ABSTRACT

RANGASAMY, LOGANATHAN. Structure and Properties of Polypropylene-Layered Silicate Nanocomposite Fibers and Nonwovens. (Under the direction of Dr.Eunkyoung Shim and Dr.Behnam Pourdeyhimi.)

Layered silicate (nanoclay) based additives have shown great potential in polymer and plastic applications because they overcome many limitations of traditional microcomposites. But there were only few studies on nanoclay-modified fiber systems. As fiber based systems are known to provide many beneficial characteristics because of their high surface area, a combination of nanocomposite technology and fiber formation is highly sought after. The main focus on this study is to analyze the structure-property relation of nanoclay-polymer composites in fiber and nonwoven formation process.

Polypropylene is selected as a host polymer matrix for this research and nanocomposite fibers of polypropylene and precompounded material of nanoclay based on organically modified montmorillonite is produced by melt spinning process. Addition of nanoclay might result in alteration of polymer melt rheology and crystallization kinetics, which are the key factors affecting microstructure formation during the fiber melt spinning. As polypropylene is semicrystalline in nature, changes in fiber fine structure will greatly affects its mechanical properties. Therefore changes in fiber fine structure parameters such as crystallinity, crystal size, crystal orientation, rate of crystallization and molecular orientation were studied using differential scanning calorimetry, wide angle X-ray diffraction, interference microscopy. Mechanical properties of nanoclay-PP composite fibers were studied and related to the changes in the microstructure caused by the addition of nanoclay.
Nanoclay types have significant effect on the polypropylene/nanoclay interaction and fiber properties. A comparison between different clay types Nanomax and Cloisite samples were carried out on nature of polymer/nanoclay dispersion, fiber fine structure and fiber properties. In order to analyze the effect of surfactant concentration, two different Cloisite samples with different surfactant concentration was chosen. Presence of compatibilizer plays a significant role in improving the compatibility between nanoclay and polypropylene. Polypropylene grafted maleic anhydride (PP-g-MA) with two different MFI values was chosen as the compatibilizer. They were mixed with PP/Cloisite type nanoclay samples in such a way that nanoclay to compatibilizer ratio is 1:2. Based on the polypropylene/nanoclay interaction, fiber fine structure changes and fiber properties, type of compatibilizer and nanoclay to compatibilizer ratio were fixed for spunbond process.

Spunbond thermal bonded fabrics were produced with different nanoclay additives at different concentration. Spunbond fabrics of polypropylene/compatibilizer samples were also produced and used as control. Changes in mechanical property and thermal behavior after nanoclay addition were analyzed and related to the structural changes caused by the presence of nanoclay particles. In order to analyze the effect of distribution of nanoclay on mechanical properties, bicomponent spunbond fibers were produced with nanoclay located either in core or sheath and compared for their mechanical properties.

Influence of nanoclay on thermal properties of PP fibers was studied using Thermo gravimetric analyzer. Using nonisothermal degradation, activation energy required for degradation in presence of nanoclay was studied. Effect of distribution on nanoclay on
thermal degradation was also studied. The mechanism by which how the presence of nanoclay affects the thermal stability of PP fibers was established.
Structure and Properties of Polypropylene- Layered Silicate Nanocomposite Fibers and Nonwovens

by
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BIOGRAPHY

Loganathan Rangasamy was born on March 1, 1982 in Tiruchengode, Tamilnadu, India. He received his Bachelor’s degree in Textile Technology from Anna University, Chennai, India in April 2004. After finishing his bachelor studies he worked for a year at Thiagarajar Spinning Mills Limited, Nilakottai, India as Research Trainee. He joined Indian Institute of Technology, Delhi in July 2005 and received his Master’s degree in Textile Technology in May 2007. In pursuit of higher studies, he joined PhD program in Fiber and Polymer Science at College of Textiles, North Carolina State University under the supervision of Dr.Eunkyoung Shim and Dr.Behnam Pourdeyhimi. In the course of his study, he obtained minor in Chemical Engineering and a graduate certificate in Nonwovens Science and Technology.
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1.1 INTRODUCTION

A composite can be defined as a material which is composed of two or more components with different properties. The advantage of composites is to utilize the properties of both the components in the system or to improve the properties of a particular component or to impart new properties to the component by adding suitable additives or fillers. The concept of nanocomposite is based on creating a very large interface between the nano sized fillers and the polymer matrix to enhance the polymer properties. Thus, nanocomposites are the class of composite material where one dimension of filler is in the nanometer range. Nanocomposites can be classified into three types based on the dimension of the dispersed fillers in nanometer. Spherical particles have all three dimensions in the nanometer range. Silica particles are the major representative of this type of nanocomposites which are mainly formed using in-situ sol-gel technology. Carbon black and precipitated calcium carbonate are the other types of particles come under this category. In the second category, two dimensions are in the nanometer range and the third dimension is much larger. Carbon nanotubes are example for this category of nanocomposites. Many studies were carried out on carbon nanotubes mainly because of their improved electrical properties. Cellulose whiskers and nanofibers are other representatives of this type of nanocomposites. In the third type of nanocomposite only one dimension is in the nanometer range. Polymer-layered silicate (nanoclay) nanocomposite comes under this category and in this silicate particles are present in the form of sheets with a thickness of few nanometers and length ranges from 100-300 nm [Alexandra et al., 2000]. This work particularly focuses on nanocomposites based on polymer-layered silicates.
As nanoclay particles have high surface area to volume ratio and its size is similar to the segment of the surround polymer chains in nanocomposite, this makes it possible to form significant bonding to polymer matrix [Dasari et al., 2005]. It may lead to improvement of many polymer properties and nanoclay has been reported as excellent reinforcement additives. Despite recent increasing studies on nanoclay composites, most studies are concentrated on film and plastic mold and only a few studies are found in nanoclay modified fiber [Joshi et al., 2006] and nonwovens [Bhat et al., 2008]. Melt-spinning is more complex process where fiber fine structure development is determined by polymer chain responses on tension, temperature, shear in the spin line and phase transition. Reported changes in polymer melt rheology by addition of nanoclay, which includes increased shear viscosity, melt fracture may alter spin line fiber forming mechanism and subsequent changes in fiber fine structures and properties. However research on this topic is fragmental at best. It also worthwhile to note that extrusion shear affects clay orientation and with highly anisotropic clay properties, clay orientation would generate anisotropic mechanical properties [Ton-That et al., 2004]. Since shear involved in fiber formation process generally greater than film or other polymer process, nanoclay-polymer composite in fibers may develop different structural characteristics form fibers from compressed molded materials. Thus this study focuses on analyzing the structure-property relation of nanoclay-polymer composites in fiber and nonwoven formation process. Specific objectives are including but not limited to:

- Test feasibility of different types of nanoclay addition in fiber/nonwoven melt extrusion process
- Study of nanocomposite morphology
• Investigate nanoclay modified fiber fine structure

• Study the property changes of the nanoclay modified composite fibers and nonwoven

Development of polymer/nanoclay composite involves melt mixing of polymers and nanoclay at suitable processing conditions. Formation of PP/nanoclay nanocomposite depends on different material and processing parameters. Chapter 2 of this research presents a brief overview of nanocomposites based on nanoclay and different factors which affects the nanocomposite properties. The different related parameters are shown in Figure 1.1

**Figure 1.1:** Parameters involved in modification of polypropylene with nanoclay additive
In this research, PP was chosen as host polymer matrix because of its great market potential in the nonwoven industry. Therefore, the type of nanoclay is a significant parameter in the formation of PP/nanoclay nanocomposite. Many studies suggest that interaction between polymer and nanoclay increases when using a precompounded polymer/nanoclay or surface modified clay. Thus for this study, two different commercially available nanoclay types, Nanomax PP (precompounded material of PP/nanoclay/compatibilizer) and Cloisite (organically modified nanoclay) were chosen. The structure-property relation of nanoclay-fiber based on Nanomax PP type nanoclay is presented in Chapter 3 and the effect of Cloisite based additive is given in Chapter 4.

Based on the results from nanoclay added PP filament properties, processing conditions of spunbond process is fixed and nonwoven fabrics were produced. In Chapter 5 of this research, spunbond nonwoven fabrics based on 2 different types of layered silicate particles were produced and their structural and mechanical properties were presented. In Chapter 6, influence of nanoclay additive on structural and mechanical properties of bicomponent spunbond fiber and nonwoven fabrics were presented. In Chapter 7, we present the thermal behavior of the PP spunbond fibers modified with nanoclay particles In Chapter 8, overall conclusion of this research and recommendation for future work is presented.

1.2 REFERENCES


CHAPTER 2

LITERATURE REVIEW
2.1 OVERVIEW OF POLYMER/NANOCLAY NANOCOMPOSITE

As mentioned previously, nanocomposites based on nanoclay have one dimension of the particles in the nanorange. Nanocomposites based on nanoclay additive found great interest because of their low cost, ready availability and improvement in mechanical, thermal, and barrier properties [Ton-That et al., 2004]. The composites based on nanoclay (layered silicates) are generally termed as polymer layered silicate nanocomposites [Giannelis, 1996]. Most of the research based on nanoclay additives has found much interest when Toyota research group successfully prepared polyamide based nanocomposites by in-situ polymerization technique [Usuki et al., 1993a, 1993b; Kojima et al., 1993]. After that many studies were carried out in different polymer systems to understand the nature of interaction between nanoclay and polymer matrix and the property improvement imparted because of the presence of nanoclay.

In this research nanoclay particulate filler was incorporated into the polypropylene matrix and the fine structure changes and property improvement were studied. This chapter gives review about nanoclay filler, challenges in achieving the nanocomposite and different research work carried out based on these composite.

2.1.1 Nanoclay

Clays are classified based on their crystal structure and the amount and locations of charge per basic cell. Crystalline clays are widely used in polymer nanocomposite applications. Clay types ranges from kaolins to smectite. Kaolins are relatively uniform in chemical
composition, whereas smectite have wide range of chemical composition. Different types of clay are as follows:

1. Kaolins
2. Serpentine
3. Illite group (mica)
4. Chlorite and vermiculites
5. Smectites or phyllosilicates

Of the above different types of clays, smectites or phyllosilicates are the widely used clay types for polymer nanocomposite applications because of its ease of separation of individual layers.

Montmorillonite (MMT) is one of the type of smectite clay which is the most common clay type used for polymer nanocomposite applications. Their crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesia is fused to two external silica tetrahedron by the tip so that the oxygen ions of the octahedral sheet do also belong to the tetrahedral sheets. The layer thickness is around 1 nm and the lateral dimension may vary from 300 Å to several microns and even larger depending on the particular silicate [Alexandra et al., 2000]. Isomorphous substitution within the layers (for example, \( \text{Al}^{3+} \) replaced by \( \text{Mg}^{2+} \) or by \( \text{Fe}^{2+} \), or \( \text{Mg}^{2+} \) replaced by \( \text{Li}^+ \)) generates negative charge on the
surface of clay that are counterbalanced by alkali or alkaline earth cations situated in the interlayer [Ray et al., 2003].

Idealized Na-MMT can be represented as \( \text{[Al}_{3.33}\text{Mg}_{0.33}(\text{Na}_{0.67})]\text{Si}_{8}\text{O}_{20}(\text{OH})_{4} \). Figure 2.1 shows the structure of the clay platelets. The layers of the nanoclay are arranged in the form of stacks with regular interlayer or galley spacing where van der Waals force exists.

Figure 2.1: Structure of 2:1 Phyllosilicate [Andreas, 2007]
Depends on the geographic locations, MMT composition at each layers differs:

1. Octahedral layer : \( \text{Al}_{3.0-4.0} \text{Mg}_{0-1.4} \text{Fe}^{3+}_{0-1.0} \)

2. Tetrahedral layer : \( \text{Al}_{0-0.8} \text{Si}_{7.2-8.0} \)

3. Exchangeable cations in the aqueous layer : \( \text{Na}_{0.67-0.8} \)

Chemical composition of typical MMT is given in Table 2.1.

**Table 2.1:** Chemical compositions in typical Montmorillonite [Utracki, 2004]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Composition, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>51.14</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>19.76</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>0.83</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.1</td>
</tr>
<tr>
<td>MgO</td>
<td>3.22</td>
</tr>
<tr>
<td>CaO</td>
<td>1.62</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>0.11</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>0.42</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>22.8</td>
</tr>
</tbody>
</table>

**2.1.2 Nanocomposite preparation method**

There are three types of preparation method of polymer/nanoclay composite according to the starting material and processing technique:
2.1.2.1 Solution method

This method is based on a solvent system in which the polymer or pre-polymer is soluble and the silicate layers are swelable. Initially the silicate layers are swollen in a solvent such as water, chloroform or toluene. When the polymer and layered silicates are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. The intercalated structure is obtained when the solvent is removed from the system.

Solution method of preparing nanocomposites has been widely used with polymers based on poly(vinyl alcohol) [Greenland, 1963; Ogata et al., 1997a], poly(ethylene oxide) [Ruiz-Hitzky et al., 1995], poly(vinylpyrrolidone) [Levy et al., 1975], poly(acrylic acid), poly(ethylene glycol) [Zhao et al., 1989], poly (propylene) [Avella et al., 2005] , poly(ε-caprolactam) [Jimenez et al., 1997] or poly(l-lactide) [Ogata et al., 1997b]. However, this process hinders the industrial application because of usage of large quantities of solvent and poor clay dispersion.

2.1.2.2 In situ polymerization

In this method, the layered silicate is swelled within the liquid monomer or a monomer solution. During polymerization, polymer formation can occur between the silicate layers. Polymerization can be initiated either by heat or radiation. The work initiated by Toyota research group [Usuki et al., 1993] on in-situ polymerization of nylon-6 based nanocomposite initiated the development of polymer layered silicate nanocomposites. They studied the ability of α,ω-amino acids \( +^1\text{H}_3\text{N}-(\text{CH}_2)_{n-1}\text{COOH}, \) with \( n = 2, 3, 4, 5, 6, 8, 11, \)
12, 18) modified Na\(^+\)-MMT to be swollen by the \(\varepsilon\)-caprolactam monomer at 100\(^{\circ}\)C and subsequently initiate its ring opening polymerization to obtain N6/MMT nanocomposites. It results in a significant improvement in thermal and mechanical properties.

The other types of nanocomposites produced by this method are based on poly (\(\varepsilon\)-caprolactone) [Messersmith et al., 1995], poly (styrene) [Akelah et al., 1996], poly (propylene) [Tudor et al., 1996], poly (ethylene) [Alexandra et al., 2002] and polyethylene terephthalate [Ke et al., 1999].

2.1.2.3 Melt blending

Melt blending is believed to be the most convenient preparation process and traditional polymer process equipment can be easily used. Vaia et al [1993] first used the melt blending technique for Polystyrene/nanoclay composite system. This method involves annealing, statically or under shear, a mixture of the polymer and nanoclay above the softening point of the polymer. Melt intercalation method of preparation of nanocomposites has been widely used with polymers based on poly (ethylene oxide) [Vaia et al., 1995], nylon 6 [Liu et al., 1999; Fornes et al., 2001; Hasegawa et al., 2003], polypropylene [Usuki et al., 1997; Kata et al., 1997; Kawasumi et al., 1997; Hasegawa et al., 1998].

The advantage of this method is that it is more flexible and environmentally benign due to the absence of chemical reactions and organic solvents. This method found to have great potential for industrial applications. Apart from this advantage, a few studies show that shear
encountered in polymer melt processing techniques helps in homogenization of the polymer-clay nanocomposite [Vaia et al., 1997; Dennis et al., 2001; Manias et al., 2001]. Due to these factors, melt intercalation method was chosen to prepare the PP/nanoclay composites. The different processing factors which affect the nanocomposite morphology will be discussed later.

2.1.3 Nanoclay/polymer composite morphology

The structure of polymer/nanoclay depends on the nature of the organoclay used and the preparation technique.

