Dupont investigation, the variation in L* and b* are much more significant than the variation of a* in white structured textile fabrics\textsuperscript{[31]}, which also reflect in our observed results (Fig. 8-11) that the coordinator value a* is irrelevant to the amount of loading concentration. So in the following fabric whiteness, we will focus on the b* value caused by adding PCC fillers in fabrics in together with the CIE-WI index.

Table 8-3: Chromaticity Index in CIE Color Spaces of Bicomponent Fibers Filled with PCC:

<table>
<thead>
<tr>
<th>Fiber Sample Info</th>
<th>Filler Loading Component</th>
<th>WI-CIE</th>
<th>Yellowness (D1925)</th>
<th>L* a* b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP Control</td>
<td>Mono</td>
<td>57.88 (0.28)</td>
<td>1.38 (0.22)</td>
<td>82.4, 0.1, 0.64</td>
</tr>
<tr>
<td>2.5% SF</td>
<td>Mono</td>
<td>67.43 (0.56)</td>
<td>-0.33 (0.08)</td>
<td>85.5, -0.14, -0.1</td>
</tr>
<tr>
<td>2.5% SF</td>
<td>Sheath</td>
<td>66.62 (0.33)</td>
<td>1.07 (0.11)</td>
<td>86.7, -0.20, 0.60</td>
</tr>
<tr>
<td>5% SF</td>
<td>Core</td>
<td>67.20 (0.38)</td>
<td>-0.05 (0.09)</td>
<td>83.4, -0.05, 0.21</td>
</tr>
<tr>
<td>5% SF</td>
<td>Sheath</td>
<td>65.70 (1.29)</td>
<td>0.46 (0.21)</td>
<td>85.6, -0.2, 0.30</td>
</tr>
<tr>
<td>5% FL+2.5% SF</td>
<td>Sheath</td>
<td>69.09 (3.34)</td>
<td>-0.65 (0.34)</td>
<td>86.0, -0.26, -0.20</td>
</tr>
<tr>
<td>5% EM</td>
<td>Core</td>
<td>64.67 (0.75)</td>
<td>-0.12 (0.35)</td>
<td>84.3, -0.16, 0.01</td>
</tr>
<tr>
<td>5% EM</td>
<td>Sheath</td>
<td>64.85 (0.42)</td>
<td>-0.05 (0.31)</td>
<td>84.0, -0.06, 0.13</td>
</tr>
<tr>
<td>2.5% EM</td>
<td>Mono</td>
<td>64.27 (1.54)</td>
<td>-0.73 (0.28)</td>
<td>83.3, -0.12, -0.30</td>
</tr>
</tbody>
</table>

Table 8-4: Whiteness CIE-value of Bicomponent Spunbond Fabrics Measured with Color-touch Technidyne System

<table>
<thead>
<tr>
<th>CIE-Whiteness (Color Touch)</th>
<th>PP control</th>
<th>5%-Mono</th>
<th>10%-Sheath</th>
<th>10%-Core</th>
<th>10%-Mono</th>
<th>20%-Sheath</th>
<th>20%-Core</th>
</tr>
</thead>
<tbody>
<tr>
<td>FiberLink</td>
<td>75.6</td>
<td>75.9</td>
<td>77.4</td>
<td>76.7</td>
<td>76.9</td>
<td>76.73</td>
<td>74.38</td>
</tr>
<tr>
<td>EMforce</td>
<td>75.6</td>
<td>78.3</td>
<td>74.0</td>
<td>73.6</td>
<td>75.1</td>
<td>72.54</td>
<td>69.4</td>
</tr>
</tbody>
</table>
8.3.3. Fabric Optical Property

Using computational method we can evaluate the color information of fabrics, but the actual visual perception of white surface is influenced by physiological function in retinal neutral system\(^{[33]}\). The color information revealed from CIE chromaticity coordinate \((L^*, a^*, b^*)\) is useful to predict the trend of reflectance from the subjects, include surface color, volume color and illumination in the space\(^{[34]}\). Added with long strands of polymers, the CaCO\(_3\) additive in polypropylene change light passage transmitted through the anisotropic fibers, however, the isotropic fiber distribution in a fibrous structure can be regarded as a synthetize function of light transmission. Different types of dissipation mechanism occur at fabric structure other than reflectance, which can weaken the effective whiteness value from the CIE color system. As shown in Table 8-4, there is hardly any change in Whiteness index on fabric. As to GCC in bicomponent fabric, filler in sheath has an improved whiteness than filler in core. The change is not that significant in whiteness index for FL, but light reflectance in Figure 8-7 shows that the influence of fiber surface roughness will actually result into more reflectance value.

The light beam energy dissipates when scattering happens at fillers surface. If we assume total incident light intensity is denoted as \(I_i\), and transmission light intensity through fabric and loss of energy through the fabrics are written as \(I_t\) and \(I_{\Omega}\). Then \(I_{\Omega}\) can be written as Equation (2) as a function related with light reflectance \(I_r\) and scattering of light through light path in the nonwoven mat \(I_s\).
Obviously the increase reflectance value should come from filler particle light reflectance itself on the standpoint of improving fabric whiteness, referred to Figure 8-7 (a) and (b), rather than roughness topography for filler concentration is lower than at least 10 wt.% As claimed by Ashizawa et al. the light transmission is monotonically decreasing with standard deviation of film surface, which means a strong correlation between film transparency with surface asperities standing on flat surface\textsuperscript{[12]}. Diffraction at particle/voids within the polymer matrix is another form of energy dissipation. Since the wavelength is comparable to particle size, according to Mie theory, the scatter of any sphere, cluster of spheres or asymmetric cylinder objectives can be coded using Maxwell function to describe the scatter radiation of electromagnetic wave\textsuperscript{[17]}. When light scattered at particles, the diffraction of light forms constructive and destructive interference which improve light scattering. In pigment technology, the light scattering on close-spacing determined the optical property of a coating layer on the wall\textsuperscript{[35]}. The back scattering coefficient per unit volume is given by:

\begin{equation}
\frac{bK_s = b(N/V)(\pi d^2/4)X_{se}}{}
\end{equation}

where \( b \) is the back-scatter fraction, \( N/V \) is the number of particles per unit volume, \( \pi d^2/4 \) is the projected area of a particle, \( K_s \) is the scattering coefficient per unit volume and \( X_{se} \) the effective scatter efficiency. In a close packed particle system, the inter particle interaction cannot be neglected in calculating the scatter, so the interference correlated with the ratio of
clearance between particles and the wavelength, \((\delta - d)/\lambda\). Define the center to center distance between particles assuming rhombohedra particle shape as \(\delta\); the particle diameter is \(d\) and wavelength is \(\lambda\). The weakened reflectance over fabric containing with 10% FL than PCC (SF and FL) reveal a closer packing of particles in the system that reduce the clearance and increase the packing efficient in the fibers.