2.1.3.1 Phase separated microcomposite:

This structure (Fig. 2.2a) is formed when the polymer chains are unable to intercalate between the silicate sheets. This will result in formation of relatively large aggregate of clays as a separate phase inside the host polymer matrix which forms continuous phase. Improved rigidity can be achieved with this type of composite but there will be reduction in elongation and toughness.

2.1.3.2 Intercalated nanocomposite:

This structure (Fig. 2.2b) is formed when a single or more extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer morphology with alternating polymeric and inorganic layers. The interlayer spacing $d_{001}$ for intercalated structures is $< 8.8\text{nm}$
2.1.3.3 Exfoliated nanocomposite:

This structure (Fig. 2.2c) is formed when the clay particles are completely and uniformly dispersed in a continuous polymer matrix. Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite [Ray et al., 2003]. The interlayer spacing $d_{001}$ for exfoliated structures is $> 8.8$ nm

![Diagram showing classification of nanoclay-polymer composite structures](image)

**Figure 2.2:** Classification of nanoclay-polymer composite structures (Lee and Goettler, 2004; Wool and Sun, 2005)

### 2.2 FACTORS AFFECTING COMPOSITE MORPHOLOGY

#### 2.2.1 The role of host polymer

Formation of nanoclay nanocomposite greatly depends on the host polymer type. As the silicate particles are polar in nature, it has good compatibility with polar polymer like Nylon. Therefore in these cases, even without surface modification and presence of compatibilizer
nanocomposite structures can be obtained. Many studies on Nylon nanocomposites showed greater improvement in the material properties because of its good compatibility with silicate particles [Li et al., 2006; Loo et al., 2004; Fornes et al., 2001; Mehrabzadeh et al., 2002; Zhang et al., 2006]. Silicate particles exhibit incompatibility with non-polar polymers like PP and PE. In these systems, the attraction between the polymer matrix and the silicate layers are very less compared to the attraction forces between the individual silicate layers. Therefore, for these polymer systems silicate particles are organically modified with surfactants and also functionalized polymers are added as compatibilizers to increase the compatibility between silicate particles and polymer. These will be discussed in detail in later parts.

2.2.2 Nanoclay types and structure

MMT in its natural form is hydrophilic in nature and commercial form of MMT is supplied in the form of powder with particle size ranges up to 8µm particle size, each containing around 3000 platelets [Utracki, 2004]. The main challenge is to first disperse the particles into individual platelets and then make a uniform dispersion in the polymer matrix.

The attraction energy of 2 platelets of equal thickness is given by Equation 1.1 [Stokes and Evans, 1997]

\[ U_{attraction} = -\frac{A_{11}}{12\pi} \left[ \frac{1}{h^2} + \frac{1}{(h + 2\delta)^2} - \frac{2}{(h + \delta)^2} \right] \] (1.1)

Where \( A_{11} \) is the Hamaker constant, \( h \) is the separation between platelets, and \( \delta \) is the platelet thickness. From the equation we can note that the attraction between the two platelets is
inversely proportional to the square of the distance between the platelets. Therefore, the main strategy for intercalation or exfoliation is to decrease the attraction between the platelets by increasing the distance between the platelets by inserting larger molecules between them. This can be achieved by chemical modification of nanoclay with suitable surfactants which increases the intergallery distance of the clay platelets.

Clay platelets consist of 3 active sites which are utilized for surface modification and reaction with host polymer matrix:

1. Presence of anionic groups on the surface of clay platelets. They are the primary active sites and utilized for the surface modification of the clay to increase the intergallery distance.

2. Presence of 4 –OH groups per unit cell are responsible for the formation of hydrogen bond and chemical reactions.

3. Positive charges at the edge of the clay platelets can attract the negatively charged ions or molecules. They are less in number and do not contribute to increase in intergallery spacing but they can enhance the clay platelet miscibility with host polymer matrix.

2.2.3 Surface modification of nanoclay

As mentioned before, intergallery spacing has to be increased to achieve intercalated or exfoliated nanocomposite. Depends on the type of method used to produce nanocomposite,
different methods are available to increase the intergallery spacing of platelets before reaction with polymer. General requirement is to have a intergallery spacing of 30-40Å.

1. Use of solvents or low molecular weight solutions such as water, alcohol, glycol or monomer solutions – widely used for solution method

2. Use of organic liquids like monomers, macromers, oligomers, polymers, copolymers and their solutions – widely used in in-situ polymerization method

3. Use of organic cations like ammonium, phosphonium or sulfonium – widely used in melt blending method

4. Use of inorganic compounds

As PP/clay composite is prepared using melt blending method, the focus here will be on intercalation by organic cations.

Treatment of clay particles with organic cations results in both increase in intergallery spacing and formation of organophilic clay. This can be done by exchange of the cations in the interlayer with cationic surfactants like alkylammonium or alkylphosphonium ions. This process lowers the surface energy of the clay and renders the nanoclay organophilic. The surface modified clay is thus called as organoclay and is compatible with organic polymers. Usuki et al [1993] first reported the organically modified clay by replacing the sodium ions present in the interlayer with ammonium cations of ω-amino acids.
The structure of the modified clay is schematically depicted in Figure 2.3.

![Diagram of surface modification of nanoclay](image)

**Figure 2.3:** Schematic of surface modification of nanoclay

In order to achieve good results on intercalation, the surfactant should have good stress transfer between clay and the polymer. The selection of cationic surfactant for a polymer matrix system based on three different aspects

1. Ability to non-ionically interact with the surface of the clay platelet
2. Ability to expand in the intergallery space
3. Miscibility with polymer matrix

Table 2.2 shows the some of the widely used cationic surfactants for clay
**Table 2.2:** Cationic surfactants used as clay intercalants [Utracki, 2004]

<table>
<thead>
<tr>
<th>Cationic surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl dibehenyl ammonium chloride</td>
</tr>
<tr>
<td>Dimethyl dilauryl ammonium or dimethyl didodecyl ammonium chloride</td>
</tr>
<tr>
<td>Dimethyl dehydrogenated tallow ammonium chloride</td>
</tr>
<tr>
<td>N,N-Dimethyl-N, N-dioctadecyl ammonium bromide or chloride</td>
</tr>
<tr>
<td>Dimethyl distearyl ammonium chloride</td>
</tr>
<tr>
<td>Dimethyl benzyl hydrogenated tallow ammonium chloride</td>
</tr>
<tr>
<td>Dimethyl benzyl octadecyl- or dimethyl benzyl stearyl ammonium chloride</td>
</tr>
<tr>
<td>Trimethyl dodecyl amine</td>
</tr>
<tr>
<td>Trimethyl dodecyl ammonium bromide</td>
</tr>
<tr>
<td>Trimethyl stearyl ammonium chloride</td>
</tr>
</tbody>
</table>

Quaternary ammonium salt is the commonly used cationic surfactant because of its good binding strength with clay platelets. The interaction with clay platelets increases with increase in number of substituents in the ammonium cation [Maes et al. 1980].

\[
NH_4^+ < RNH_3^+ < R_2NH_2^+ < R_3NH^+ < R_2N^+\]
The disadvantage of quaternary ammonium ions is that they start to decompose at a processing temperature of 200°C and it results in decrease of the gallery spacing. But it is widely used in industrial scale because of its nature of binding with clay platelets.

Thus surface modification of clay with cationic surfactant results in increase in the intergallery space between the platelets as shown in Figure 2.3. The factors which mainly influence the amount of increase of intergallery spacing during surface modification are Cation Exchange Capacity (CEC) and structure of cationic surfactant.

2.2.3.1 Cation exchange capacity

CEC is the amount of cations in the interlayer of nanoclay structure that can be substituted with other cations. It is expressed in meq/100 g. It was reported that for good intercalation, clay particles should have preferred CEC values between 50 – 200 meq/100g. If CEC is < 50 meq/100g , the ion exchange will be insufficient and if CEC > 200 meq/100g, then the interlayer bonding is too strong for the intercalation to takes place. CEC value for MMT is near to 110 meq/100g. When the amount of cationic surfactant during the ion-exchange reaction is lesser than the CEC value of nanoclay, the process involves just neutralization of the negative charge on the surface of the clay. When the amount of cationic surfactants is greater than the CEC values, then the presence of excess surfactants results in increase in thickness of the gallery spacing.
Natural occurring Na-MMT has an intergallery spacing of 12 Å, commercially available 2 types of organo clay which is modified with 2 different organic modifier concentrations of 125 meq/100gram and 95 meq/100gram has a gallery spacing of 31.5 Å and 28 Å respectively. Thus presence of higher modifier concentration results in higher gallery spacing in the former case. Study on surfactant shows that PP/nanoclay composite with higher organic modifier concentration results in exfoliated composite structure because of the higher gallery spacing obtained, which facilitates the exfoliation of the polypropylene chains between the clay layers.

2.2.3.2 Structure of cationic surfactant

The structure of cationic surfactant plays an important role in the organoclay properties and thus affects the nature of composite. Typical structure of alkylammonium cations are of the form \([(CH_3)_3NR]^+\). Fornes et al. [2002] studied the effect of number of alkyl tail on the Nylon/nanoclay nanocomposite structure. They found that exfoliation of nanoclay particles is better when alkylammonium cations with one alkyl tail is used that that of two alkyl tail. As nylon itself has some attraction to the pristine clay particles because of its polar nature, presence of two polar ends in the surfactants hinders the interaction between nanoclay and nylon. But for non-polar polymers like PP and PE, which does not have any interaction with nanoclay, use of two alkyl chains found to have better exfoliation compared to one alkyl tail. Another study by Fornes et al. [2003] explains about the effect of functional group attached to the amine. They found that clay exfoliation is better for surfactants which consist of methyl groups on the amine rather than presence of hydroxyl-ethyl groups.
Study by Osman et al. [2004] and Reichert et al. [2000] suggests that when the alkyl chain length is greater than 8 carbon atoms, there is greater increase in the thickness of the gallery spacing, which is a favorable condition for the polymer chains to intercalate between the clay layers. Study by Usuki et al. [1997] shows that when the carbon number is increased from 2 to 18, the gallery spacing is increased from 1.27 nm to 2.82 nm and facilitates the intercalation or exfoliation of the clay particles.

2.2.4 Presence of compatibilizer

As mentioned before, achieving intercalation or exfoliation is the main challenge in polypropylene clay composite. First clay particles are to be intercalated in the polypropylene matrix to achieve exfoliated structure. For intercalation to take place, following three steps are important to achieve:

1. Increase in interlayer spacing
2. Reduction of solid-solid interaction between the platelets
3. Improve interactions between clay and matrix

Increase in interlayer spacing is achieved by cationic exchange reaction with organic modifier which results in increase in the interlayer spacing between the two clay platelets. As mentioned in the above equation (1), increase in interlayer spacing results in decrease of the van der Waals interaction between the two platelets. To improve the interaction between clay and matrix, suitable compatibilizers are used to improve the interaction with host polymer matrix.
For Polypropylene based clay composites, organo-clay still could not provide enough nanoclay-polymer interaction to produce high degree of dispersion. Kawasaki et al. [1997] first used maleic anhydride grafted PP as a compatibilizer for PP/nanoclay composites. In this they found that presence of compatibilizer improves the interaction between polypropylene and organically modified clay with stearyl ammonium. Intercalation arises because of the formation of hydrogen bond between maleic anhydride group and the oxygen groups of the silicate. Many studies were carried out later [Chen et al., 2003; Lertwimolnum et al., 2005; Wenyi et al., 2006] based on maleic anhydride-modified PP and found improvement in clay dispersion and mechanical properties. However, addition of low molecular weight PP-g-MA can result in lower mechanical properties of the final composite. Therefore concentration of PP-g-MA should be optimized. Few studies show that to obtain intercalated or exfoliated composite optimal clay to compatibilizer should be 1 (clay): 2-3 (compatibilizer) [Pascual et al., 2009].

Figure 2.4: Schematic of reaction of nanoclay with compatibilizer
Ton-That et al. [2004] studied the effect of molecular weight of compatibilizer on clay exfoliation and mechanical properties. They found that compatibilizer based on higher molecular weight facilitates clay exfoliation and improved strength. Although polymer chain mobility is high for low molecular weight compatibilizer and it easily intercalates into the clay layers because of smaller chain length, co-crystallization with PP matrix is low and hence its compatibility is low. Compatibilizer based on higher molecular weight has good interaction with PP because of its longer chain length. Similar result was obtained by Svoboda et al [2002] on PP/nanoclay composites in presence of three different types of compatibilizers.

There are few studies [Ristolainen et al., 2005] which are based on hydroxyl-functional PP were carried out and found to be effective compatibilizer for PP.

### 2.2.5 Processing conditions

Processing conditions employed in the melt intercalation technique has a significant effect on the composite morphology. The main factors which affect the interaction between polymer and clay particles are temperature, stress, screw type, number of steps.

A Study by Modesti et al. [2005] shows that PP/nanoclay composite produced at higher stress (high screw speed) results in intercalated and exfoliated composite with better property improvement than the composite produced at lower stress. Also combination of higher shear...
rate and lower temperature is optimal to get better interaction between clay and polymer, as higher temperature results in degradation of the material.

Effect of shear on composite structure was studied by Ko et al. [2002] and Kim et al [2002]. They found that primary factor which affects the clay exfoliation is shear stress although diffusion of polymer chains also affects the exfoliation.

Zhu et al. [2004] studied the effect of the composite morphology and its properties based on the number of steps involved in the preparation of the composite. The results show that 2-step processes results in intercalated or exfoliated composites compared to 2-step process as the amount of stress involved in 2-step process is higher and it helps in better dispersion of the clay particles in the polymer matrix. Similar result was obtained by Cho et al. [2001] on Nylon composites.

Dennis et al. [2001] demonstrated that both shear intensity and residence time are important factors in improving the clay dispersion and hence exfoliation. But excessive shear intensity results in degradation of the samples.

Based on the study of processing conditions on polymer/nanoclay morphology, Dennis et al., [2001] and Fornes et al., [2001] proposed 2 steps on the nature of intercalation and dispersion of nanoclay in polymer matrix:
1. Formation of smaller tactoids by breakdown of clay agglomerates due to processing stresses.

2. Penetration of polymer chains between the gallery layers by a combined diffusion and shear controlled processes.

### 2.3 EFFECT OF NANOCLAY ADDITION ON COMPOSITE FINE STRUCTURE

As PP is semicrystalline in nature, changes in the crystallization behavior because of the presence of clay particles will greatly affect its mechanical properties [Yu et al., 2000]. Presence of nanoclay plays two roles in the crystallization process [Svoboda et al., 2002; Xu et al., 2001].

1. Nanoclays act as a nucleating agent and facilitates the crystallization

2. Nanoclays act as a physical hindrance to the polymer chains and retard the crystallization

Many studies [Hambir et al., 2002; Varga et al., 1999] were carried out to study the effect of nanoclay on overall crystallinity, crystallization rate and size of spherulites.

Ma et al. [2002] first studied the crystallization behavior of PP-nanoclay composites produced using in-situ polymerization method. They found that presence of nanoclay results in significant increase in the crystallization rate of PP chains. The increase in crystallization rate is attributed to the exfoliation of the clay particles. Clay exfoliation causes increase in the number of heterogeneous nuclei in the composite and hence crystallization of
PP/nanoclay composite systems follow heterogeneous nucleation. It was well established that heterogeneous nucleation starts simultaneously as soon as the sample reaches crystallization temperature whereas homogeneous starts spontaneously by chain aggregation below the melting temperature. Thus heterogeneous nucleation process takes less time for crystallization and time taken to reach maximum degree of crystalline order is less in heterogeneous nucleation process.

The size of spherulites also significantly affected by the presence of nanoclay. Ma et al. [2002] shows that there is decrease in spherulite size from 200µm to 60µm or less after the addition of nanoclay at a clay loading of 4.6 wt%. Optical microscopy images of their study are shown in Figure 2.5. The decrease in spherulites size is because of the exfoliation of the clay layers in the PP matrix. The growth of the spherulites is limited by the presence of nanoclay and decreases its size. Thus presence of nanoclay results in increase in number of nuclei but at the same time size of the spherulite is decreased. Overall, this result in reduction in crystallinity of the nanoclay based composites.
Figure 2.5: Effect of change in spherulite size after nanoclay addition [Ma et al., 2002]

Similar results of decrease in spherulites size was obtained by Seo et al. [2000] on PP/nanoclay composites in presence of PP-g-MA as a compatibilizer. They also analyzed the effect of presence of PP-g-MA on crystallization rate and spherulites size. They found that presence of PP-g-MA also results in increased crystallization rate and decrease in size of the spherulites. This suggests that PP-g-MA itself acts as a nucleating agent for PP. But presence of nanoclay has greater influence on both crystallization rate and spherulites size compared to compatibilizer.

Study by Joshi et al [2004] on PP/nanoclay filaments in presence of compatibilizer obtained increase in crystallinity at lower clay loading but decrease in crystallinity was obtained at
higher clay loading. This is attributed to the better dispersion of the clay particles in the polymer matrix and not interfering with the crystallization process.

2.4 EFFECT OF NANOCLAY ADDITION ON COMPOSITE PROPERTIES

2.4.1 Mechanical properties

Polymer layered silicate nanocomposites has found to improve many properties of the host polymer. One of the main properties under study by most of the researchers is mechanical property. Mechanical property of the nanocomposite is directly related to the amount of intercalation or exfoliation of the nanoclay particles. When the nanoclay particles are well dispersed and exfoliated in the polymer matrix, the load bearing capacity will increase and it results in good improvement in mechanical properties. Tsagaropoulos et al. [1995] state that stiffness of the silicate layers creates immobilized or partially immobilized polymer phases at the interphase regions is the one of the main factor for the improved mechanical property. Specific surface area of the clay particles is another reason for the improved mechanical properties. Specific surface area of the clay particles increases with decrease in particle size. Decrease in particle size contributes to increase in volume of the interfacial regions and it contributes to better stress transfer. In the conventional microcomposites, the particles are in micrometer range and hence the thickness of the interfacial regions can be neglected as they are in nanometer range. But in nanocomposite, the effect of interfacial region is also significant as the particles are in nanoscale range. Ji et al. [2002] developed a model to predict the tensile modulus of the nanocomposites by taking into account of interfacial
region. The study shows that increase in interfacial region contributes to increase in tensile strength.

Study by Hasegawa et al. [2000] shows increase in Young’s modulus up to 30% for PP based nanocomposites in presence of PP-g-MA as compatibilizer. Although there is greater increase in young’s modulus, there is no improvement in maximum tensile stress at break. This is due to the lack of interfacial adhesion between PP and nanoclay, presence of PP-g-MA helps in compensating the interfacial adhesion and maintains the maximum stress at break comparable to that of PP.

Most of the studies on nanoclay based PP composite were done on polymer films, Joshi et al. [2006] studied the PP/nanoclay composite based on monofilament samples in presence of PP-g-MA as a compatibilizer. Improved tensile and modulus was obtained for filaments even at a clay loading at 0.25 to 0.5 wt%. The greater increase in strength is attributed to the improvement orientation of the molecular chains obtained during drawing.

2.4.2 Thermal stability

Many studies on Nanoclay composites show significant improvement of thermal stability [Hambit et al., 2002, Qin et al., 2005; Nejad et al., 2007; Ma et al., 2001]. Nanoclay acts as a superior insulator and mass transport barrier to the volatile products generated during the decomposition process and improves the thermal stability. Improved thermal stability based on nanoclay composite was first reported by Blumstein [1965] on intercalated PMMA/clay
composites. PMMA/clay composites found to have 40-50°C higher decomposition temperature. Improved thermal stability is attributed to the intercalation or exfoliation of the clay particles. Due to intercalation, the polymer chains between the clay layers have restricted thermal motion and thus there is improved thermal stability. Study by Giannelis and Burnside [1995] on cross-linked poly (dimethylsiloxane) nanocomposite system shows up to 150°C increase in decomposition temperature at 50% degradation. The improvement in thermal stability is attributed to the restriction of the diffusion of the volatile decomposition products formed during degradation, as presence of nanoclay particles decreases the permeability.

The mechanism of improved thermal stability based on nanoclay composites is due to the following factors:

1. As the clay particles are inorganic in nature, they act as a heat barrier and enhance the thermal stability of the nanoclay composite system.

2. In the initial stage, silicate layers absorbs the heat supplied and in the later stage this accumulated heat along with supplied heat is used to degrade the sample. Therefore there is a rapid degradation of the nanoclay composite obtained at the later stage.

2.4.3 Dyeability

Polypropylene fibers are difficult to dye because of its nonpolar nature. PP can be chemically modified by graft copolymerization of fibers with monomers such as acrylic acid, vinylpyridine, acrylonitrile, styrene and vinyl acetate and dyeing can be achieved. These
methods are commonly used in pilot production. For industrial applications, PP is physically modified by the addition of low-molecular and polymer compounds containing functional groups which are able to bind the dyes. Commonly used techniques are as follow [Marcincin, 1999]:

i. Addition of organometallic compounds such as Al, Cu, Zn, Ni in the form of salts of organic acids, alcoholates, phenolates, amines, triazols etc.

ii. Oligomer and polymer additives with primary, secondary amino groups or with tertiary nitrogen able which are able to bind water-soluble dyes containing acid groups.

iii. Addition of oligomers such as ethylene and vinyl acetate copolymers, polyethylene terephthalate and its copolymers, polyamides etc.

iv. Mass coloration by the pigmentation process. Widely used pigments for PP is carbon black and TiO$_2$.

Recent studies by Fan et al. [2003], Mani et al. [2003] and Razafimahefa et al. [2008] shows that PP can be dyed by using nanoclay additives. It was reported that presence of nanoclay in the PP matrix creates a polar group and hence PP can be dyed with the use of suitable dyes like disperse acids or acid dyes. The main factors which decide the dyeing of PP are van der Waals forces and ionic interaction between nanoclay and dyes [Yang et al., 2005].

Based on the dyeing study on PP modified nanoclay Fan et al. [2003] developed a model which states that exfoliation of the clay particles greatly influences the dyeing behavior of
PP. The disperse dyes penetrate into the clay layers and remain in the intergallery spacing of the clay. Therefore exfoliation results in high surface area and hence number of active spots for dye increases and hence dye absorption.

Mani et al., [2003] used disperse and acid dyes to dye the nanoclay modified PP film produced by solution method. They obtained uneven dyeing on the polypropylene film which is due to the improper dispersion of nanoclay particles in the PP matrix. The intensity of dyeing increases with nanoclay loading as the number of active sites increases with increase in nanoclay particles.

Razafimahefa et al., [2008] carried out dyeing of PP/nanoclay produced using melt intercalation method in presence of PP-g-MA as compatibilizer. They found that compared to acid dyes disperse dyes was effective in dyeing PP fibers modified with nanoclay. They also found that type of cationic surfactant used to modify the nanoclay has a great influence on the nature of dyeing. Cationic surfactant with alkyl groups found out to have good interaction with disperse dyes than cationic surfactants with hydroxyl groups.

2.4.4 Reinforcement effect of nanoclay

Solid-state mechanical properties of the composites such as modulus are one of indirect measure of the extent of dispersion of clay particles in the polymer matrix. Also, this study of visco-elastic properties of polymer nanocomposites is mainly important for load bearing applications where the stress is applied for longer period of time.
Dynamic mechanical analysis (DMA) measures the response of the material to a cyclic deformation as a function of the temperature. Three main parameters are obtained from DMA:

a. The storage modulus ($E'$) - represents the elastic response to deformation
b. The loss modulus ($E''$) – represents the plastic response to deformation
c. $\tan \delta = \frac{E'}{E''}$, for determining the occurrence of molecular mobility transitions such as the glass transition temperature

All 3 parameters are useful to analyze the nature of interaction between the polymer matrix and the clay particles.

For polymer/nanoclay systems, a marked improvement in storage modulus represents good interaction between polymer chains and the nanoclay particles. When the clay particle intercalates or exfoliates in the polymer matrix, the polymer chains between the clay platelets will have restricted chain mobility and hence there will be increase in storage modulus. Kawasumi et al., [1997] first studied the reinforcement effect of the nanoclay particles on PP matrix. PP nanoclay composites were prepared based on 2 different compatibilizers. Relative storage moduli was found to be 1.3 to 1.4 times that of PP below Tg and it increases up to 1.7 to 2.0 above Tg at a temperature range of 50-80°C. The increase in storage moduli is due to the good dispersion of the nanoclay particles on the polymer matrix. PP nanoclay composites based on higher molecular weight compatibilizer found to have higher storage moduli compared to compatibilizer based on lower molecular weight. This is because of the good
miscibility obtained with the presence of higher molecular weight compatibilizer. The results were supported by XRD and TEM results where shift in the basal spacing to higher intergallery distance and proper dispersion of clay particles were noticed. Similar trend of increase in storage modulus below Tg and greater increase in storage modulus above Tg were observed for composite samples based on PLA, Nylon.

Study by Joshi et al., [2001] showed up to 2-order increase in storage modulus for PP based nanoclay added samples even for a lower clay loading of 0.5%. PP-g-MA was used as compatibilizer for the system with clay to compatibilizer ratio as 1:2. The increase in storage modulus denotes increase in the elastic component of the nanocomposite filaments.

In general, both loss modulus and tan delta increases with decrease in storage modulus with increase in temperature till glass transition temperature. The rise in loss modulus is due to the increase in the structure mobility of the polymer, a relaxation process that permits motion along larger portions of the individual polymer chains than would be possible below the transition temperature. As the material becomes soften above Tg, the reinforcement effect by the silicate layers is prominent due to the restricted movement of polymer chains.

2.5 REFERENCES


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Structure and Tensile properties of Nanoclay-PP fibers produced by Melt Spinning

ABSTRACT
Nanocomposite fibers of polypropylene and montmorillonite-based organoclay were produced by a melt-spinning process, and their structures and mechanical properties were studied. The addition of nanoclay in polypropylene increased the rate of crystallization and altered the microstructures of the fibers. Increases in the crystal size and a reduction in the molecular orientation were observed in the nanoclay–polypropylene composite fibers. The tensile properties of nanoclay composite fibers were also studied, and decreases in the fiber modulus and tenacity and increases in the strain at break were observed.

3.1 INTRODUCTION
One of the interesting developments of nanomaterials in polymer engineering is that of nanoclay particulate additives. Nanoclay-based additives have shown great potential in polymer and plastic applications because they overcome many limitations of traditional microcomposites. Many previous studies have demonstrated their excellent properties, including superior balance of modulus, impact strength, improved thermomechanical performance, fire resistance, and enhanced barrier properties. (Chen et al. 2003, Brule and Flat, 2006, Dasari, et. al., 2005; Drodoz and Christiansen, 2007; Valera-Zaragoza, et al., 2006). The reason behind these unique behaviors is the nanostructures created by the nanoclay layer/polymer molecular chain.
The structures of nanoclay-polymer composite can be classified by the degree of dispersion (Lee and Goettler, 2004; Wool and Sun, 2005). Traditional microcomposites [Figure. 3.1(a)] are formed when the polymer chain is unable to penetrate between the silicate layers. As the results, the clays forms relatively large aggregates as a separate phase inside the host polymer matrix, which forms continuous phase. Improved rigidity can be achieved with this type of composite, but there are reductions in the elongation and toughness. An intercalated structure is formed when a single or more extended chain is intercalated between the nanoclay silicate layers; this results in a well-ordered multilayer with alternating polymeric and inorganic clay layers [Figure. 3.1(b)]. The structure with the highest degree of dispersion is called an exfoliated or delaminated structure, where the silicate layers are completely opened up and dispersed in a disorderly and uniform manner in a continuous polymer matrix [Figure 3.1(c)]. Both intercalated and exfoliated structures are considered nanocomposites, which can provide significant performance enhancements. (Wool and Sun, 2005).

Nanoclay particles have high surface-area-to-volume ratios and their sizes are similar to the segment of the surrounding polymer chains in nanocomposites; this makes it possible for the nanoclay particles to form significant bonding with the polymer matrix (Dasari, et. al., 2005). This may lead to improvements in many of the polymer properties, and nanoclays have been reported to be excellent reinforcement additives. Increases in the tensile strength, modulus, and crack resistance have been achieved, even at low concentrations (Chen et al. 2003). A reduction in the creep behavior has also been found in some nanoclay–polymer composites (Drodoz and Christiansen, 2007). A higher nanoclay loading does not always improve the
mechanical properties, but property degradation due to the coagulation of nanoclays has been observed (Chen et al. 2003). The ability to achieve good performance at low inorganic loading can provide an added advantage: a lighter reinforced composite. Nanoclays also impart outstanding diffusional barrier properties, enhanced chemical resistance, and flame retardancy (Brule and Flat, 2006; Valera-Zaragoza, et al., 2006).

Figure 3.1: Classification of the nanoclay-polymer composite structures (Lee and Goettler, 2004; Wool and Sun, 2005)

Nanoclay–polymer composite structures are highly dependent on the preparation process and conditions, polymer–nanoclay interaction, and the presence of other chemicals, such as compatibilizers (Frounchi, et. al. 2006; Lei, et. al. 2006). The achievement of proper
polymer–nanoclay interactions has been an important issue in nanocomposite development. The silicate surface of the nanoclay is hydrophilic in nature, and it hinders homogeneous dispersion in organic polymer matrixes. To achieve the required properties, a good dispersion of nanoclay in the polymer matrix and a good interface between the two phases are essential (Ton-That et al. 2004). One way to improve the compatibility between the hydrophilic inorganic clay and the oleophilic organic polymer is to modify the surface of the clay through an ion-exchange reaction. This involves the exchange of hydrophilic cations on the clay surface with short-chain organic cations, such as alkyl ammonium ions (Ding et al. 2005; Marchant and Jayaraman, 2002). The surface modification of clay, often referred as organoclay, has shown improved compatibility with the polymeric matrix (Frounchi et al. 2006; Ding et al., 2005).

In some polymer matrices, especially highly hydrophobic polyolefin polymers, organoclay could still not provide enough nanoclay–polymer interactions to produce a high degree of clay dispersion. The use of compatibilizers, such as maleic anhydride modified polypropylene (PP), has been reported, and the use of this method has caused improvements in the clay dispersion and the mechanical properties (Chen et al., 2003; Kato et al. 1997; Kawasumi et al. 1997; Lertwimolnun and Vergnes, 2005; Wenyi et al., 2006).

There are three types of preparation methods for polymer/nanoclay composites: \textit{in situ} polymerization, the solution method, and melt blending. One of the earliest methods used in the Toyota laboratory was \textit{in situ} polymerization, where the polymerization reaction of a
monomer occurred in the presence of nanoclay. The solution process may provide a better and more stable dispersion of nanoclay in host–polymer matrix, but more complex process steps are involved, and it also considered environmentally unfriendly. (Avella et. al., 2005). Melt blending is believed to be most convenient preparation process, and traditional polymer process equipment can easily be used. However, some researchers have reported that nanoclays prepared with melt blending can be unstable for reprocessing and high processing temperatures may transform the nanocomposite into microcomposites (Avella et. al., 2005).

Despite recent increasing interest in nanoclay, most studies have concentrated on films and plastic molds and we found only a few studies on nanoclay-modified fibers (Joshi et. al., 2006). Compared to films, fiberbased systems are known to provide many beneficial characteristics because of their high surface areas, so a combination of nanocomposite technology and fiber formation is highly sought after. However, melt spinning is a more complex process, where fiber fine structure development is determined by polymer-chain responses to tension, temperature, and shear deformation in the spin line. It has been reported that nanoclay incorporation alters the polymer melt rheology and crystallization kinetics (Ma et. al. 2002; Zhang et. al., 2004; Seo at. al, 2000; Varga and Karger-Kocsis 1995), which are the key factors affecting microstructure formation during the fiber melt spinning. Several authors have reported nanoclay–polymer composite fiber properties, but their findings have been contradictory and fragmented at best (Wenyi et. al. 2006; Joshi et. al. 2006; Svoboda et. al., 2002). Because the properties of polymeric fibers are highly influenced by the microstructures of how the polymer chains are aligned, to further determine the effect of
nanoclay addition on melt-spun systems, one should look not only at the dispersion of nanoclay layers in polymeric materials but also at their impact on the fiberforming mechanism and the crystalline structures of fibers related to their properties.