Since shear force in fiber spinning increases the amount of micro voids, which generate interphases at air-polymer boundary within those fibers in size of 16\(\mu\)m (1.8 denier). So light may be diffused by refraction from polymer to the air voids due to the different refractive index at two phase material. So the parallel light beams curves at the multiple internal voids resulted into blurring at the back of scatter. Therefore, fabric opacity at 10% loading in mono-component spunbond has reached to the highest points compare with other two PCC particle types (Fig. 8-10), and from the instantly rise from 5% elucidating the refraction cause more light dissipation when transmit through the fabrics. Light path diffraction around particulate fillers may enhance the amount of light scattered from the adjacent region of fillers.

\[
K_{s-web} + K_{s-fiber} + K_{s-back} = K_s
\]  

(4)

Where \(K_{s-web}\) is scattering at small fibers constructed air-fiber surface, \(K_{s-fiber}\) is the scattering coefficient when the parallel beam are scattered at the heterogeneous surface at those fibers, \(K_{s-back}\) is scattering coefficient caused by backscatter which especially refers to the fillers embedded within the bicomponent inner structure. For bicomponent fibers there is
interface between sheath/core especially when the refractive index potentially changed due to adding in two different polymers for each component.

Then the scattering coefficient is separated to the partially scattered at fiber sheath at those standing particle asperities and those being scattered within the polymer matrix. When light intensity reduces by multiple scattering at beam hitting at fiber sheath component, transmission decreases represent by an improvement in opacity. The fiber surface roughness is one of reason to cause light scattering, surface loading fraction of particulate CaCO$_3$ affect the actual reflectance of fabrics. As shown in Figure 8-7(a), 15% of GCC-FL in mono-component fibers and 10% in sheath component both contribute to a higher reflectance because densely packed surface topography especially enhance the surface scatter. The particle size contribute to the scattering performance, that larger the particle size the more light reflectance on the particle surface, while as particle size decreases, light tend to scattering more intensely around those particles [17]. As compare FL with PCC (Fig. 8-7 (b)), using FL incorporated in fiber sheath has resulted the reflectance above a certain level to SF and EM filled fabrics. Although such GCC particle forms of fillers does not obtain as much raw material reflectance as PCC particles illustrated in Figure 8-1, the effect onto element structure in nonwoven reflect from a rougher fiber surface. Abnormally, if use bico fibers with core component loaded with FL fillers, we can see the opposite reflectance for SF and EM because the finer particles cause more backscatter when light penetrate through the polymer medium.
Figure 8-7: Fabrics sample light reflectance compare different filler loading configuration in mono-component and sheath/core bicomponent fabrics with in 50/50 ratio.
From whiteness in CIE (L*, a*, b*) color system the information reflected that both lightness and chromaticity coordinates will affect the visual perception of fabric whiteness especially when whiteness index consistently reduce as shown Table 8-4. Generally, a more white coated surface gives a tint of blue as bluish white appears to be more whiter than yellowish white [22, 26]. First, from Figure 8-9, calcium carbonate particles preferentially raises up the lightness level comparing to polypropylene fabric, though difference between control samples may be due to the impurities involved FL, EM and SF residuals imposed onto PP fabrics. Additionally based on GCC compared with PCC (EM and SF) it may argued that PCC tends to perform more significant improvement on lightness compared with GCC contained fabrics as shown Figure 8-9. It indicates lightness improvement greatly may come from such densely compaction in sheath component. Higher concentration determines the denser packing fraction, thereafter the brightness from pigments itself impact the whole fabric. Among three types of calcium carbonate, PCC-SF stands out in lightness correlation with filler loading concentration in sheath/core configuration (Fig. 8-9). Loading filler in core component just cover the high bright filler particles beneath pure PP shell, therefore, do not contribute to much on fabric lightness. The characteristic in lightness is one contributor to fabric visual perceptual white from SF filled fabrics. However, the b* value which imposed yellowish tint to SF and EM filled fabrics modify light reflectance onto filled particle surface. Whiteness of SF filled fibers show a dependent on loading configuration in sheath/core bicomponent fibers, 10% of loading in sheath impose higher lightness value than loading 5% in mono-component fibers. It is also pointed out the meaning of loading filler in sheath, to use a sufficient denser packing to scatter light as much as it can be.
Figure 8-8: Melt spun fiber morphology contained with 10% fillers within mono fibers (a,b, d). 5% FL + 2.5% SF a mixture of two fillers within the fiber sheath component in (c).

Include in Table 8-4, bicomponent fabrics evaluated over the CIE-whiteness index with a larger aperture (20cm). Coarser calcium carbonate fillers (GCC-FL) can sustain WI-CIE value at same level as PP without fillers. While PCC-EM only achieve higher whiteness index at 2.5~5% of loading, but further increasing up loading reduce the WI-CIE index. While for PCC, since overloaded up to 10% induce a tint to the fabric, so it is hard to keep the WI-CIE value as expected. In this case, it should accordingly reduce the amount of...
loading for PCC, but relatively increase the GCC filler concentration on sheath component. When higher b* index is inevitably increases we must use GCC to replace the PCC to maintain the targeted aesthetic effect. Evaluation of whiteness is not only connected with light reflectance value showing different levels of lightness (Figure 8-9), but also influenced by yellowness tint of fabrics that the intrinsic reflectance from calcium carbonate powder associate the color from mineral pigment with the matrix it fill into [35]. From the study of Uchida et al. on whiteness of dental restoration material, we learn that whiteness is a combination effect of shade, hue, lightness and color saturation [30]. It is not only judged from lightness, but more use chromaticity coefficient as an indicator of the color effect of fabric in visual perception. From Figure 8-11, b* incline to 2~3 for loading PCC SF and EM in the fabrics up to 20 wt. %, comparing with that, GCC-FL restrain b* within 1~1.5.
Figure 8-9: Lightness value of fabrics made with bicomponent fibers filled with 10% of 3 different types of calcium carbonate as mainly comparing to the 5% in mono-component.
Figure 8-10: Fabric whiteness influenced by filler loading configuration with 10% in sheath/core compared to 5% in mono-component.

We should be aware that CIE whiteness index is applied for paper brightness and whiteness evaluation, and paper brightening agent seek for an improved light reflectance at short wavelength range. So it is better to absorb yellow and red wavelength and more reflect the blue light, as perception of bluish white usually looks whiter. It can be directly related to the more scattering but less reflecting at the blue wavelength band from precipitated CaCO$_3$ fillers, which reduce the amount of CIE-whiteness value of produced fabrics shown in Table 8-4. At higher lightness scattered by particles on those fibers increase the amount of reflectance at larger wavelength band. Using the other whiteness index from TAPPI standard demonstrate a clearly positive effect of general greater amount of light reflected back which enhance the fabric white. Among them, only SF loaded onto sheath has much increased the
Tappi-whiteness value (Figure 8-10) which because SF fill out on sheath impose higher lightness, especially enhance the reflectance above 500 nm (Fig. 8-7). Meanwhile, with less than 0.5 μm of filler particles has the ability to form a rather smooth coating on fibers. By scattering at the fiber surface, it is expected that contrast ratio which represent the opacity of fabric is also increased. Both the contrast ratio and ISO opacity for PCC-SF filled fabrics peak out when fiber surface morphology is filled out with SF (Fig. 8-12). This indicated higher surface scattering caused from finer SF particle feature must contribute more to hiding from the black backing. The other EM fillers do not bring much variation on the light scattering of spunbond fabrics made of PCC fillers, which elucidate probably enhanced scattering coming at fiber surface where EM particle prominent improve the surface smoothness. But for GCC fillers, the dominate factors that contribute to opacity improvement at (10~20%) must be associated with roughened surface. In the following section, we will learn from the structure of fibrous medium of spunbond fabrics to reveal the geometry of fiber diameter on the diffusion of light in transmission.

The chromaticity coefficient as shown in Figure 8-11 demonstrated that b* grows positively with loading of three types of inorganic fillers. This is especially the case for PCC both types of fillers, because the finer particles impose more yellowish component from the powder form (Table 8-2). At the bicomponent fiber structure, 10% loaded in both components intensify the increment on b* as to PCC-EM and PCC-SF, because the internal packing structure become denser as compared to 5% -mono fibers. When light transmit through the fiber polymer the high loading density of fillers could greatly enhance the light scattering, as
a result light at lower wavelength (blue band) must scatter even strongly. As those fine particles aggregated by cohesive tendency in a higher volume fraction, the inter-particle spacing is coordinately narrowed. This enhance diffraction effect of light transmit through the fabrics, if regard those narrowed spacing as optical grafting that has effect on the portion of light with long wavelength (yellow to red), theoretically form the interference effect in the surrounding space. The resulted displacement of light wave could change the constructive and destructed effect as well as the light propagation directions. The longer wavelength in the chromaticity coordinator represent in the larger yellowness and less reflectance of bluish white. While the irregular cubic GCC fillers do not impose that much constructed yellow light band from the particles, and keep b* a slight increases at 10% in sheath, but not significant (Fig. 8-11).

![Graph showing chromaticity coefficients a* and b* for spunbond fabrics containing 10% CaCO3 in Sheath/Core.](image)

Figure 8-11: Chromaticity coefficient value a* and b* of spunbond fabrics containing 10% CaCO3 in Sheath/Core.
Figure 8-12: Opacity of bicomponent spunbond fabric
Figure 8-13: Thermal bonded nonwoven structured in random entanglement of fibers and its bonding pads (a): FL 20%-50gsm-135°C; (b) FiberLink fillers (FL) emerge from polymer matrix to the air.

Figure 8-14: Chromaticity coordinates in blue-yellow axis in CIE color space.
8.3.4. Fabric Geometry on Whiteness

8.3.4.1. Basis Weight

Figure 8-15: Calcium carbonate whitening effect based on thickness (basis weight) of spunbond fabrics: 50 gsm and 100 gsm containing with different amount of fillers.

Basis weight is an important geometrical factor to be considered for nonwoven production, and this index is correlated with belt moving velocity, polymer density and throughput from the spinneret. The plot based on two basis weight 50 gsm comparing with 100 gsm in Figure 8-15 gives us idea of how does fabric whiteness vary with fabric thickness with varying amount of GCC particles. As shown in the figure, adding 2.5% and 20% to polypropylene fabrics impose an increasing whiteness effect, however, comparative increment in 50 gsm comes more apparent. Even with lower whiteness for PP-50 gsm than PP-100 gsm, after
loading 20% of GCC, the 50 gsm fabric has higher whiteness value. But 100 gsm fabrics only changed in this index a little compare to the base level. With fabric basis weight reduce, the thermal calendar tend to press the bonded region thoroughly from surface to mid-plane, with particles that stayed near fiber surface can be squeezed outside of polymers. Figure 8-13 posture one of spots on 50 gsm spunbond containing with 20% of fillers, we noticed that as fibers are compressed by calendar, these dispersed particles escape outside of polymer matrix and flow on top of it. Such surface particle can impose more lightness from its intrinsic optical characteristics from calcium carbonate powder. Therefore, thin fabrics improve whiteness index apparently with thinner fashion fabrics with calcium carbonate fillers.

Figure 8-16: Loading of filler GCC-FiberLink at 30% in spunbond melt and bind together at those bridge fibers caused by convection of heat.
8.3.4.2. Fiber Diameter

Light reflectance at fabric surface correlate with surface topography which constitutes with different fiber diameter, fiber surface roughness, depth of bonds under thermal calendar bonding. Light diffuse on that calendared pattern fabric surface, with relative flatness on bonding region. As to fine fibers, inner geometry in porous structure adds up multiple reflections and scattering which promote dissipation through the medium. As we already discussed, lustering sheen from smooth fiber surface may impose plastic-like feel of spunbond fabrics. When spun fibers from the spinneret, different mass throughput levels based on fiber diameter requirement can influence fiber surface smoothness. Surface scattering at the heterogeneous asperities related with CaCO₃, will impose matte effect in replace of lustering of fabrics, shown in Figure 8-15. This changing in whitening effect has been addressed in patents [4, 6], which were discussed from aesthetic improvement of fiber forming products applied in wipes and diapers. Surface roughness of single fibers at different levels concentration of CaCO₃ in fibers is the main reason for CIE-whiteness value improvement for both fibers and fabrics. However, the filler concentration is not the only attributor to fiber morphology changes, other than that, fiber spinning process dependent fiber diameter can also contribute to fabric whiteness varying (Figure 8-17).
Table 8-5: Fabric Opacity Related to Polymer Crystal Size after Thermal Calendaring of Embossed Roll and Smooth Roll:

<table>
<thead>
<tr>
<th></th>
<th>PP Spunbond</th>
<th>Spunbond Drawn Fiber</th>
<th>SF 10%-Sheath SB +Calendar</th>
<th>SF 10%-Sheath Spunbond + Heat Press (2000 psi, 20 second)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonding Temp.</td>
<td>140–145˚C</td>
<td>n/a</td>
<td>135˚C</td>
<td>135˚C</td>
</tr>
<tr>
<td>Crystal Size (Å)</td>
<td>131</td>
<td>88</td>
<td>149</td>
<td>108</td>
</tr>
<tr>
<td>Contrast Ratio (%)</td>
<td>54.3</td>
<td>n/a</td>
<td>59.9</td>
<td>64.0</td>
</tr>
</tbody>
</table>