In this study, nanocomposite fibers of PP and montmorillonite-based organoclay were produced by a melt-spinning process, and their structures and mechanical properties were investigated.

3.2 EXPERIMENTAL

3.2.1 Materials

Spunbond-grade PP (PP CP360H), with an average melt flow rate of 35 g/10 min, was supplied by Sunoco Chemicals (Philadelphia, PA). A commercially available, precompounded, montmorillonite-based organoclay–PP (Nanomax PP) was purchased from Nanocor (Arlington Heights, IL).

Nanomax PP contained about 50% Nanomer nanoclay (i.e., surface-modified montmorillonite clays), PP, and a maleic anhydride modified polyolefin compatibilizer and was prepared by melt compounding, on the basis of patented technology (Qian et al. 2002, Qian et. al., 2003), to produce intercalated structures.
3.2.2 Melting spinning of Nanoclay/PP composite fibers

Even Nanomax PP precompounded Masterbatch pellets containing PP, nanoclay, and compatibilizer and good processability were reported in various plastic processing equipment, our initial attempt to spin the composite fibers by the direct mixing of Nanomax PP and PP and extrusion in fiber-spinning equipment caused a series of spinning problems, including melt fractures, filter blockages, spin-line breakages, and large agglomeration of the clay particles. Therefore, Nanomax PP and PP were meltcompounded further to reduce the clay loading. Nanoclay–PP composite pellets with nanoclay loadings of 5 wt % were prepared by melt compounding at 205°C in a TechmerPM (Clinton, TN). Then, nanoclay–PP composite pellets were again mixed and extruded with PP to produce nanoclay–PP composite fibers with the Hills Homofilament Research line in the Nonwovens Institute, North Carolina State University (Raleigh, NC). The spinning speed was 2000 m/m, and the spin-head temperature was 265°C. A melt throughput was maintained at 1 g hole⁻¹ minute⁻¹. Nanoclay–PP fibers with a clay load of 0.5–3% were produced. As a control, PP without nanoclay was melt-extruded under the same conditions. The fiber sizes of all of the samples were about 5 denier.

3.2.3 Transmission Electron Microscope

Cross sections of the nanoclay–PP composite fibers were investigated under a Hitachi HF 2000 transmission electron microscope to study the nanoclay dispersion in PP. We prepared the samples by embedding the fiber samples in Spurr’s epoxy and microtoming them to 70 nm thick.
3.2.4 Differential Scanning Calorimeter (DSC)

The melting and crystallization behaviors of the composite were analyzed with a PerkinElmer differential scanning calorimeter (Perkin Elmer, Norwalk, CT). Nanoclay–PP composite fibers (4.5 ± 0.5mg) were heated in a nitrogen atmosphere from 25 to 190 °C and allowed to stand for 10 min at 190 °C and then cooled from 190 to 25 °C. In all cases, the heating/cooling rate was maintained at 5 °C /min.

The crystallinity of the samples was calculated using the following formula:

\[
%\text{Crystallinity} = \frac{\Delta H}{\Delta H_{pp}^0} \times 100
\]

(3.1)

where, \( \Delta H \) is the enthalpy of fusion of the sample (J/g) and \( \Delta H_{pp}^0 \) is the enthalpy of fusion of completely crystalline PP (~ 207 J/g) (Karger-Kocsis, 1995).

3.2.5 Isothermal Crystallization

The isothermal crystallization of the nanoclay–PP composites were also investigated with the Perkin-Elmer differential scanning calorimeter. The samples were heated at a rate of 20 °C /min to 190 °C and kept at 190 °C for 10 min; then, they were cooled down at a rate of 50 °C /min to crystallization temperatures ranging from 124 to 128 °C and allowed to crystallize there for 10 min.
3.2.6 Birefringence

The birefringence of the fibers was measured with an Aus Jena Interference microscope. The wavelength of the polarized light used was 546 nm. The fibers were immersed in oil with a matching refractive index (Cargill), and the refractive indexes parallel and perpendicular to the fiber axis were measured from the interference fringe shifts.

Then, the birefringence of the samples was calculated with the following formula:

\[ \Delta n = \left| n_\parallel - n_\perp \right| \]  

(3.2)

\( n_\parallel \) - refractive index of the samples parallel to the direction of orientation

\( n_\perp \) - refractive index of the samples perpendicular to the direction of orientation.

3.2.7 Wide angle X-ray Diffraction (WAXD)

The crystallinity and crystal size of the samples was calculated with an Omni Instrumental X-ray diffractometer (Biloxi, MS). 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 onto the sample holder and placed in the sample holder. The samples were scanned in the 2\( \Theta \) range 3° to 30° with an increment of 0.05°. From the scattering pattern, the crystal sizes of the samples were calculated with Scherer’s equation (Cullity et al., 2001):

\[ t = \frac{0.9 \times \lambda}{B \times \cos \theta_B} \]  

(3.3)

where, \( t \) is Crystal size (Å), \( \lambda \) is Wavelength of X-ray (1.54 Å), \( B \) is Full Width at Half Maximum (radian) and \( \theta_B \) is Bragg angle (degree).
3.2.8 Single Fiber Tensile Properties

The single-fiber tensile properties of the nanoclay–PP composite fibers were evaluated according to ASTM D 3822-07 in an Instron MTS instrument with a 50-g load cell (Canton, MA). The gauge length was 2.54 cm, and the rate of extension was 15 mm/min. The tenacity, secant modulus at 5% strain, toughness, and strain at break were calculated from the tensile stress–strain curve, and the average of 10 samples are reported.

3.3 RESULTS AND DISCUSSION

3.3.1 Nanoclay dispersion in PP fibers

TEM images of the nanoclay–PP fiber cross sections showed that the nanoclay layers were uniformly distributed at both 1 and 3% clay loadings [Figure. 3.2(a,c)]. It was apparent that the nanoclay platelets were stacked to thickness ranges of 10–100 nm, and the thickness of the platelet stacks was not affected by the nanoclay loading. Observations at higher magnifications revealed more details of the nanoclay platelet arrangements in the polymer matrix. It was very apparent that dark clay platelets and thin polymer layers were alternating, and this confirmed that the nanoclay platelets and host polymers were well intercalated. However, there were dark areas where clay layers were aggregated without polymer chain penetrating between the layers. In addition, areas where platelets were arranged in a less ordered manner were also observed; this suggested the possible presence of exfoliated structures in the fibers. No significant effect of clay loading on the clay platelet distribution was observed (Frounchi and Dourbash, 2009).
Figure 3.2: TEM images of cross sections of nanoclay–PP composites fibers with nanoclay concentrations of (a) 1% (8000x magnification), (b) 1% (60,000x magnification), (c) 3% (8000x magnification), and (d) 3% (60,000x magnification).
3.3.2 DSC Analysis

As illustrated in Figure 3.3, nanoclay addition affected the thermal transition temperature, both in the heating and cooling processes. The melting endotherm, shown in Figure 3.3(a), indicated a slight increase in the melting temperature. It was even more interesting that changes in the shape of the melting endotherm implicated a possible alteration of the fiber microstructure as the result of nanoclay addition, although there were few changes in the overall crystallinity. The melting endotherm of the PP control fibers were broad and consisted of two distinct melting peaks. The first peak, at a low melting point, indicated the presence of small and imperfect crystallites. When nanoclay particles were present, the melting peaks became narrower, and the two peaks became less distinct. This indicated that they had narrower ranges of crystal sizes. A slight increase in the melting temperature with increasing clay loading suggested that the crystallites became larger and more perfect (Table 3.1). However, there were few changes in the overall crystallinity measured from the total area of the melting endotherm (Table 3.1).

This may have been due to an alteration in the crystallization behavior, as observed in Figure 3.3(b). The onset crystallization temperatures detected in the DSC cooling curve increased slightly in the Nanomax PP samples. The area of the crystallization peak in the cooling curve further converted to relative crystallinity, and the results are shown in Figure 3.4. It was very clear that the addition of nanoclay increased the crystallization rate. To gain more understanding of the effect of the nanoclay in the crystallization kinetics, the isothermal
crystallization of the nanoclay–PP composite fibers was studied, and the results are reported in the next section.

Table 3.1: Melting and crystallization temperature and % crystallinity of nanoclay-PP fiber samples

<table>
<thead>
<tr>
<th>Nanoclay loading</th>
<th>On-set Crystallization Temp (°C)</th>
<th>Peak Crystallization Temp (°C)</th>
<th>On-set Melting Temp (°C)</th>
<th>1st Peak, Melting temperature Tm, (°C)</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>123.8</td>
<td>120.2</td>
<td>158.4</td>
<td>161.0</td>
<td>50</td>
</tr>
<tr>
<td>0.5%</td>
<td>124.7</td>
<td>121.5</td>
<td>159.3</td>
<td>163.1</td>
<td>49</td>
</tr>
<tr>
<td>1.0%</td>
<td>124.8</td>
<td>121.6</td>
<td>159.4</td>
<td>163.9</td>
<td>49</td>
</tr>
<tr>
<td>1.5%</td>
<td>125.3</td>
<td>121.8</td>
<td>160.3</td>
<td>163.8</td>
<td>47</td>
</tr>
<tr>
<td>2.0%</td>
<td>126.5</td>
<td>123.5</td>
<td>160.3</td>
<td>164.2</td>
<td>49</td>
</tr>
<tr>
<td>2.5%</td>
<td>126.7</td>
<td>123.2</td>
<td>160.3</td>
<td>164.4</td>
<td>47</td>
</tr>
<tr>
<td>3.0%</td>
<td>126.8</td>
<td>123.3</td>
<td>160.2</td>
<td>164.3</td>
<td>47</td>
</tr>
</tbody>
</table>

Figure 3.3: DSC thermograms of nanoclay–PP composite fibers: (a) heating thermogram of the melting endotherm and (b) cooling thermogram of the crystallization exotherm.
3.3.3 Isothermal Crystallization

The isothermal crystallization kinetics of nanoclay–PP composite fibers at different crystallization temperature were analyzed according to the Avrami equation (Avrami, 1939; Avrami 1940).

\[ 1 - X_t = \exp(-kt^n) \quad \text{or} \]
\[ \ln(-\ln(1 - X_t)) = n \ln t + \ln k \]  

Figure 3.4: Nonisothermal crystallization of nanoclay–PP at a cooling rate of 5°C.
Where, $X_t$ is the relative crystallinity at different crystallization time $t$, $k$ is the crystallization rate constant, and $n$ is the Avrami exponent constant.

Avrami plots of $\ln(-\ln(1-X_t))$ versus $\ln t$ of 1% nanoclay–PP fibers and the PP control fibers are shown in Figure 3.5. From these Avrami plots, $n$ and $k$ values were obtained from the slope and intercept of the linear line fitting, and the results are given in Table 3.2. In the entire crystallization temperature range studied, 1% nanoclay addition led to an increase in $k$ and reductions in the crystallization half-time. This indicated faster crystallization in the samples with added nanoclay. This result agreed well with those of other studies (Ma et. al. 2002; Zhang et. al., 2004; Seo et. al, 2000; Varga and Karger-Kocsis 1995). Ma et. al. (2002) and Zhang et. al.(2004) concluded that the exfoliation of silicate layers results in an increase in the number of heterogeneous nuclei and, thus, increases the crystallization rate. Therefore, the presence of clay particles acted as a heterogeneous nucleating agent and led to a higher crystallization rate, and the crystallization of the PP–clay-added composite fiber samples followed the heterogeneous nucleation mechanism. This was further supported by $n$, also given in Table 3.2. The $n$ value is an indicator of the crystal growth mechanism. In the PP polymer, $n$ was around 3.5–3.6; this value represented spherulite crystalline growth and some nucleating. With a 1% addition of nanoclay, the $n$ values increased to 3.6–3.9 with increasing heterogeneous nuclei formation. Therefore, the nanoclay particles acted as a heterogeneous nucleating agent in the polymer matrix and increased the crystallization rate of the host polymer.
Fiber formation during melt spinning is the process of phase transition from an entangled polymer melt to ordered semicrystalline materials with complex microstructures. Because the crystallization behavior of materials greatly affects the fiber fine structures developed during melt spinning, changes in the crystallization kinetics with the addition of nanoclay can lead to significant changes in the microstructure of fibers.

**Figure 3.5:** Avrami plots of $\ln(-\ln(1-X_t))$ versus $\ln t$ for (a) PP (b) 1% Nanoclay/PP
Table 3.2: Kinetic parameters of the isothermal crystallization of nanoclay–PP composite fibers with a 1% nanoclay concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameter</th>
<th>Crystallization temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>124</td>
</tr>
<tr>
<td>PP</td>
<td>Half-time (min)</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>3.56</td>
</tr>
<tr>
<td></td>
<td>k</td>
<td>0.0381</td>
</tr>
<tr>
<td>1% nanoclay</td>
<td>Half-time (min)</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>3.89</td>
</tr>
<tr>
<td></td>
<td>k</td>
<td>0.0944</td>
</tr>
</tbody>
</table>

3.3.4 Crystalline Structures: Wide Angle X-ray Diffraction

Nanoclay particles added in the melt-spinning process affects the fiber-formation process and the fiber fine structures. Changes in the crystalline morphology were observed with WAXD. The X-ray diffractogram of pure PP showed a broad crystalline peak at a 2θ value of 15.1; this corresponded to the mesomorphic form of isotactic PP (Figure. 3.6). The crystalline peaks were not well defined, so this indicated imperfect and not well-defined crystalline structures of the PP fibers. When nanoclay was added to the fibers, the crystalline peaks were sharper and more distinct. In the case of the addition of 1% nanoclay–PP fibers, distinct crystalline peaks occurred at 2θ values of 15.0, 17.8, 19.5, 22.1, and 26.4; this corresponded to the α-crystalline form of isotactic PP. As the percentage of clay loading increased, the positions of the crystalline peaks did not changes, but the peaks became shaper. This may have been caused by nanoclay actions during the spinning and fiber formation process. Sharper and more distinct peaks also indicated an increase in the crystalline size. Table III gives details about the Bragg angle associated with the individual peaks, interplanar d-
spacing, and crystal size. The sizes of the crystals were significantly higher in all of the nanoclay-containing samples than in the control PP. These results agreed well with the DSC results of the melting peak shift.

These changes in the crystalline structures (α- crystalline formation and larger crystalline size) could be explained by the effect of nanoclay addition on the crystallization behavior. As explained previously, the nanoclay particles acted as nucleating agents and increased the crystallization rate, which may have caused changes in the crystalline form and crystal size (Zhang et al., 2004).

**Figure 3.6:** X-ray diffractograms of PP and nanoclay-PP composite fibers
Table 3.3: Crystallite sizes of PP and nanoclay-PP composite fibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ</th>
<th>d(Å)</th>
<th>Crystal size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>15.1</td>
<td>5.86</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>22.2</td>
<td>4.01</td>
<td>-</td>
</tr>
<tr>
<td>PP and 1% Nanoclay</td>
<td>15.0</td>
<td>5.89</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>17.8</td>
<td>4.98</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>19.5</td>
<td>4.55</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>22.1</td>
<td>4.01</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>26.4</td>
<td>3.37</td>
<td>228</td>
</tr>
<tr>
<td>PP and 2% Nanoclay</td>
<td>14.9</td>
<td>5.94</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>17.7</td>
<td>5.00</td>
<td>118</td>
</tr>
<tr>
<td></td>
<td>19.4</td>
<td>4.58</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>21.9</td>
<td>4.05</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>26.3</td>
<td>3.38</td>
<td>179</td>
</tr>
<tr>
<td>PP and 3% Nanoclay</td>
<td>14.9</td>
<td>5.94</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>17.7</td>
<td>5.00</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>19.4</td>
<td>4.58</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>26.3</td>
<td>3.38</td>
<td>204</td>
</tr>
</tbody>
</table>

3.3.5 Birefringence

The birefringence of PP and the PP–nanoclay fibers given in Table 3.4 shows that the birefringence of the nanoclay–PP composite fibers was lower than that of the PP fibers. This indicated that the addition of clay particles resulted in a reduction in the molecular orientation of PP molecules. This reduction in the molecular orientation of the fibers highly impacted the mechanical properties of the fibers. However, we still did not fully understand the reason behind these changes. The molecular orientation of a fiber developed during the melt-spinning process is
strongly affected by the spinning conditions and also by the polymer-chain properties, including the crystallization behavior (White et al., 1986). The presence of nanoclay alters the chain rigidity and polymer rheology, so this may hinder the alignment of molecules by spin tension at given spinning speed (Peltola et al., 2006; Solomon et al., 2001). In addition, changes in the crystallization behavior caused by nanoclay addition could influence the molecular orientation development because crystallization and orientation development occur simultaneously during spinning and they are highly interrelated (White et al., 1986; Katayama et al., 1968).

**Table 3.4:** Birefringence of nanoclay-PP composite fibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Birefringence (X10⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>20.3</td>
</tr>
<tr>
<td>PP + 0.5% Nanomax</td>
<td>19.6</td>
</tr>
<tr>
<td>PP + 1% Nanomax</td>
<td>19.1</td>
</tr>
<tr>
<td>PP + 1.5% Nanomax</td>
<td>18.7</td>
</tr>
<tr>
<td>PP + 2% Nanomax</td>
<td>18.4</td>
</tr>
<tr>
<td>PP + 2.5% Nanomax</td>
<td>18.2</td>
</tr>
<tr>
<td>PP + 3% Nanomax</td>
<td>17.9</td>
</tr>
</tbody>
</table>
3.3.6 Fiber Tensile Properties

Figure 3.7 compares the specific stress–strain curves for the PP and nanoclay–PP fiber samples. It was apparent that the addition of nanoclay altered the shape of the stress–strain curve and, thus, the tensile behaviors: it reduced the tenacity and increased the strain at break. In general, the tensile behavior of polymeric fibers is the result of the inherent polymeric chain properties (chain rigidity, secondary bond strength between polymeric chains, and molecular weight of the polymers used) and the microstructures of the fibers formed by polymer-chain alignment. Because the microstructures of fibers were highly dependent on the melt-spinning conditions, the tensile properties in the nanoclay–PP composite fibers were the combined results of the alteration of the polymer-chain properties and microstructural changes. In this case, nanoclay addition in PP were caused by changes in the material properties, which included an alteration in the mobility or rigidity of the polymer chain through intercalation or exfoliation, and the introduction of defect formations when some of the nanoclay formed microcomposite structures. However, as we demonstrated in a previous section, changes in the microstructure were observed with the addition of nanoclay, and this resulted in changes in the crystallization behavior. The shape of the stress–strain curves implicated that the reduction of molecular orientation occurred with the incorporation of nanoclay, although all of these fibers were produced with exactly the same spinning conditions. This agreed well with what we observed in the birefringence measurement (Table 3.4). Regardless of its clay concentration, the fibers with added nanoclay exhibited plateaus after the yield points, where the fibers were elongated greatly without added stress. This is a hallmark behavior of a fiber with an unoriented chain, which realigns parallel to the fiber axis
when stressed. This induces an increase in the fiber length without added stress. At a higher clay loading, no further changes in the stress–strain curve were observed, but this caused premature tensile failure compared to the sample with a low clay loading. This may be due to structural defects in the fibers when a high concentration of nanoclay was added. The effect of clay loading on the tensile properties are further summarized in Figure 8, where the tenacity, strain at break, secant modulus at 5%, and toughness were calculated from the stress–strain curves of single fibers. At all clay loading levels, the tenacity was found to be lower than that of PP. There was a greater decrease in the tenacity with increasing clay loading above 1%. As pointed out previously, the reduction of tenacity could be explained by a reduction in the orientation and possible defect formation with the addition of nanoclay. The fiber modulus also exhibited decreasing trends with clay addition. In contrast, the strain at break was dramatically enhanced when nanoclay was added, and it reached its peak at a 1% nanoclay loading level and decreased thereafter. The reduction of orientation could have also been one reason for the higher strain at break in the nanoclay–PP composite fibers. However, the increase in the strain at break was more drastic than changes in the birefringence and fiber tenacity. It reached its peak at the 1% nanoclay loading, where the strain at break almost doubled compared to the PP control. The fiber toughness also increased and reached about 1.5 times that of the PP control at the 1% nanoclay loading. Because the molecular orientation had little impact on the fiber toughness, nanoclay addition in PP caused fundamental changes beyond the alteration of the molecular alignment and led to fibers with more ability to absorb energy before failure. This effect was diminished when the clay loading increased, and the defect formation deteriorated and initiated premature
tensile failure. The crystalline structures observed by WAXD (Figure 3.6) at the 1% clay loading were significantly different that of the PP control. However, any additional amount of clay changed the X-ray diffraction pattern (Table 3.3) only slightly, and a slight reduction in the crystallinity was also observed.

Figure 3.7: Stress-strain curves of nanoclay-PP composite fibers under tensile deformation
CONCLUSIONS

Nanocomposites fibers of PP and montmorillonite based organoclay were produced by a melt-spinning process, and their structures and mechanical properties were studied. Nanoclay addition altered the crystallization kinetics of PP and resulted in changes in the microstructure of the nanoclay–PP composite fibers. Higher $n$ and $k$ values for the nanoclay–PP composite fibers suggested that the nanoclay particles acted as heterogeneous nucleating agents in the polymer matrix and increased the crystallization rate of the host polymer. Nanoclay addition also led to increases in the crystal size, as observed by WAXD and DSC.

Figure 3.8: Single fiber tensile properties. Single-fiber tensile properties of nanoclay–PP fibers: (a) tenacity, (b) strain at break, (c) toughness, and (d) 5% secant modulus.
However, a reduction in the fiber orientation was also observed in the nanoclay–PP nanocomposite fibers and resulted in significant changes in the tensile deformation behavior of fibers. Decreases in the fiber modulus, tenacity, and toughness with increasing strain at break were observed. These changes suggested that nanoclay particles were involved in a fiber-formation process and interacted with polymer chain; then, the composite structures created were highly affected by the material and processing parameters, both on the microscale and nanoscale.

3.5 REFERENCES


8. Ding C., Jia D., He H., Guo B., Hong H., Polymer testing, 24 (2005), 94-100.


CHAPTER 4

STRUCTURE AND TENSILE PROPERTIES OF
NANOCLAY-PP FIBERS PRODUCED BY MELT
SPINNING: EFFECT OF CLAY AND
COMPATIBILIZER TYPE
Structure and Tensile properties of Nanoclay-PP Fibers Produced by Melt Spinning: Effect of Clay Type and Compatibilizer Type

ABSTRACT
Nanocomposites fibers of polypropylene (PP) and montmorillonite-based organo-clay were produced by melt spinning process and their structures and mechanical properties are studied. Polypropylene grafted maleic anhydride is used as a compatibilizer to improve the compatibility between non-polar PP and polar organoclay. Addition of nanoclay in PP increases rate of crystallization and alters microstructures of fibers. Increases in crystal size as well as reduction in molecular orientation were observed in nanoclay-PP composite fibers. Tensile properties of nanoclay composite fibers were also studied and decreases in fiber modulus, tenacity and increases in strain at break were observed.

4.1 INTRODUCTION
Nanocomposites based on nanoclay additive found great interest because of their low cost, ready availability and improvement in mechanical, thermal, and barrier properties [Ton-That et al., 2004]. The composites based on nanoclay (layered silicates) are generally termed as polymer layered silicate nanocomposites [Giannelis, 1996]. Most of the research based on nanoclay additives has found much interest when Toyota research group successfully prepared polyamide based nanocomposites by in-situ polymerization technique [Usuki et al., 1993a, 1993b; Kojima et al., 1993]. After that many studies were carried out in different
polymer systems to understand the nature of interaction between nanoclay and polymer matrix and the property improvement imparted by the presence of nanoclay.

The structures of nanoclay-polymer composite can be classified by the degree of dispersion (Lee and Goettler, 2004; Wool and Sun, 2005). Traditional microcomposites [Figure 4.1(a)] are formed when the polymer chain is unable to penetrate between the silicate layers. As the results, the clays form relatively large aggregates as a separate phase inside the host polymer matrix, which forms continuous phase. Improved rigidity can be achieved with this type of composite, but there are reductions in the elongation and toughness. An intercalated structure is formed when a single or more extended chain is intercalated between the nanoclay silicate layers; this results in a well-ordered multilayer with alternating polymeric and inorganic clay layers [Figure. 4.1(b)]. The structure with the highest degree of dispersion is called an exfoliated or delaminated structure, where the silicate layers are completely opened up and dispersed in a disorderly and uniform manner in a continuous polymer matrix [Figure 4.1(c)]. Both intercalated and exfoliated structures are considered nanocomposites, which can provide significant performance enhancements (Wool and Sun, 2005).

Polypropylene (PP) is one of the most widely used thermoplastic polymers for many industrial applications. Many studies on polymer nanocomposites with montmorillonite based organo-clay were carried out by different researchers to improve different properties. Melt blending method of producing polypropylene based nanocomposite is found to be the most appealing method for commercial use. However, achieving exfoliated or fully dispersed
nanoclay particles in PP matrix is very difficult because of the absence of polar groups in PP. The silicate surface of the nanoclay is hydrophilic in nature, and it hinders homogeneous dispersion in organic polymer matrixes. To achieve the required properties, a good dispersion of nanoclay in the polymer matrix and a good interface between the two phases are essential (Ton-That et al., 2004).

Figure 4.1: Classification of nanoclay-polymer composite structures (Lee and Goettler, 2004; Wool and Sun, 2005)

One way to improve the compatibility between the hydrophilic inorganic clay and the oleophilic organic polymer is to modify the surface of the clay through an ion-exchange reaction. This involves the exchange of hydrophilic cations on the clay surface with short-
chain organic cations, such as alkyl ammonium ions (Ding et al. 2005; Marchant and Jayaraman, 2002). The surface modification of clay, often referred as organoclay, has shown improved compatibility with the polymeric matrix (Frounchi et. al. 2006; Ding et. al., 2005).

For Polypropylene based clay composites, organoclay still could not provide enough nanoclay-polymer interaction to produce high degree of dispersion. Kawasaki et al. [1997] first used maleic anhydride grafted PP as a compatibilizer for PP/nanoclay composites. In this they found that presence of compatibilizer improves the interaction between PP and organically modified clay with stearyl ammonium. Intercalation arises because of the formation of hydrogen bond between maleic anhydride group and the oxygen groups of the silicate. Many studies [Chen et al., 2003; Lertwimolnum et al., 2005; Wenyi et al., 2006] found improvement in clay dispersion and mechanical properties when maleic anhydride-modified PP was used. However, addition of low molecular weight PP-g-MA can result in lower mechanical properties of the final composite. Therefore concentration of PP-g-MA should be optimized. A few studies show that optimal clay to compatibilizer ratio is should be about 1 (clay): 2-3 (compatibilizer) to obtain intercalated or exfoliated composite [Pascual et al., 2009]. Ton-That et al. [2004] studied the effect of molecular weight of compatibilizer on clay exfoliation and mechanical properties. They found that compatibilizer based on higher molecular weight facilitates clay exfoliation and improved strength. Although polymer chain mobility is high for low molecular weight compatibilizer and it easily intercalates into the clay layers because of smaller chain length, co-crystallization with PP matrix is low and hence its compatibility is low. Compatibilizer based on higher molecular
weight has good interaction with PP because of its longer chain length. Similar result was obtained by Svoboda et al [2002] on PP/nanoclay composites in presence of three different types of compatibilizers. There are few studies [Ristolainen et al., 2005; Usuki et.al., 1997] which are based on hydroxyl-functional PP were carried out and found to be effective compatibilizer for PP.

In this chapter, melt spun PP fibers were produced with the addition of montmorillonite based organoclay and their structure-property relationship was analyzed. Also, effect of compatibilizer on the compatibility between organoclay and PP was studied.

4.2 EXPERIMENTAL

4.2.1 Materials

Spunbond grade PP (PP CP360H) with an average melt flow rate of 35g/10 minute was supplied by Sunoco chemicals (Philadelphia, PA). Organically modified nanoclay (Natural montmorillonite modified with a quaternary ammonium salt) samples of Cloisite 20A and Cloisite 15A were obtained from Southern Clay products (Gonzales, TX). Cloisite 20A and Cloisite 15A are organically modified with dimethyl, dehydrogenated quaternary ammonium salt (Figure 4.2). The concentration of organic modifier in Cloisite 20A and Cloisite 15A is respectively 95 and 125 meq/100 g of clay.
Two different compatibilizers, Epolene G-3015 (Eastman Chemicals) and Fusabond M613-05 (Dupont) were used as a compatibilizer for Cloisite 15A and 20A samples. Both the compatibilizers are based on PP grafted with maleic anhydride with a maleic anhydride grafting content of <1 wt%. Epolene G-3015 has a melt flow rate of 40 and Fusabond M613-05 has a melt flow rate value of 120.

**4.2.2 Melt spinning of the nanoclay-PP composite fibers**

Nanoclay/PP composite pellet with nanoclay loading 10 wt. % were prepared by melt compounding at 205°C in TechmerPM (Clinton, TN, USA). The ratio of clay to compatibilizer is maintained as 1:2. A control sample of PP and PP-g-MA compatibilizer is produced in order to analyze the compatibilizer effect.

The produced masterbatch pellet were then mixed and extruded with PP to produce nanoclay/PP composite fibers with the Hills Homofilament Research line in the Nonwovens Institute, North Carolina State University (Raleigh, NC, USA). Spinning speed was
maintained at 2000 m/m and spin head temperature was 265°C. A melt throughput of 1 g hole$^{-1}$ minute$^{-1}$ was maintained. Nanoclay-PP fibers with a clay loading of 0.5-1.5% were produced. As a control, PP without nanoclay was melt extruded at the same condition and to analyze the compatibilizer effect, control samples of PP and PP-g-MA were also produced at the same conditions. Fiber sizes of all samples were about 5 denier. The details of the fibers produced are given in Table 4.1

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Nanoclay type</th>
<th>Compatibilizer type</th>
<th>Concentration of clay, wt%</th>
<th>Concentration of PP-g-MA, wt%</th>
<th>Average Denier</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>PP</td>
<td></td>
<td>---</td>
<td>---</td>
<td>5.2</td>
</tr>
<tr>
<td>C20A-Epolene-0.5</td>
<td>Cloisite 20A</td>
<td>Epolene</td>
<td>0.5</td>
<td>1</td>
<td>4.8</td>
</tr>
<tr>
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<td>Cloisite 20A</td>
<td>Epolene</td>
<td>1.0</td>
<td>2</td>
<td>5.0</td>
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<tr>
<td>C20A-Epolene-1.5</td>
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<td>1.5</td>
<td>3</td>
<td>4.8</td>
</tr>
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<td>4.8</td>
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<td>Epolene</td>
<td>1.0</td>
<td>2</td>
<td>5.0</td>
</tr>
<tr>
<td>C15A-Fusabond-1</td>
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<td>Fusabond</td>
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<td>4.7</td>
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<td>Epolene -1</td>
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<td>PP-g-MA</td>
<td>Fusabond</td>
<td>---</td>
<td>2</td>
<td>4.7</td>
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<tr>
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<td></td>
<td>Epolene</td>
<td>---</td>
<td>3</td>
<td>4.9</td>
</tr>
</tbody>
</table>
4.2.3 Transmission Electron Microscope (TEM)

Cross sections of the nanoclay–PP composite fibers were investigated under a Hitachi HF 2000 transmission electron microscope to study the nanoclay dispersion in PP. We prepared the samples by embedding the fiber samples in Spurr’s epoxy and microtoming them to 70 nm thick.