100 gsm Fabric containing with varying amount of filler from 2.5% to 30% is also varying in fiber diameter as illustrated in Figure 8-17. At 10%–15% when fiber diameter increases from 20μm to 22μm, the CIE-whiteness value is dropped correspondingly. Then whiteness recover at 20% is due to a reversely return down on smaller fiber diameter as volumetric throughput is turning down accordingly. As fiber diameter decreases, the particle size of calcium carbonate stands out of smooth curve that forming surface roughness of fiber units. We believe fiber surface roughness contributes to light reflectance value from filler particle phases which impose higher whitening to fabrics. Especially as concentration reach to 15% to 20%, more filler loaded in fibers result in an unevenness of fibers, which diffuse light in the reflectance evaluation. Therefore, whiteness is related with bumpy fiber surface under higher amount of loading. Figure 8-18 gives us a better idea that how does raising spin throughput from 0.6 ghm to 0.8 ghm may modify fiber surface unevenness at a constant spinning speed and filler concentration at 10 wt.%.
However, it was noticed from 100 gsm fabric CIE-whiteness as shown in Figure 8-16, that sharp rise in fiber diameter at varying concentration of GCC from 5% to 15% first increase the whiteness level followed by a leveling down at 20~30% of loading. Fabric whiteness is closely related to nonwoven porous structure and finer pore size can aid light scattering at multiphase involving polymer-air interphase, filler-filler and fill-polymer interphase. For polymer-air interphase, torturous geometry interlacing by finer fiber diameter enhances light scattering intensity. This is further supported by two throughput levels - 0.6 ghm with 0.8 ghm (Figure 8-17). Finer fibers will with finer pores and high solid volume fraction during packing, which enhance the scattering of light. Meanwhile, Particle sticking outside of fibers surface can also generate a more heterogeneous scattering sites. Spun fiber loaded with 2.5%~30% CaCO₃ impose different surface roughness that the heterogeneous light scattered at surface of fibers and embossed bonding points. Peng et al. claimed bicomponent fibers surface texture improves using a mineral fillers additive incorporating in sheath, if the particle size is larger than sheath thickness, it will stick outside of fibers [21].

Fabric structures have been studied from fabric thickness and its formation under several levels of calendar bonding temperature. Among such fabric forming structure, fiber diameter and the destructive fiber structure under calendar heat conduction and radiation is sensitive to amount of filler inside of spunbond fabrics. As represent in the 50 gsm fabric CIE-whiteness plot with filler concentration, monotonous increase from zero percent loading to 20 wt.%. Except for above 20%, increasing filler amount vary little based on different throughput
elucidating fiber surface dominate optical properties. For 0.8 ghm, further adding fillers above 10 wt.% does not varying much on the fabric whitening effect. Previous study by Huck and Clegg [11] has conducted the opacity of LDPE film under different melt extrusion condition, and brought up two mechanisms dominating the film surface roughness which may influence opacity or haze. One is extrusion haze, and another is crystallization haze [11, 24]. As bumpy surface extruded in the molten phase correlated with the roughness, therefore modification at the die pack to impose surface unevenness to the solidified film or any other geometrical objective will help to improve the haze, white and opacity [24]. This means at higher throughput polymer from the spinneret will impose more close wrapping around those fillers particles, not as protruded as in the case of 0.6 ghm. Figure 8-19 well explain the morphology changes with throughput level, and surface become less rough after raising up to 0.8 ghm. For the latter crystallization haze, it is mainly contribute to the light scattering effect at those small aggregates of crystallites on or close to the surface of the film [24]. As shown from Table 8-5, with crystal size in spunbond fabric increases from 131Å to 149Å, the contrast ratio of PP fabric is also improved by 5.6% after incorporating 10% of PCC-SF in sheath component. As previous results in Chapter VII (Table 7-5) reveals, the spunbond fabric after thermally bonded, the crystal size increased from 126Å to 138Å. Fibers are bonded by embossed rolls can be regarded as pad of PP containing with SF fillers. We find that the even higher contrast ratio is reached for sample bonded with double smooth rolls, which may because of smaller crystal size generate more scattering of light.
Figure 8-17: Single fiber diameter with varying of filler concentration from 5%, 10%, 15% to 20% and 30%, included in graph (a). Fabric (100 gsm) whiteness (CIE-WI) (b).
Figure 8-18: Varying of fabric whiteness compared mass throughput level 0.6 ghm (gram per hole per minute) and 0.8 ghm. (Throughput impact on fabric whiteness)

Figure 8-19: Throughput effect on fiber morphology in surface roughness, representing the smoothness improvement containing with 10% of FL-GCC at 0.8 ghm (b) compare to 10% of FL-GCC at 0.6 ghm (a).
8.3.4.3. **Bicomponent Sheath/Core Ratio of Fiber**

One issue associate with spunbond nonwovens is plastic feel that always accompanied with using thermoplastic polymers, since light lustering from fabric appearance are mainly due to lack of texture on the fiber surface. Fibers made from polymers added with calcium carbonate filler may change the undesired plastic-feel because surface of fibers change the mirror reflection to more scattering of light during the scattering onto the fabrics. Opacity of polypropylene spunbond, especially those applied for hygiene products, owe to the spinnability of particulate fillers into the fibers, will be improved up to certain extent. Especially in nonwoven structure with large porosity but less solid volume fraction, the likelihood of light transmitting through and see through from the back, will depend on fiber diameter and cross-section shape, fabric thickness and basis weight, pore size and pore geometry. But changing filler particle loading configuration within bicomponent fibers, it can modify opacity to the fabric without change much on other geometric parameters. Because the reason light transmission is declined is because there are sufficient light scatter on the rough fiber surface generated by filler particles.

Loading fillers in sheath and core of bicomponent spunbond fibers bring different opacity effect as expected, that filler loading in the sheath improve opacity (Figure 8-20). Following steps in opacity evaluation is by keeping constant loading at 20% in S/C fibers, but with varying S/C ratio at 25/75, 50/50 and 75/25. Amount of fillers in whole fiber equal to 5%, 10% and 15% by varying three S/C ratio. Increasing core ratio from 25% to 75% in whole volume, filler loading dominate more in fiber center. There is less increment in whole fabric
opacity. When put calcium carbonate filler in fiber sheath, there has been large extent of improvement in opacity. This diffuse more incident light, as well as the reflected light which actually improve the hiding power of the nonwoven medium. Standing on this point, if adding calcium carbonate into thin nonwoven mat for the purpose of improving fabric opacity, it is better to load filler in the outer shell of fibers to enhance the light diffusion.

Figure 8-20: Comparison of bicomponent fabric filled with 20% of FiberLink in S/C 25/75, 50/50 and 75/25.
As compare fabric contrast ratio of fabrics containing with 5%, 10% and 15%, to the same weight fraction but only appear in bicomponent sheath component with 20%. Such dense layer cover around a pure polypropylene core inside, as ratio of core reduces from 75 vol. % to 25 vol. %., as shown in Figure 8-20, PP control cannot possess with as comparable contrast ratio as those fabrics containing with CaCO₃. This is represented in a lower $R_0$ which represent polypropylene made fabrics have less coverage over black background, so light beams are likely to be absorbed by the darkness on the back. Because the fibers are filled with CaCO₃, then fabrics containing with more inorganic fillers can gives more efficient light reflectance even backed with background. This is what indicated in Figure 7-17, that concentration of fillers work positively towards to a larger contrast ratio value. That bicomponent containing with 20% of CaCO₃ in a 25 vol.% sheath layer would perform even better opacity over 5% in mono-component. Specifically, the light reflectance of CaCO₃ contained fibers perform its reflectance path from incident throw onto fiber surface, to a refractive, diffractive light wavelength being distracted at shallow surface of fibers. Incorporating filler particles which can diffract light more efficiently than pure polymer structure would find it works directly towards incident light beam when the configuration of loading is on sheath rather than in the core. This is proved from Figure 8-20, that loading in core configuration is not competent with loading filler in sheath.
Figure 8-21: Scattering power of fabrics filled with 20% GCC on sheath component at varying of sheath/core ratio at 25:75, 50:50, 75:25.
8.4. CONCLUSION

Different particle size and shape of calcium carbonate fillers influence spunbond fabric optical properties in light reflectance and whiteness index. GCC particles will improve fibers and fabric whiteness up to 20 wt.% of loading concentration. Fiber incorporated with 10 wt.% obtain higher light reflectance than 2.5%, because light scattering on the rough fiber surface is related with the weight fraction. PCC fillers, especially EMforce have more lightness and whiteness than Superpflex, which has higher brightness but at the same time possess with reddish and yellowish tint. As for spunbond incorporated with fillers in either mono-component or bicomponent, it has been found that improving filler fraction in fiber sheath works efficiently in improving light reflectance value. While further add up above 5% of PCC will result in a less whiteness surface, which results from higher b* value, compare to GCC fillers.

Spunbond fabrics filled with calcium carbonate change the fabric optical properties from light scattering, reflection and diffraction. Scattering of light will reduce light lustering onto pure polypropylene fibers, therefore makes fabric obtain matte effect. Two main contributors to surface scattering is fiber diameter and filler weight fraction in loading. Surface unevenness associated with higher loading (>15 wt.%) is minimized by using higher spinning throughput because of larger fiber diameter compare to filler particle top cut. Secondly, light reflecting on fabric smooth surface depend on processing condition of thermal point bonding. Our results indicate fabric whiteness decreases with calendar roll temperature (bonding temperature). This must review our previous Chapter V and Chapter VI, where we conduct
fabric bonding structure and mechanical properties under different temperature levels. And we conclude the reducing whiteness is because of overbonding, that nip pressure will reduce the bonding film thickness and sinking geometry. Finally, finest portion of CaCO₃ particle size dominate light diffraction in that short wavelength range. PCC-Superpflex, 0.7μm, and a larger portion in finest particle size compare to GCC-FiberLink, influence more light absorption from optical microscopy image, because in wavelength 380~500 nm the light diffraction is enhanced by those fine PCC fillers embedded in fibers.

Advantage of using bicomponent spunbond composed with calcium carbonate in sheath component is for fabric optical performance. Rough surface give more diffusion on incident light beams resulting into better opaque effect. Opaque effect is also enhanced by loading increasing amount of fillers into spunbond fibers for both any levels of fabric thickness from 50 gsm to 100 gsm. For fabric in the application of wipes, coversheet for diapers etc. a good opacity for even thin and light fabric but without compromising opacity and whiteness is a general trending in product development. By combining calcium carbonate fillers in spunbond nonwoven, especially loaded in the sheath/core bicomponent fibers, fabric thickness and solid volume fraction reduces because of fiber density increases.
REFERENCES


CHAPTER 9 CONCLUSION AND FUTURE WORK

This dissertation mainly discuss the structure-property relationship in polymer melt spinning and spunbond nonwoven processing. We have been applied three different types of inorganic fillers, GCC-FiberLink, PCC-EMforce and PCC-Superpflex into melt extrusion, and mainly investigate filler loading concentration, thermal calendar bonding temperature and bicomponent configuration on their impact of spunbond nonwoven structure. These types of fillers consistently prove that adding up to 20% of inorganic fillers can be successful to produce nonwoven products; more significantly, thermal bonded fabrics containing fillers will keep the same tensile strength as polypropylene fabric. Our target of applying inorganic filler to reduce the dependence on thermoplastic polymer has been achieved, which also efficiently reduce the cost, reduce the thermal energy input for calendaring, make the line speed faster for roll fabrics. The mechanism of difference between bonding efficiency of spunbond fabric is explained by investigating single fiber tensile property, polymer melting and recrystallized structure under bonding and fiber crystal size influenced by different thermal bonding temperature. The very important results on bicomponent fiber configuration is depending on filler particle shape, the one with higher aspect ratio (EMforce) will works out with higher fiber strength, bonding efficient and closer lamellae packing (d-spacing) when embedded in sheath layer. However, the cubic and spherical particles (FiberLink and Superpflex) both support that incorporation within core configuration will improve the thermal bonding structure and properties.
Melt viscosity determine several key parameters in melt spinning, wherein melt strength should be the most important work that must be addressed in the future. Next as to viscosity under different calcium carbonate fillers loading respond to the melt strength in polymer solidification, especially at higher straining rate. Therefore, the filler interaction with polymer shear flow at shear rate range of $100\ \text{s}^{-1}$ to $10,000\text{s}^{-1}$ may bring a future work on packing of fillers with polymer flow under different aspect ratio of fillers. It also related to a potential issue on the extrusion instability such as melt fracture with a critical volume fraction of fillers, so that by characterizing extrudate from capillary rheometer could find hidden problem in polymer extrusion out of spinpack capillary.

Next potential challenge is on winding the fibers onto spin godet, because our previous results show a high spinline tension induced fanning out on the godet. We think spin finish is rejected by adding one type of PCC particles onto PP fiber. So it brings up the next question how to select the applicable spin finish to enhance the adhesion and reduce higher friction, but also stabilize the online spinning performance.

On spunbond fiber orientation in the fabrics, we believe it is the fiber rotational rigidity and fiber size that determine the randomness in web lay-down formation. As certain part of fabric web surface appear fiber bundles without sufficiently opening, so we suggest keeping investigating the web laid down formation influenced by inorganic filler particles. Possibly to learn the static effect that might accumulate onto fibers with a roughened surface.
About other properties of nonwoven fibrous medium comprise calcium carbonate fillers, it is highly recommended to keep research on air filtration performance. If meltblown technology is durable with certain amount of fillers, it may give a fiber mat with nano size fiber diameter. So when select the filler particle size, it is important to consider both the melt viscosity and fiber diameter in both ways. In the future, the pressure drop and filtration efficient will be an interesting area for study. Precipitated calcium carbonate provide an optional to select particle size within 500 nm range, however, it also brings up high requirement for surface treatment of fillers to enhance the dispersion in polymers. Meanwhile, to solving the chemical affinity between inorganic filler particle with polymer melt is the fundamental problem to overcome filler agglomeration.
Table 3-7: Parameter Settings for Melt Spinning of Fibers Containing FiberLink CaCO₃