4.2.4 Differential Scanning Calorimeter (DSC)

The melting and crystallization behaviors of the composite were analyzed with a PerkinElmer differential scanning calorimeter (Perkin Elmer, Norwalk, CT). Nanoclay–PP composite fibers (4.5 ± 0.5mg) were heated in a nitrogen atmosphere from 25 to 190 °C and allowed to stand for 10 min at 190 °C and then cooled from 190 to 25 °C. In all cases, the heating/cooling rate was maintained at 5 °C /min.

The crystallinity of the samples was calculated using the following formula:

\[ %\text{Crystallinity} = \frac{\Delta H}{\Delta H_{pp}^0} \times 100 \] (4.1)

where, \( \Delta H \) is the enthalpy of fusion of the sample (J/g) and \( \Delta H_{pp}^0 \) is the enthalpy of fusion of completely crystalline PP (~ 207 J/g) (Karger-Kocsis, 1995).
4.2.5 Isothermal Crystallization

The isothermal crystallization of the nanoclay–PP composites were also investigated with the Perkin-Elmer differential scanning calorimeter. The samples were heated at a rate of 20 °C /min to 190 °C and kept at 190 °C for 10 min; then, they were cooled down at a rate of 50 °C /min to crystallization temperatures ranging from 124 to 128 °C and allowed to crystallize there for 10 min.

4.2.6 Birefringence

The birefringence of the fibers was measured with an Aus Jena Interference microscope. The wavelength of the polarized light used was 546 nm. The fibers were immersed in oil with a matching refractive index (Cargill), and the refractive indexes parallel and perpendicular to the fiber axis were measured from the interference fringe shifts.

Then, the birefringence of the samples was calculated with the following formula:

\[ \Delta n = |n_\parallel - n_\perp| \]  \hspace{1cm} (4.2)

- \( n_\parallel \) - refractive index of the samples parallel to the direction of orientation
- \( n_\perp \) - refractive index of the samples perpendicular to the direction of orientation.

4.2.7 Wide angle X-ray Diffraction (WAXD)

The crystallinity and crystal size of the samples were measured with an Omni Instrumental X-ray diffractometer (Biloxi, MS). 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 onto the sample holder and placed inside the chamber of the sample holder. The samples were scanned in the 2θ range 3° to 30° with an increment of 0.05°. From the scattering pattern, characteristics interplanar d-spacing of nanoclay platelets was calculated using Bragg’s equations (Cullity et al., 2001).

$$\lambda = 2d \sin \theta_B$$  \hspace{1cm} (4.3)

Where $\lambda$ is wavelength of X-ray (1.54 Å), $d$ is interplanar spacing (Å) and $\theta_B$ is Bragg angle in degree.

The crystal sizes of the samples were also calculated with Scherer’s equation (Cullity et al., 2001):

$$t = \frac{0.9 * \lambda}{B * \cos \theta_B}$$ \hspace{1cm} (4.4)

Where,

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$</td>
<td>Crystal size (Å)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength of X-ray (1.54 Å)</td>
</tr>
<tr>
<td>$B$</td>
<td>Full Width at Half Maximum (radian)</td>
</tr>
<tr>
<td>$\theta_B$</td>
<td>Bragg angle (degree)</td>
</tr>
</tbody>
</table>
4.2.8 Single Fiber Tensile Properties

The single-fiber tensile properties of the nanoclay–PP composite fibers were evaluated according to ASTM D 3822-07 in an Instron MTS instrument with a 50-g load cell (Canton, MA). The gauge length was 2.54 cm, and the rate of extension was 15 mm/min. The tenacity, secant modulus at 5% strain, toughness, and strain at break were calculated from the tensile stress–strain curve, and the average of 10 samples is reported.

4.3 RESULTS AND DISCUSSION

4.3.1 Nanoclay dispersion in PP fibers

TEM images (Figure 4.3) of the composite PP fibers with Cloisite 15A and Cloisite 20A nanoclay types shows distribution on the nanoclay particles in the fiber cross-section. Diffusion of polymer chains into the intergallery layer of nanoclay that results in peeling-off of nanoclay layers from one end is clearly observed from Figure 4.3 (c-d). The platelet layers are peeled-off during shear in the compounding and extrusion, which makes way for polymer chains to intercalate between the clay platelets. This phenomenon of “peeling-off” effect is reported in various studies of nanoclay composite systems (Ton-That et.al., 2004, Giannelis, 1996). However, there were some regions where clay layers were aggregated without polymer chain penetration between the nanoclay layers.
Figure 4.3: TEM images of cross sections of nanoclay–PP composites fibers of (a) C15A-Epolene-1 (50000x magnification), (b) C20A-Epolene-1 (50,000x magnification), (c) C15A-Epolene-1 (100000x magnification), and (d) C20A-Epolene-1 (100000x magnification).
As the layered silicate particles are arranged in orderly fashion, they have a characteristic d-spacing which is the sum of thickness of single clay layer and the intergallery spacing. This is reflected in the (001) crystal plane. X-ray diffraction (XRD) is used to measure the intergallery spacing of the nanoclay structures. Clay intercalation or exfoliation can be analyzed with the shift in this interplanar d-spacing of clay particles. As shown in Figure 4.4, the characteristics interplanar d-spacing for the Cloisite 20A clay powder was found out to be 24.0 Å, which corresponds to a 2θ value of 3.67°. With the addition of Cloisite 20A in PP/PP-g-MA system, there is a shift in the interplanar d-spacing observed at lower 2θ angles as shown in Figure 5, which shows that clay particles are either intercalated or exfoliated in the PP/PP-g-MA system. This characteristics peak at 2θ value of 3.67° is not seen with 1% clay loading in the nanoclay-PP fibers indicates the shift in the interplanar d-spacing to lower angles. This indicates that in the nanoclay-PP fiber composite, there is increase in the interplanar d-spacing which is caused by the intercalation of polymer chains between the clay layers.
**Figure 4.4:** X-ray diffractograms of Cloisite 20A clay powder and C20A-Epolene-1 fiber sample at lower Bragg angle

### 4.3.2 DSC Analysis

Figure 4.5 shows the DSC heating and cooling thermogram of fibers. Presence of nanoclay affected both the melting and crystallization behavior of the PP fibers. From Figure 4.5a, it can be inferred that there is slight increase in the melting temperature with the addition of nanoclay. The change in the shape of the melting endotherm with the addition of nanoclay suggests there is a possible alteration of the fiber microstructure caused by the presence of nanoclay. It can clearly be observed that this change arises only from the presence of
nanoclay as the shape of the melting endotherm for compatibilizer added fibers is same as that of PP control. The melting endotherm of PP and PP-compatibilizer control fibers were broad and consisted of two distinct melting peaks. The first peak, at low melting point indicated the presence of small and imperfect crystallites. The narrowness of the melting endotherm for the nanoclay added samples suggests narrower range of crystal sizes. Also the melting point is slightly increased with the presence of nanoclay (Table 4.2).

Cooling thermogram as shown in Figure 4.5b shows that there is alteration in the crystallization behavior. Both the onset and peak crystallization temperature decreased with the presence of nanoclay. It can also be noticed that these values were even decreased when only compatibilizer is added in the PP fiber. For further understanding of the effect of nanoclay on crystallization behavior of PP fibers, isothermal crystallization for the fibers was carried out to analyze the crystallization kinetics.
Figure 4.5: DSC thermograms of nanoclay–PP composite fibers: (a) heating thermogram of the melting endotherm and (b) cooling thermogram of the crystallization exotherm
**Table 4.2:** Melting and crystallization temperatures and crystallinity (%) of nanoclay-PP composite fibers

<table>
<thead>
<tr>
<th>Nanoclay loading</th>
<th>Onset crystallization temperature (°C)</th>
<th>Peak crystallization temperature (°C)</th>
<th>Onset melting temperature (°C)</th>
<th>First peak melting temperature (°C)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>123.8</td>
<td>120.2</td>
<td>158.4</td>
<td>161.0</td>
<td>50</td>
</tr>
<tr>
<td>C15A-Epolene-1</td>
<td>123.1</td>
<td>119.3</td>
<td>159.0</td>
<td>162.7</td>
<td>52</td>
</tr>
<tr>
<td>C20A-Epolene-1</td>
<td>121.4</td>
<td>118.9</td>
<td>159.1</td>
<td>163.0</td>
<td>48</td>
</tr>
<tr>
<td>Epolene-2</td>
<td>122.7</td>
<td>118.7</td>
<td>158.1</td>
<td>160.7</td>
<td>49</td>
</tr>
</tbody>
</table>

**4.3.3 Isothermal crystallization**

The isothermal crystallization kinetics of nanoclay/PP composite fibers at different crystallization temperature was analyzed according to Avrami equation (Avrami, 1939; Avrami 1940).

\[ 1 - X_t = e^{(-kt^n)} \]

or

\[ \ln(-\ln(1 - X_t)) = n \ln t + \ln k \]

where \( X_t \) is the relative crystallinity at different crystallization time \( t \), \( k \) is the crystallization rate constant and \( n \) is the Avrami exponent constant.

Avrami plots of \( \ln(-\ln(1-X_t)) \) vs. \( \ln t \) of 1% nanoclay/PP fibers and PP control fibers are shown in Figure 4.6 – 4.7. From these Avrami plots, \( n \) and \( k \) values were obtained from the slope and intercept of the linear line fitting and results are given in Table 4.3. In all the
crystallization temperature range studied, 1% nanoclay addition leads to an increase in rate constant $k$ and reductions in the crystallization half time regardless of clay. It is worth note that addition of PP-g-MA alone significantly slow down the crystallization process, but this is easily overcome by clay addition. It indicates faster crystallization of nanoclay added samples. This result agrees well with other studies (Ma et. al. 2002; Zhang et. al., 2004; Seo at. al., 2000; Varga and Karger-Kocsis 1995). Ma et. al. (2002) and Zhang et. al.(2004) concluded that the exfoliation of the silicate layers results in increase in the number of heterogeneous nuclei and thus increases the crystallization rate. It can also be noticed with only the presence of compatibilizer, crystallization half time is increased and decrease in rate constant $k$. It indicates that compatibilizer hinders the crystallization process and increase in the crystallization as observed in the nanoclay added samples arises only from the presence of nanoclay. Therefore the presence of clay particles acts as a heterogeneous nucleating agents leading to higher crystallization rate and the crystallization of PP-clay added composite filament samples follow heterogeneous nucleation mechanism. This can be further supported by Avrami exponent constant, $n$, also given in Table 4.3. Avrami exponent constants are indicators of crystal growth mechanism. In PP polymer, $n$ is around 3.5~3.6 representing spherulite crystalline growth and some nucleating. With 1% addition of nanoclay n values increase to 3.6~3.8 due to increase in the heterogeneous nuclei formation. Therefore, it can be concluded that nanoclay particles act as a heterogeneous nucleating agent in the polymer matrix and increase the crystallization rate of the host polymer.

Fiber formation during melt spinning is the process of phase transition from entangled polymer melt to ordered semicrystalline materials with complex microstructures. Since
crystallization behavior of materials affect fiber fine structure developed during the melt spinning greatly, changes in crystallization kinetics by addition of nanoclay can lead significant changes in microstructure of fibers.

**Figure 4.6**: Avrami plots of \( \ln(-\ln(1-X_t)) \) versus \( \ln t \) for (a) PP (b) C15A-Epolene-1
Figure 4.7: Avrami plots of $\ln(-\ln(1-X_t))$ versus $\ln t$ for (c) C20A-Epolene-1 (d) Epolene-2
Table 4.3: Kinetic parameters of the isothermal crystallization of nanoclay-PP composite fibers with a 1% nanoclay concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameter</th>
<th>Crystallization temperature (°C)</th>
<th>124</th>
<th>125</th>
<th>126</th>
<th>127</th>
<th>128</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>Half-time (min)</td>
<td></td>
<td>2.22</td>
<td>2.8</td>
<td>3.51</td>
<td>4.47</td>
<td>5.78</td>
</tr>
<tr>
<td>n</td>
<td></td>
<td></td>
<td>3.56</td>
<td>3.47</td>
<td>3.48</td>
<td>3.5</td>
<td>3.46</td>
</tr>
<tr>
<td>k</td>
<td></td>
<td></td>
<td>0.0381</td>
<td>0.0181</td>
<td>0.0082</td>
<td>0.0035</td>
<td>0.0015</td>
</tr>
<tr>
<td>C15A-Epolene-1</td>
<td>Half-time (min)</td>
<td></td>
<td>2.05</td>
<td>2.60</td>
<td>3.30</td>
<td>4.23</td>
<td>5.42</td>
</tr>
<tr>
<td>n</td>
<td></td>
<td></td>
<td>3.80</td>
<td>3.81</td>
<td>3.84</td>
<td>3.82</td>
<td>3.78</td>
</tr>
<tr>
<td>k</td>
<td></td>
<td></td>
<td>0.0445</td>
<td>0.0185</td>
<td>0.0075</td>
<td>0.0030</td>
<td>0.0013</td>
</tr>
<tr>
<td>C20A-Epolene-1</td>
<td>Half-time (min)</td>
<td></td>
<td>2.11</td>
<td>2.61</td>
<td>3.23</td>
<td>4.10</td>
<td>5.26</td>
</tr>
<tr>
<td>n</td>
<td></td>
<td></td>
<td>3.84</td>
<td>3.75</td>
<td>3.69</td>
<td>3.58</td>
<td>3.53</td>
</tr>
<tr>
<td>k</td>
<td></td>
<td></td>
<td>0.0390</td>
<td>0.0189</td>
<td>0.0090</td>
<td>0.0044</td>
<td>0.0020</td>
</tr>
<tr>
<td>Epolene-2</td>
<td>Half-time (min)</td>
<td></td>
<td>3.10</td>
<td>4.47</td>
<td>5.83</td>
<td>7.53</td>
<td>9.48</td>
</tr>
<tr>
<td>n</td>
<td></td>
<td></td>
<td>3.68</td>
<td>3.65</td>
<td>3.46</td>
<td>3.39</td>
<td>3.35</td>
</tr>
<tr>
<td>k</td>
<td></td>
<td></td>
<td>0.0107</td>
<td>0.0034</td>
<td>0.0016</td>
<td>0.0007</td>
<td>0.0004</td>
</tr>
</tbody>
</table>

4.3.4 Crystalline structures: WAXD

X-ray diffractograms of fiber samples given in Figure 4.8 indicated that presence of nanoclay changes the crystalline morphology of PP. PP control samples showed a broad crystalline peak at a 2θ value of 15.1 corresponds to mesomorphic form of i-PP. Similar behavior is observed for PP fiber samples which contains only compatibilizer. But with the addition of nanoclay particles the crystalline peaks were sharper and more distinct. Distinct crystalline peaks were observed at 2θ values of 15.0, 17.8, 19.5 and 22.1 which corresponds to the (110), (040), (130) and (111) diffraction planes of α-crystalline form of i-PP. This may be caused by nanoclay actions during the spinning and fiber formation process. Sharper and distinct peaks also indicate increase in crystalline size. Table 4.4 gives detail about Bragg
angle associated with each peaks, interplanar d-spacing and the crystal size. Sizes of crystals were significantly higher in all nanoclay containing samples than those in control PP. This results well agrees with DSC results of melting peak shift.