<table>
<thead>
<tr>
<th>Design of Experiment Parameters</th>
<th>Trial I</th>
<th>Trial II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filler Concentration (%)</td>
<td>5~20 and PP control</td>
<td>20~40 and PP</td>
</tr>
<tr>
<td>Spin Speed (meter per min)</td>
<td>500, 1250, 2000</td>
<td>1250~2000</td>
</tr>
<tr>
<td>Draw Ratio ($\frac{v_{\text{draw roll}}}{v_{\text{feed roll}}}$)</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Spin Finish (Motor Rate, %) *</td>
<td>10</td>
<td>20~40</td>
</tr>
<tr>
<td>Quenching (Motor Rate, %)</td>
<td>20</td>
<td>20, 50</td>
</tr>
<tr>
<td>Throughput (cc/hole/minute)</td>
<td>0.635</td>
<td>0.766 and 1.155</td>
</tr>
</tbody>
</table>

Note: Spin finish: Lurol PP-912 lubricant is applied
Table 3-8: The Cost Estimation of Varying of Loading Level of Calcium Carbonate Fillers and the Relevant Throughput Changes:

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Cost (US$/Tonne)</th>
<th>Density (gram/cc)</th>
<th>Consuming Total weight of PP + CaCO₃ Raw Material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Unfilled</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>300</td>
<td>2.7</td>
<td>0</td>
</tr>
<tr>
<td>Additive**</td>
<td>1500</td>
<td>0.94</td>
<td>0</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>1200</td>
<td>0.936</td>
<td>1200</td>
</tr>
<tr>
<td>Compounder***</td>
<td>250</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Total Cost</td>
<td>1200</td>
<td></td>
<td>1200</td>
</tr>
</tbody>
</table>

|                          |                   |                   |                   |                   |                   |                   | Volume fraction of Filler (vl.%): 0 | 0.88 | 1.4  | 3.0  | 4.6  | 6.4  | 10.5 |
|                          |                   |                   |                   |                   |                   |                   | Polymer Solid Density (g/cc): 0.936| 0.952| 0.961| 0.989| 1.017| 1.049| 1.121|
|                          |                   |                   |                   |                   |                   |                   | Polymer Melt Density (g/cc): 0.78  | 0.797| 0.809| 0.839| 0.873| 0.909| 0.992|
|                          |                   |                   |                   |                   |                   |                   | Mass Throughput (gr/hole/min): 0.6  | 0.61 | 0.62 | 0.64 | 0.67 | 0.70 | 0.75 |

* Assuming 1.5 wt.% stearic acid additive

** Masterbatch is 70:30 compounded with 70% of CaCO₃ and 30% of PP, where fillers are coated with 1.5% of stearic acid.

*** Volume fraction is calculated from melt density of each component in filled PP. \( m_{\text{filler}} = 2.7 \text{ g/cc}, m_{\text{PP}} = 0.739 \text{ g/cc} \).
Appendix B  Thermal Degradation

Spinpack blocking was not observed during our 5 minutes spinning using the GCC-FL particles, furthermore, in the subsequent 15 minutes running, compare GCC and other two PCC fillers (EM and SF), there was more screen pack clogging in PCC particles.

Table 3-9: Fiber Sample TGA Information:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Target Residue (%)</th>
<th>Wt.% Residue</th>
<th>On-set Degradation Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-2000B</td>
<td>0</td>
<td>0.31</td>
<td>401.10</td>
</tr>
<tr>
<td>Ca20-2000B*</td>
<td>20</td>
<td>20.72</td>
<td>379.49</td>
</tr>
<tr>
<td>Ca30-2000B</td>
<td>30</td>
<td>30.87</td>
<td>410.76</td>
</tr>
<tr>
<td>Ca40-2000B</td>
<td>40</td>
<td>37.08</td>
<td>392.87</td>
</tr>
<tr>
<td>Ca40-2000A*</td>
<td>40</td>
<td>41.70</td>
<td>397.05</td>
</tr>
<tr>
<td>Ca30-2000A</td>
<td>30</td>
<td>28.32</td>
<td>379.12</td>
</tr>
<tr>
<td>Ca30-1250B</td>
<td>30</td>
<td>30.46</td>
<td>384.12</td>
</tr>
<tr>
<td>Ca40-1250B</td>
<td>40</td>
<td>39.39</td>
<td>389.88</td>
</tr>
</tbody>
</table>

*: A and B represent two spun draw roll speed ratio. A=DR 1:1, B= DR 1:2.
Figure 9-1: True loading of inorganic fillers in melt spun fibers
Figure 9-2: Diameter of melt spun fibers under varying of throughput and draw ratio

Diameter of melt spun fibers compare the theoretical level (dashed line) with experimental values, acquired from two throughput (TH5- 0.635cc/hole/min; TH9-1.155cc/hole/min); Two spinning speed levels (1250 and 2000 mpm) at two draw ratio DR =1:1 and DR =1:2.
Appendix D  Fiber Spinnability Related to Types of CaCO₃

Table 4-11: Fiber Spinning Performance:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Filler Type</th>
<th>Filler Conc. (%)</th>
<th>Spinning Speed (mpm)</th>
<th>Pump pressure</th>
<th>Spinning Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP -1</td>
<td>EMforce</td>
<td>2.5</td>
<td>1000/2000</td>
<td>361</td>
<td>10 min running for each</td>
</tr>
<tr>
<td>EM2.5</td>
<td>EMforce</td>
<td>2.5</td>
<td>1000/2000</td>
<td>362</td>
<td>Filaments break out down in the quenching zone</td>
</tr>
<tr>
<td>EM10</td>
<td>EMforce</td>
<td>10</td>
<td>1000/2000</td>
<td>366</td>
<td></td>
</tr>
<tr>
<td>EM25</td>
<td>EMforce</td>
<td>25</td>
<td>1000/2000</td>
<td>362</td>
<td></td>
</tr>
<tr>
<td>PP-2</td>
<td>Superflex</td>
<td>2.5</td>
<td>1000/2000</td>
<td>352</td>
<td></td>
</tr>
<tr>
<td>SF2.5</td>
<td>Superflex</td>
<td>2.5</td>
<td>1000/2000</td>
<td>347</td>
<td>Fanning out, Refuse taking up spin finish</td>
</tr>
<tr>
<td>SF10</td>
<td>Superflex</td>
<td>10</td>
<td>1000/2000</td>
<td>335</td>
<td></td>
</tr>
<tr>
<td>SF25</td>
<td>Superflex</td>
<td>25</td>
<td>1000/2000</td>
<td>302</td>
<td>Fiber breaking on drawing godets</td>
</tr>
<tr>
<td>PP-3</td>
<td>FiberLink</td>
<td>2.5</td>
<td>1000/2000</td>
<td>352</td>
<td></td>
</tr>
<tr>
<td>FC2.5</td>
<td>FiberLink</td>
<td>2.5</td>
<td>1000/2000</td>
<td>354</td>
<td></td>
</tr>
<tr>
<td>FC10</td>
<td>FiberLink</td>
<td>10</td>
<td>1000/2000</td>
<td>348</td>
<td>Fanning out at draw rolls</td>
</tr>
<tr>
<td>FC25</td>
<td>FiberLink</td>
<td>25</td>
<td>1000/2000</td>
<td>361</td>
<td>Fibers fanning out severely, dancing on the godets</td>
</tr>
</tbody>
</table>

Fibers spinning instability comes from frequently breakage on spinline, one is below the spinneret when polymer is still molten, another is on godet when the high friction between fiber and godet surface impose higher friction. Although spin finish is adjusted to fully charged, but the adhesion to metal surface is still not promised, spin finish lubrication is
easily applied onto smooth PP fibers, but not onto CaCO$_3$ filled fibers. Severe problem comes when PCC-Superpflex is filled into fibers, fibers reject to take up spin finish at early stage. Superpflex fillers not just cause instable fiber spinning performance, but also result into frequently breaking. Fiber surface unevenness affect the relative movement at spin-draw godet, and will influence the actually take-up velocity and the true draw ratio between two velocity of draw roll to the feed roll.
Figure 9-3: Melt viscosity of PP masterbatch with PCC fillers.
### Appendix F

Table 6-6: Bico Fiber Spinnability in Spin-Draw Performance at Varying of Loading Concentration in Sheath/Core Bicomponent Configuration

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Filler Type</th>
<th>Conc. wt.%</th>
<th>Spin Speed (mpm)</th>
<th>Pump Pressure (psi) on Two Extruders</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sheath</td>
<td>Core</td>
</tr>
<tr>
<td>PP-control-1</td>
<td>NA</td>
<td>0</td>
<td>2000</td>
<td>724</td>
<td>673</td>
</tr>
<tr>
<td>EM5-sheath</td>
<td>EMforce</td>
<td>2.5</td>
<td>2000</td>
<td>566</td>
<td>691</td>
</tr>
<tr>
<td>EM10-sheath</td>
<td>EMforce</td>
<td>5</td>
<td>2000</td>
<td>555</td>
<td>680</td>
</tr>
<tr>
<td>EM20-sheath</td>
<td>EMforce</td>
<td>10</td>
<td>2000</td>
<td>552</td>
<td>681</td>
</tr>
<tr>
<td>EM5-core</td>
<td>EMforce</td>
<td>2.5</td>
<td>2000</td>
<td>556</td>
<td>684</td>
</tr>
<tr>
<td>EM10-core</td>
<td>EMforce</td>
<td>5</td>
<td>2000</td>
<td>559</td>
<td>687</td>
</tr>
<tr>
<td>EM20-core</td>
<td>EMforce</td>
<td>10</td>
<td>2000</td>
<td>558</td>
<td>692</td>
</tr>
<tr>
<td>EM2.5-mono</td>
<td>EMforce</td>
<td>2.5</td>
<td>2000</td>
<td>728</td>
<td>695</td>
</tr>
<tr>
<td>EM5-mono</td>
<td>EMforce</td>
<td>5</td>
<td>2000</td>
<td>726</td>
<td>702</td>
</tr>
<tr>
<td>EM10-mono</td>
<td>EMforce</td>
<td>10</td>
<td>1600</td>
<td>724</td>
<td>705</td>
</tr>
<tr>
<td>EM20-mono</td>
<td>EMforce</td>
<td>20</td>
<td>1600</td>
<td>721</td>
<td>703</td>
</tr>
<tr>
<td>PP-control-2</td>
<td>NA</td>
<td>0</td>
<td>2000</td>
<td>725</td>
<td>703</td>
</tr>
<tr>
<td>SF2.5-sheath</td>
<td>Superpflex</td>
<td>1.25</td>
<td>2000</td>
<td>726</td>
<td>704</td>
</tr>
<tr>
<td>SF5-sheath</td>
<td>Superpflex</td>
<td>2.5</td>
<td>2000</td>
<td>566</td>
<td>691</td>
</tr>
<tr>
<td>SF10-sheath</td>
<td>Superpflex</td>
<td>5</td>
<td>2000</td>
<td>555</td>
<td>680</td>
</tr>
<tr>
<td>SF1.25-mono</td>
<td>Superpflex</td>
<td>1.25</td>
<td>2000</td>
<td>725</td>
<td>694</td>
</tr>
<tr>
<td>SF2.5-mono</td>
<td>Superpflex</td>
<td>2.5</td>
<td>1600</td>
<td>729</td>
<td>696</td>
</tr>
<tr>
<td>SF5-mono</td>
<td>Superpflex</td>
<td>5</td>
<td>1600</td>
<td>735</td>
<td>692</td>
</tr>
</tbody>
</table>
Table 6-6 Continued

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Filler Type</th>
<th>Conc. wt.%</th>
<th>Spin Speed (mpm)</th>
<th>Pump Pressure (psi) on Two Extruders</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF10-mono</td>
<td>Superflex</td>
<td>10</td>
<td>1600</td>
<td>759</td>
<td>724</td>
</tr>
<tr>
<td>SF15-mono</td>
<td>Superflex</td>
<td>15</td>
<td>1600</td>
<td>751</td>
<td>732</td>
</tr>
<tr>
<td>SF5-core</td>
<td>Superflex</td>
<td>2.5</td>
<td>1600</td>
<td>748</td>
<td>700</td>
</tr>
<tr>
<td>SF10-core</td>
<td>Superflex</td>
<td>5</td>
<td>1600</td>
<td>739</td>
<td>707</td>
</tr>
<tr>
<td>SF15-core</td>
<td>Superflex</td>
<td>7.5</td>
<td>2000</td>
<td>738</td>
<td>722</td>
</tr>
<tr>
<td>SF20-core</td>
<td>Superflex</td>
<td>10</td>
<td>2000</td>
<td>737</td>
<td>729</td>
</tr>
<tr>
<td>SF30-core</td>
<td>Superflex</td>
<td>15</td>
<td>2000</td>
<td>740</td>
<td>772</td>
</tr>
</tbody>
</table>

Fine and weak, spin speed had to be lowered down

Spinning improved, less fanning out, stable

A few breaking at draw rolls
Free fall filaments were collected down below the spinneret. Pictures taken by Canon camero below the spinneret as shown in Figure 6-21, no distinctive melt fracture or melt dripping during processing.

![Figure 9-4: Spinneret from bicomponent melt spinning unit shows fibers without CaCO₃ (left) and 30% of CaCO₃ (right)](image)

Behavior of filaments on godet rolls was influence by filler loading concentration. During 3 mins running on the spin-line, godet spinning speed and spin finish of fibers were delicately adjusted to achieve better fiber spinnability when gradually increase the amount of filler in fiber component. It has been found that loading filler in bico sheath, fibers tend to be severely fanning out on draw rolls. This issue really cause processing problem when loading concentration increase up to 10%, we must lower down the spinning speed to make it spinnable. Spin finish was applied in vol. 10% of Lurol 912 at pump motor speed of 35%. However, rise up motor from 35% to 45% did not improve this instability condition. This phenomenon is due to a high spin-line tension which is controlled by coefficient of friction.
Appendix I

Heat Capacity of Polymer Material

Table 7-10: I. Theoretical heat capacity calculated from rule of mixture using PP and CaCO₃ pure material tested in MDSC results. II. Experimental results from MDSC of heat capacity of polymer with and without CaCO₃ filler:

I.