![X-ray diffractograms of PP and nanoclay-PP composite fibers](image)

**Figure 4.8:** X-ray diffractograms of PP and nanoclay-PP composite fibers

**Table 4.4:** Crystallite size of PP and nanoclay-PP composites fibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ</th>
<th>d(Å)</th>
<th>Crystal size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>15.1</td>
<td>5.86</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>22.2</td>
<td>4.01</td>
<td>-</td>
</tr>
<tr>
<td>C15A-Epolene-1</td>
<td>15.0</td>
<td>5.92</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>17.8</td>
<td>4.99</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>19.4</td>
<td>4.57</td>
<td>101</td>
</tr>
<tr>
<td>C20A-Epolene-1</td>
<td>15.0</td>
<td>5.92</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>17.8</td>
<td>4.95</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>19.5</td>
<td>4.56</td>
<td>101</td>
</tr>
<tr>
<td>Epolene-2</td>
<td>15.1</td>
<td>5.86</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>22.2</td>
<td>4.01</td>
<td>-</td>
</tr>
</tbody>
</table>
4.3.5 Birefringence

The birefringence of PP and the PP-nanoclay fibers given in Table 4.5 shows that the birefringence of the nanoclay-PP composite fibers was lower than that of the PP fibers. It can be observed birefringence value of PP-compatibilizer fibers were even lower than that of the PP fibers. It indicates that addition of both compatibilizer and clay particles causes reduction in the molecular orientation of PP molecules. This reduction is more apparent in PP/Closite 20A fibers. As the molecular orientation is directly related to the mechanical properties, this reduction in the molecular orientation in the fibers affected the mechanical properties of the fibers. The molecular orientation of a fiber developed during the melt-spinning process is strongly affected by the spinning conditions and also by the polymer-chain properties including the crystallization behavior [White et al., 1986]. During melt-spinning process, presence of nanoclay particles may hinder the alignment of the molecules. From DSC results it was observed that presence of nanoclay affects the crystallization behavior of the fibers, this might also influence the molecular orientation of the fibers as the crystallization and orientation development occur simultaneously during spinning and they are highly interrelated [White et al., 1986; Katayama et al., 1968].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Birefringence</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>0.0203</td>
</tr>
<tr>
<td>C15A-Epolene-1</td>
<td>0.0183</td>
</tr>
<tr>
<td>C20A-Epolene-1</td>
<td>0.0165</td>
</tr>
<tr>
<td>Epolene-2</td>
<td>0.0192</td>
</tr>
</tbody>
</table>
4.3.6 Fiber tensile properties

Figure 4.9 compares the specific stress-strain curves for the PP, PP/PP-g-MA and nanoclay-PP fiber samples for a clay loading of 1%. It was observed that there is a decrease in specific stress and increase in % strain at break with the addition of PP-g-MA compatibilizer. After the addition of clay particles, there is greater decrease in the specific stress with increase in % strain at break. The decrease in tenacity can be related to the reduction of molecular orientation caused by the addition of clay particles, which can be confirmed by the decrease in birefringence value. Also partly, the presence of compatibilizer also contributes to the decrease in specific stress. From the initial stress-strain curve of the filament samples, it is observed that with the addition of PP-g-MA there is a decrease in the initial modulus, which is regained after the addition of the clay particles. This can be noticed from the values of secant modulus in Figure 4.11d. This shows that addition of clay particles in fact improves the modulus of PP/PP-g-MA system, but lesser than PP. Figure 4.10 - 4.11 shows the overall mechanical properties of PP and PP/nanoclay composite filaments at different clay loadings. As can be seen from secant modulus plot, secant modulus remains same with the addition of 1% PP-g-MA, but at higher compatibilizer percentages there is a greater decrease in the secant modulus compared to 100%PP. Further addition of clay particles, improves the secant modulus of the PP/PP-g-MA system. The improvement in modulus is due to the dispersion of the clay particles in nanometer level and intercalation with PP. This results in confinement of the segmental motion of the PP polymer chains, which results in improvement of modulus [Ding et al., 2005]. This shows the possible intercalation or exfoliation of silicate layers between the polymeric chains, which improves the modulus of PP/PP-g-MA/nanoclay
composites. At all clay loading levels, tenacity is found to be lower than that of PP. There is a greater decrease in tenacity with increasing clay loading above 1%. This is because of the decrease in birefringence values with clay addition. Part of the contribution arises from the presence of PP-g-MA, which also causes decrease in birefringence and hence decreases in tenacity. In contrast, strain at break dramatically enhances when nanoclay were added and reaches its peak at 1% nanoclay loading level and decrease thereafter. The reduction of orientation can also be one reason of higher strain at break in nanoclay-PP composite fibers.

![Stress-strain curves of nanoclay-PP composite fibers under tensile deformation](image)

**Figure 4.9:** Stress-strain curves of nanoclay-PP composite fibers under tensile deformation

However, increasing in strain at break is more drastic than changes in birefringence and fiber tenacity. It can also be noticed that overall mechanical properties of Cloisite 15A clay fiber samples has higher tenacity than that of Cloisite 20A fiber samples. This is because of the
higher organic modifier concentration in Cloisite 15A clay (125 meq/gram) compared to the Cloisite 20A clay (95 meq/gram). It was reported that higher modifier concentration helps in increase in better bonding with the compatibilizer and this helps in better dispersion of clay particles in the PP fiber matrix.

**Figure 4.10**: Single-fiber tensile properties of nanoclay–PP fibers: (a) tenacity, (b) strain at break.
Figure 4.11: Single-fiber tensile properties of nanoclay–PP fibers: (c) toughness, and (d) 5% secant modulus.
4.3.7 Effects of compatibilizers on fiber properties

In order to investigate influences of compatibilizers’ properties on nanoclay/PP composite formation, 2 different types of compatibilizers, Epoline G-3015 with MFI of 40 and Fusabond M613-05 with MFI of 120 were studied. The melt spun fibers were tested for their mechanical properties and Figure 4.12 compares the stress-strain curves for fibers with different compatibilizers and mechanical properties of the fiber samples are given in Table 4.6. It was found that addition of both the compatibilizers’ results in decrease in tenacity and increase in breaking strain. The decrease in tenacity is due to the reduction in molecular orientation because of the presence of maleic anhydride, which can be confirmed by birefringence values as given in Table 4.7. It can be noticed that birefringence of Epoline based samples are higher compared to that of Fusabond based samples, which is also evident from the higher tenacity values for Epoline based samples as compared to that of Fusabond based samples. The differences may be contributed to the differences of MFI between Epoline G-3015 and Fusabond M613-05. Fusabond M613-05 with MFI of 120 has lower molecular weight compared to host PP (MFI=35) and it may hinder homogenous blending of PP and the compatibilizer, while Epoline G3015 has similar MFI with host PP.
**Figure 4.12:** Effect of compatibilizer type on stress-strain curves of nanoclay-PP composite fibers under tensile deformation

**Table 4.6:** Effect of different compatibilizers on fiber mechanical properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tenacity, gf/denier</th>
<th>% Strain at break</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>2.8 (0.07)</td>
<td>215 (7)</td>
</tr>
<tr>
<td>Epolene-2</td>
<td>2.5 (0.03)</td>
<td>282 (8)</td>
</tr>
<tr>
<td>Fusabond-2</td>
<td>2.2 (0.08)</td>
<td>328 (27)</td>
</tr>
<tr>
<td>C15A-Epolene-1</td>
<td>2.2 (0.09)</td>
<td>264 (11)</td>
</tr>
<tr>
<td>C15A-Fusabond-1</td>
<td>1.8 (0.07)</td>
<td>322 (21)</td>
</tr>
</tbody>
</table>
Table 4.7: Effect of different compatibilizers on fiber Birefringence

<table>
<thead>
<tr>
<th>Sample</th>
<th>Birefringence (X10⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>0.0203</td>
</tr>
<tr>
<td>Epolene-2</td>
<td>0.0192</td>
</tr>
<tr>
<td>C15A-Epolene-1</td>
<td>0.0183</td>
</tr>
<tr>
<td>Fusabond-2</td>
<td>0.0189</td>
</tr>
<tr>
<td>C15A-Fusabond-1</td>
<td>0.0180</td>
</tr>
</tbody>
</table>

4.4 CONCLUSIONS

Nanocomposites fibers of PP and montmorillonite based organoclay were produced by a melt-spinning process in presence of PP-g-MA as compatibilizer, and their structures and mechanical properties were studied. Nanoclay addition altered the crystallization kinetics of PP and resulted in changes in the microstructure of the nanoclay–PP composite fibers. Higher $n$ and $k$ values for the nanoclay–PP composite fibers suggested that the nanoclay particles acted as heterogeneous nucleating agents in the polymer matrix and increased the crystallization rate of the host polymer. Nanoclay addition also led to increases in the crystal size, as observed by WAXD and DSC. However, a reduction in the fiber orientation was also observed in the nanoclay–PP nanocomposite fibers and resulted in significant changes in the tensile deformation behavior of fibers. Decreases in the fiber modulus, tenacity, and toughness with increasing strain at break were observed. These changes suggested that nanoclay particles were involved in a fiber-formation process and interacted with polymer chain; then, the composite structures created were highly affected by the material and
processing parameters, both on the microscale and nanoscale. Nanocomposite fiber samples of montmorillonite based organoclay with higher organic modifier concentration (Cloisite 15A) showed better property improvement compared to organoclay with lower organic modifier concentration (Cloisite 20A). This could be attributed to the increased gallery spacing with higher modifier concentration and improved compatibility. Also compatibilizer with low melt flow index has better compatibilization and improved property when compared to high melt flow index compatibilizer.

4.5 REFERENCES

8. Ding C., Jia D., He H., Guo B., Hong H., Polymer testing, 24 (2005), 94-100.


CHAPTER 5

STRUCTURE AND PROPERTIES OF NANOCLAY

ADDED SPUNBOND FIBERS AND NONWOVEN
Structure and Properties of Nanoclay added Spunbond Fibers and Nonwovens

ABSTRACT
Nanoclay incorporated PP spunbond thermal bonded nonwoven fabrics were produced with a basis weight of 50gsm and characterized for their structure and mechanical properties. Tensile property of nanoclay added spunbond fibers are comparable to that of PP as presence of nanoclay does not affect the orientation of PP chains. It was found that with the addition of nanoclay there is up to 20% increase in maximum stress and up to 50% increase in breaking strain obtained for nonwoven samples. The improvement in tensile property in nonwoven fabric is attributed to the changes in the bonding mechanism and improved thermal stability caused by presence of nanoclay. Thermal stability in presence of nanoclay is supported by heat ageing studies where no strength reduction is observed for nonwoven fabric containing nanoclay. Thermal degradation studies using TGA shows increase in onset degradation temperature up to 100°C with the addition of nanoclay.

5.1 INTRODUCTION
During the last 3 decades, organic-inorganic nanocomposites have attracted great research and industrial focus. These composites are based on organic polymer and inorganic filler system. The most commonly used inorganic filler is the layered silicate and among these, montmorillonite based nano clay are widely used in polymeric system. The research on this particular topic was of great interest among researchers only after the research by Toyota
group on nylon nanocomposites and followed by commercial production of the nanocomposite (Fukushima et al., 1988; Usuki et al., 1993). Owing to its size range and aspect ratio, it was expected that complete exfoliation or intercalation of these materials in the polymeric system will result in improvement in properties like mechanical, thermal, barrier, and chemical resistance. The reason behind these unique behaviors is the nanostructures created by the nanoclay layer/polymer molecular chain. Unfortunately, the expected improvement in properties is not achieved always as preparation of nanocomposite systems is quite complex and there are many processing and material parameters which determines the final composite structure.

Nanoclay particles being hydrophilic in nature, has good compatibility between polar polymers such as nylon and hence method of nanocomposite preparation based on nylon is comparatively easy and many studies on nylon nanocomposites showed greater improvement in the material properties because of its good compatibility with silicate particles (Li et al., 2006; Loo et al., 2004; Fornes et al., 2001; Mehrabzadeh et al., 2002; Zhang et al., 2006). Silicate particles exhibit incompatibility with non-polar polymers like PP and PE. In these systems, the attraction between the polymer matrix and the silicate layers are very less compared to the attraction forces between the individual silicate layers. Therefore, for these polymer systems silicate particles are organically modified with surfactants and also functionalized polymers are added as compatibilizers to increase the compatibility between silicate particles and polymer. Kawasaki et al.(1997) first used maleic anhydride grafted PP as a compatibilizer for PP/nanoclay composites. In this they found that presence of
Compatibilizer improves the interaction between polypropylene and organically modified clay with stearyl ammonium. Intercalation arises because of the formation of hydrogen bond between maleic anhydride group and the oxygen groups of the silicate. Many studies were carried out later (Chen et al., 2003; Lertwimolnum et al., 2005; Wenyi et al., 2006) based on maleic anhydride-modified PP and found improvement in clay dispersion and mechanical properties. However, addition of low molecular weight PP-g-MA can result in lower mechanical properties of the final composite. Therefore concentration of PP-g-MA should be optimized. Few studies show that to obtain intercalated or exfoliated composite optimal clay to compatibilizer should be 1 (clay): 2-3 (compatibilizer) [Pascual et al., 2009].

Despite recent increasing interest in nanoclay, most studies have concentrated on films and plastic molds and we found only a few studies on nanoclay-modified fibers (Joshi et. al., 2006) and only one reported work on nanoclay incorporation in spunbond fibers and nonwoven webs (Bhat et al., 2008). Nanoclay containing fibers and nonwovens can have great potential in various application areas. Improved mechanical properties coupled with lighter weight and enhanced flame and thermal resistance may be beneficial in fiber based composite used in automotive applications. In packaging and medical applications, higher barrier properties may add value of the products. Beyond physical and chemical performance, it may provide added benefit of the appearance of product by improved dyeability and changes in opacity.
In this study, montmorillonite based organoclay containing spunbond fibers and nonwovens fabrics were produced at different bonding temperature, and their structures and mechanical properties were investigated.

5.2 EXPERIMENTAL

5.2.1 Materials

PP pellet (PP CP360H), which has an average melt flow rate of 35g/10 minute was obtained from Sunoco chemicals. Commercially available pre-compounded montmorillonite based organo-clay/PP- Nanomax® PP was purchased from Nanocor (Arlington Heights, IL, US) and used for the study. Nanomax® PP contains about 50% Nanomer® Nanoclay that is surface modified montmorillonite clays, PP, and maleic anhydride modified polyolefin compatibilizer and is prepared by melt compounding to produce intercalated structures based on patented technology (Qian et al. 2002, Qian et. al., 2003).

Organically modified nanoclay (Natural montmorillonite modified with a quaternary ammonium salt) samples of Cloisite 15A was obtained from Southern Clay products. Cloisite 15A is organically modified with dimethyl, dehydrogenated quaternary ammonium salt (Figure 5.1). The concentration of organic modifier in Cloisite 15A 125 meq/100 g of clay

\[
\text{CH}_3 \quad \text{HT – Hydrogenated Tallow ~} \\
\text{CH}_3 - N^+ - \text{HT} \quad 65\% \text{ C18; ~30\% C16; ~5\% C14} \\
\text{HT} \\
\]

**Figure 5.1:** Structure of dimethyl dehydrogenated quaternary ammonium salt
Epolene G-3015 (Eastman Chemicals) was used as a compatibilizer for Cloisite 15A samples. The compatibilizer is based on Polypropylene grafted with maleic anhydride (PP-g-MA) with a maleic anhydride grafting content of <1 wt% and a melt flow rate of 40. The ratio of Cloisite 15A to PP-g-MA is maintained at 1:2.

5.2.2 Nonwoven production

Nanomax® PP and PP were melt compounded further to reduce clay loading to 5 wt%. Masterbatch preparation was carried out with the help of Techmer (Clinton, TN). For Cloisite 15A, masterbatch samples with a 10wt% nanoclay loading was produced and ratio of clay to compatibilizer was maintained as 1:2. A control of PP and PP-g-MA compatibilizer is produced in order to analyze the compatibilizer effect. The details of the master batches are given in Table 5.1. Master batch samples were produced at a temperature of 205°C with a screw speed of 225 rpm.