<table>
<thead>
<tr>
<th>Rule of Mixture C_p (J/g·°C)</th>
<th>PP (experimental)</th>
<th>5% CaCO₃</th>
<th>10% CaCO₃</th>
<th>15% CaCO₃</th>
<th>20% CaCO₃</th>
<th>30% CaCO₃</th>
<th>CaCO₃ Powder (experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C</td>
<td>2.579</td>
<td>2.5069</td>
<td>2.4168</td>
<td>2.3267</td>
<td>2.2366</td>
<td>2.0564</td>
<td>0.795</td>
</tr>
<tr>
<td>135°C</td>
<td>2.683</td>
<td>2.59385</td>
<td>2.5047</td>
<td>2.41555</td>
<td>2.3264</td>
<td>2.1481</td>
<td>0.900</td>
</tr>
<tr>
<td>220°C</td>
<td>3.644</td>
<td>3.52705</td>
<td>3.4101</td>
<td>3.29315</td>
<td>3.1762</td>
<td>2.9423</td>
<td>1.305</td>
</tr>
</tbody>
</table>

II.

<table>
<thead>
<tr>
<th>CaCO₃ Filer Concentration (%)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>100 (CaCO₃ Powder)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C</td>
<td>2.597</td>
<td>2.238</td>
<td>2.35</td>
<td>2.282</td>
<td>2.234</td>
<td>2.034</td>
<td>0.795</td>
</tr>
<tr>
<td>135°C</td>
<td>2.683</td>
<td>2.168</td>
<td>2.538</td>
<td>2.538</td>
<td>2.082</td>
<td>2.081</td>
<td>0.900</td>
</tr>
<tr>
<td>220°C</td>
<td>3.644</td>
<td>2.898</td>
<td>2.924</td>
<td>2.924</td>
<td>3.099</td>
<td>2.786</td>
<td>1.305</td>
</tr>
</tbody>
</table>
Figure 9-5: Heat capacity of raw Calcium Carbonate with surface treatment, measuring by modulated DSC from 25°C to 220°C heating at 10°C/min
Appendix J

Spunbond Processing Performance

In filler processing, constant volume of polymer is pumped into the spinpack and split into thousands of spinneret channels. Since polymer density changes after loading in particulate form of calcium carbonate, pump rate must be adjusted with the increased melt density by turning down the volumetric flow rate to keep at a constant mass throughput. Pump pressure is not only influenced by amount of polymer pump rate, but also by a clear pathway across the screen filter. Accumulation of fillers at mesh screen increases the burden of the pump. If without sufficient wetting filler tend to agglomerate in polymer extruding and mixing, continuously pumping to spinpack is not achievable. Therefore, pump pressure should be well monitored throughout the processing.

For example, spunbond is processed using constant mass throughput 0.6 gram per hole per minute (ghm). Loading 20% of CaCO₃ melt density raised from 0.78 g/cm³ for pure polypropylene to 0.91 g/cm³ and pump speed is correspondingly lowered down from 7.4 RPM to 6.4 RPM. The pressure of pump is dropping from 512 psi to 504 psi which means there was few mesh screens blocking issue, or no severe agglomerates captured at the mesh screen. The pump pressure for each concentration level of FiberLink is compared with three calcium carbonate filler types, FiberLink, EMforce and Superpflex, listed in Table 4. EMforce caused pressure shooting up at 25% of filler loading. This type of precipitated filler
has larger specific surface area than FiberLink. The pressure problem occurred at high concentration because of accumulating of particles with in a gradient of loading from 2.5% to 20%. As shown in Figure 2, particles residual left at breaker plate and spinneret. Such build-up of particulate filler hinders long time running using same filter. Periodical replacement of clogged screen filter is necessary. If pump pressure keeps at high rate means there is a blockage of fillers at normal flow passage. Overloading of fillers should be avoided to keep pump at pressure range below safety range, because when screen start clogging, further purging may not flow out the dirt accumulated. We purge both extruder with polypropylene right at the moment pressure shoot to 2000 psi, but pressure did not go back to normal level even after 30 minutes. Among three filler types, FiberLink possess with the most stable pressure level as compare to Superpflex and EMforce. There is not clogging and pump pressure issue at melt spinning of fibers with 20~30 wt. %, even though maximum loading thicken the melt flow but it still follow shear thinning behavior at high shear rate (Fig. 3-20).
Table 7-11: Pump pressure (unit: psi) for filler concentration at 2.5%-30% in primary and secondary extruder pump in constant mass throughput of 0.3 ghm for each pump

<table>
<thead>
<tr>
<th>Primary Pump pressure</th>
<th>PP-control</th>
<th>2.5%</th>
<th>5%</th>
<th>10%</th>
<th>20%</th>
<th>25%</th>
<th>30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FiberLink</td>
<td>405</td>
<td>402</td>
<td>N/A</td>
<td>404</td>
<td>405</td>
<td>N/A</td>
<td>404</td>
</tr>
<tr>
<td>EMforce</td>
<td>401</td>
<td>400</td>
<td>401</td>
<td>399</td>
<td>401</td>
<td>438</td>
<td>N/A</td>
</tr>
<tr>
<td>Superpflex</td>
<td>371</td>
<td>N/A</td>
<td>369</td>
<td>367</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Secondary Pump pressure</th>
<th>PP-control</th>
<th>2.5</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>25</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>FiberLink</td>
<td>512</td>
<td>503</td>
<td>N/A</td>
<td>505</td>
<td>504</td>
<td>N/A</td>
<td>502</td>
</tr>
<tr>
<td>EMforce</td>
<td>467</td>
<td>462</td>
<td>466</td>
<td>473</td>
<td>471</td>
<td>784</td>
<td>N/A</td>
</tr>
<tr>
<td>Superpflex</td>
<td>437</td>
<td>N/A</td>
<td>429</td>
<td>2099</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 9-6: Particulate fillers agglomerates at mesh screen filter
Some striped polymer resin across the clogged mesh screen has been noticed at one of the calcium carbonate fillers – Superpflex (PCC) with maximum loading at 10%, from which we suspect there was high pressure gradient on each side. Furthermore, such sign was prominent in the mesh screen connecting to sheath extruder. This extruder has smaller screw dimension (63.5mm) and higher extruder speed (23.8 RPM). So when polymer melt was metered equally at 0.3 ghm for sheath and core extruder, the fillers tend to agglomerate in sheath extruder as kneading force impose too much pressure at the shallow barrel clearance. Conversely, the larger screw extruder (75mm) connected to core component reduced the risk of overloading on pump pressure. Distribution of polymer over the breaker plate allow polymer flow across two meshed plates connected with primary extruder, but across only one mesh plate into the sheath component. So the pressure imposing onto each component in the
spinneret will be different. As shown in Figure 3 and Table 4, breaking polymer flow into two primary mesh filter flow out particulate fillers smoothly and did not raise up pump pressure significantly.

Figure 9-8: Schematic graph of spunbond spinpack