Table 5.1: Master batch composition

<table>
<thead>
<tr>
<th>Masterbatch</th>
<th>PP, wt%</th>
<th>Clay, wt%</th>
<th>Compatibilizer, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanomax PP</td>
<td>95</td>
<td>5</td>
<td>0.1 to 0.6</td>
</tr>
<tr>
<td>Cloisite 15A</td>
<td>70</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>PP-g-MA</td>
<td>80</td>
<td>--</td>
<td>20</td>
</tr>
</tbody>
</table>

Spunbond nonwoven fabrics were produced in Hill’s spunbond line at Nonwoven Institute’s pilot lab as shown in Figure 5.2. Spunbond nonwoven fabrics with clay additive Nanomax PP
and Cloisite 15A were produced. Along with, control samples of PP and PP/PP-g-MA were also produced. The extrusion temperature was set at 240°C and a throughput of 0.8 g/hole/minute was maintained. The web basis weight was maintained at 50 g/m². Table 2 shows the details of produced spunbond fabrics. Spunbond fibers were also collected for characterization.

Figure 5.2: Schematic of spunbond process (Fedorova, 2006)
Table 5.2: Spunbond nonwoven fabric details

<table>
<thead>
<tr>
<th>Nanoclay type</th>
<th>Concentration of clay, wt%</th>
<th>Average fiber denier</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>---</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Nanomax PP</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Cloisite 15A</td>
<td>1</td>
<td>1.9</td>
</tr>
</tbody>
</table>

The produced spunbond fabrics were thermal calendared at 5 different temperatures of 140, 145, 150, 155 and 160°C.

5.2.3 Differential Scanning Calorimeter (DSC)

Melting and crystallization behavior of the composite was analyzed using Perkin-Elmer differential scanning calorimeter (DSC). 4.5 ± 0.5mg of nanoclay/PP composite fibers were heated in a nitrogen atmosphere from 25 to 190°C and allowed to stand for 10 minute at 190°C and then cooled from 190°C to 25°C. In all cases the heating/cooling rate was maintained at 10°C/min.

The crystallinity of the samples was calculated using the following formula:

\[
\%\text{Crystallinity} = \frac{\Delta H}{\Delta H_{pp}^0} \times 100
\]

(5.1)
where $\Delta H$ is the enthalpy of fusion of the sample (J/g) and $\Delta H_{PP}^0$ is the enthalpy of fusion of completely crystalline PP (~ 207 J/g) (Karger-Kocsis, 1995).

### 5.2.4 Birefringence

The birefringence of the fibers was measured with an Aus Jena Interference microscope. The wavelength of the polarized light used was 546 nm. The fibers were immersed in oil with a matching refractive index (Cargill), and the refractive indexes parallel and perpendicular to the fiber axis were measured from the interference fringe shifts.

Then, the birefringence of the samples was calculated with the following formula:

$$\Delta n = |n_\parallel - n_\perp|$$  \hspace{1cm} (5.2)

$n_\parallel$ - refractive index of the samples parallel to the direction of orientation

$n_\perp$ - refractive index of the samples perpendicular to the direction of orientation.

### 5.2.5 Tensile property

In order to analyze the effect of nanoclay on change in mechanical properties, single fiber tensile testing and spunbond nonwoven fabrics tensile properties were carried out.

#### 5.2.5.1 Tensile properties of single fibers

Single fiber tensile testing was carried out according to ASTM standard D 3822-07, in Instron MTS using 50g load cell. The gauge length used was 2.54cm and the rate of
extension used was 15 mm/minute. The average of 10 samples was reported. Following parameters are obtained from tensile testing.

- **Tenacity**: Specific stress at maximum force expressed in gram force/denier.
- **Toughness**: Area under the specific stress vs. strain curve expressed in gram force/denier.
- **Strain at break**: Strain at break expressed in %.

5.2.5.2 *Tensile properties of spunbond nonwoven*

Tensile properties of fabrics were measured according to ASTM standard D3035, in Instron tensile tester using 45.36 kg load cell. The gauge length used was 7.62 cm and the fabrics were extended at a rate of 300 mm/minute. Five specimens per sample of width 2.54cm and 15.24cm wide were cut in both machine and cross direction of the thermal bonded nonwoven fabric. The average force required to break the nonwoven fabric and elongation at break are reported.

5.2.6 *Thermal Properties of Spunbond Fabrics*

5.2.6.1 *Thermal degradation*

Thermal degradation of the samples was analyzed using Perkin-Elmer diamond Thermo gravimetric analyzer. Samples of weight (5-10mg) were placed in the sample pan and heated from 25°C to 600°C in N₂ atmosphere. Onset degradation temperature was measured at a temperature where 10% degradation of the sample occurs at heating rate of 10°C/minute.
5.2.6.2 Tensile strength retention after heat exposures

Thermal bonded spunbond nonwoven fabric, which is bonded at a bonding temperature of 145°C were annealed at 100°C for 36 hours and tested for their mechanical properties to analyze the effect of heat treatment on the mechanical properties. % Loss in mechanical property was calculated as follows:

\[ \% \text{Loss} = \frac{T_0 - T_a}{T_0} \times 100 \]  

(5.3)

T₀ – Tensile property of thermal bonded spunbond nonwoven fabric

Tₐ – Tensile property of heat aged thermal bonded spunbond nonwoven fabric.

5.2.7 Dynamic Mechanical Properties

Nonwoven samples of 10 x 6.0 x 0.32 were clamped between 2 clamps of Dynamic mechanical analyzer (DMA). Cyclic deformations of 1Hz were applied to samples in a temperature range from -100 to 150°C. The samples were heated at a heating rate of 2°C/minute.

5.3 RESULTS AND DISCUSSION

5.3.1 DSC analysis

Heating and cooling thermogram of PP and nanoclay-PP spunbond fiber samples are given in Figure 5.3. The melting endotherm of both PP and nanoclay-PP spunbond fiber samples exhibit two distinct melting peaks. For nanoclay added PP fibers the second peak is less
distinct with increase in nanoclay loading. Presence of two melting peaks suggests broad range of crystal sizes and with addition of nanoclay crystal sizes become narrower. Although there is no change in overall crystallinity was observed for nanoclay added fiber samples (Table 5.3).

As shown in Figure 5.4, there is some modification in the crystallization behavior with the presence of nanoclay. Onset crystallization temperature is decreased with the addition of nanoclay particles and this causes decrease in crystallization temperature as well. To further understand the crystallization behavior, the isothermal crystallization of the nanoclay-PP composite fibers was studied and the results are reported in the next section.

![Figure 5.3: DSC thermograms of nanoclay–PP composite fibers: Heating thermogram of the melting endotherm](Image)

Figure 5.4: DSC thermograms of nanoclay–PP composite fibers: Cooling thermogram of the crystallization exotherm.

Table 5.3: Melting and crystallization temperatures and crystallinity (%) of nanoclay-PP composite fibers

<table>
<thead>
<tr>
<th>Nanoclay loading</th>
<th>Onset crystallization temperature (°C)</th>
<th>Peak crystallization temperature (°C)</th>
<th>Onset melting temperature (°C)</th>
<th>First peak melting temperature (°C)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>124.1</td>
<td>120.6</td>
<td>160.3</td>
<td>162.4</td>
<td>44</td>
</tr>
<tr>
<td>Nanomax PP-1%</td>
<td>123.7</td>
<td>120.1</td>
<td>160.2</td>
<td>162.9</td>
<td>44</td>
</tr>
<tr>
<td>Nanomax PP-2%</td>
<td>123.4</td>
<td>119.7</td>
<td>160.1</td>
<td>163.0</td>
<td>44</td>
</tr>
<tr>
<td>Nanomax PP-3%</td>
<td>123.6</td>
<td>119.9</td>
<td>160.0</td>
<td>163.1</td>
<td>43</td>
</tr>
</tbody>
</table>
5.3.2 Molecular orientation

Birefringence for PP and PP-nanoclay fibers given in Table 5.4 shows that low concentration of nanoclay addition does not affect molecular orientation of nanomax/PP fibers produced by spunbond process while it cause reduction in birefringence in filament spinning process at same clay loading as reported previously [Rangasamy et al., 2011]. The difference of fibers between spunbond process and multifilament spinning may be caused by differences in spinning speed and quenching conditions. Larger scale and high speed spun bond process may provide more uniform blending of nanoclay and PP as well as high spinline. However, higher clay load still cause some reduction in birefringence even in spunbond process.

Table 5.4: Effect of different clay types on birefringence

<table>
<thead>
<tr>
<th>Sample</th>
<th>Birefringence (X10^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spunbond process</td>
</tr>
<tr>
<td></td>
<td>(Spinning speed =3500m/min)</td>
</tr>
<tr>
<td>PP</td>
<td>26.2</td>
</tr>
<tr>
<td>Nanomax PP-1%</td>
<td>26.1</td>
</tr>
<tr>
<td>Nanomax PP-2%</td>
<td>25.7</td>
</tr>
<tr>
<td>Nanomax PP-3%</td>
<td>25.2</td>
</tr>
<tr>
<td>Cloisite 15A-1%</td>
<td>25.9</td>
</tr>
</tbody>
</table>
5.3.3 Tensile properties of spunbond fiber

The mechanical properties of the spunbond fibers are given in Table 5.5 and Figure 5.5 compares the specific stress vs. % strain for PP and PP/nanoclay fiber samples.

Table 5.5: Mechanical properties of PP and PP/clay composite filament samples at 1% clay loadings. Standard error is given in parenthesis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Denier</th>
<th>Tenacity, gf/denier</th>
<th>Breaking strain, %</th>
<th>Toughness, gf/denier</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>2.0 (0.06)</td>
<td>2.0 (0.06)</td>
<td>233 (12.77)</td>
<td>3.7 (0.27)</td>
</tr>
<tr>
<td>Nanomax PP – 1%</td>
<td>2.0 (0.03)</td>
<td>1.9 (0.06)</td>
<td>257 (20.72)</td>
<td>3.2 (0.41)</td>
</tr>
<tr>
<td>Nanomax PP – 2%</td>
<td>2.1 (0.05)</td>
<td>1.7 (0.07)</td>
<td>286 (19.82)</td>
<td>3.3 (0.41)</td>
</tr>
<tr>
<td>Nanomax PP – 3%</td>
<td>2.2 (0.07)</td>
<td>1.6 (0.04)</td>
<td>310 (10.69)</td>
<td>3.5 (0.18)</td>
</tr>
<tr>
<td>Cloisite15A-1%</td>
<td>1.9 (0.07)</td>
<td>1.8 (0.07)</td>
<td>206 (16.03)</td>
<td>2.6 (0.24)</td>
</tr>
<tr>
<td>PP-g-MA – 2%</td>
<td>2.1 (0.08)</td>
<td>1.9 (0.06)</td>
<td>265 (19.09)</td>
<td>3.6 (0.37)</td>
</tr>
</tbody>
</table>

It can be noticed that there is only slight decrease in tenacity with the addition of nanoclay at lower loading levels. The obtained trend is different from the tenacity values of multifilaments based on nanoclay as reported in our previous chapters, where greater decrease in tenacity was observed with the addition of clay. Unlike the SS curve for filament samples, SS curves for spunbond fibers are similar to that PP fibers with oriented structure. The difference may be because of the higher spinning speed and change in extrusion condition at spunbond process. This can be further confirmed from the birefringence values.
given in Table 5.5, where the presence of nanoclay doesn’t affect the molecular orientation at lower nanoclay loadings.

![Stress-strain curve of PP and PP/nanoclay spunbond fibers](image)

**Figure 5.5:** Typical Stress-strain curve of PP and PP/nanoclay spunbond fibers

### 5.3.4 Tensile properties of thermal bonded spunbond nonwoven

Interestingly, thermal bonded nonwoven fabrics with nanoclay additives showed significant increases both in breaking strength and strain at break, even strengths of single fibers in spunbond web was similar or slightly lower than that of PP control (Figure 5.5). Table 5.6 shows the value of average force required to break the nonwoven fabric and % strain at break for spunbond fabric samples which are thermally bonded at a temperature of 145°C. It indicates about 17% increase in breaking stress and 45% increases in breaking strain in
nonwovens with 1% nanomax PP compared to 100% PP control fabrics. C15A samples also showed similar trends in lesser degree.

**Table 5.6:** Mechanical properties of PP and PP/nanoclay spunbond thermal bonded nonwoven fabric (bonding temperature – 145°C) along machine direction at 1% nanoclay loading

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak load , lbf</th>
<th>Breaking strain, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>16.7</td>
<td>48</td>
</tr>
<tr>
<td>Nanomax PP-1%</td>
<td>19.4</td>
<td>70</td>
</tr>
<tr>
<td>Cloisite 15A-1%</td>
<td>17.7</td>
<td>65</td>
</tr>
</tbody>
</table>

This trend of high strength and breaking strain in nanoclay incorporated nonwovens were observed in all bonding temperature ranges observed (140-150°C). Regardless of nanoclay addition, strengths of thermal bonded fabrics are highly dependent on bonding temperature as demonstrated in Figure 5.6a. It shows the relationship of maximum stress with bonding temperature for PP and clay added samples at a clay loading of 1%. At 140°C, the fabrics are under-bonded and results in lesser strength compared to that of the bonding temperature at 145°C. Similarly above 145°C, the fabrics are over-bonded and brittle in nature and results in decrease in maximum stress. Optimum bonding temperature was found out to be 145°C.
Figure 5.6: Effect of different nanoclay addition on breaking stress (a) and breaking strain (b) of thermal bonded spunbond nonwovens (along machine direction)
Figure 5.7: Effect of different nanoclay addition on breaking stress (a) and breaking strain (b) of thermal bonded spunbond nonwovens (along cross direction)
Breaking strain (Figure 5.7b) also affected by bonding temperatures and for PP and nanoclay samples at a clay loading of 1%, optimum breaking strain occurs at the bonding temperature of 145°C. The percent increase in breaking strain decreases as bonding temperature increases as that observed for maximum stress. For Cloisite 15A based samples, breaking strain at 140°C is similar to that of breaking strain at 145°C. Even nanoclay added fabrics showed better tensile strength and strain at break at all temperature ranges; it is worthwhile to note that these differences are more distinct at lower temperature.

The effect of clay loading on tensile properties is given in Figure 5.8. It can be noticed that with increase in clay loading there is increase in maximum stress at all temperatures and with 3% Nanomax clay loading, there is up to 20% increase in breaking stress and 50% increase in breaking strain is obtained as compared to PP. At lower bonding temperatures, there is greater increase in maximum stress with clay addition and increases with increase in clay loading. But at higher bonding temperature, the percent increase in maximum stress with clay loading is less and optimizes at clay loading of 1%, further addition of clay loading at 2 and 3% doesn’t have much effect on the maximum stress. For all clay loading, optimum bonding temperature was found out to be 145°C except for a clay loading of 3%, which has an optimum bonding temperature at 140°C. Tensile properties of spunbond fabrics at optimum bonding temperature are summarized in Table 5.7.
Figure 5.8: Effect of nanoclay loading on breaking stress of Nanomax PP thermal bonded nonwoven fabric along (a) machine direction (b) cross direction
Table 5.7: Mechanical properties of PP and PP/nanoclay spunbond thermal bonded nonwoven fabrics at optimum bonding temperature

<table>
<thead>
<tr>
<th>Polymer/Clay</th>
<th>Conc. %</th>
<th>Optimum Bonding Temp. (°C)</th>
<th>Maximum Stress (N/mm)</th>
<th>Breaking Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>MD</td>
<td>CD</td>
</tr>
<tr>
<td>PP</td>
<td>--</td>
<td>145</td>
<td>2.92 (0.06)</td>
<td>1.72 (0.03)</td>
</tr>
<tr>
<td>Nanomax PP-SB</td>
<td>0.5%</td>
<td>145</td>
<td>3.30 (0.07)</td>
<td>2.00 (0.03)</td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>145</td>
<td>3.40 (0.13)</td>
<td>1.96 (0.09)</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>145</td>
<td>3.24 (0.06)</td>
<td>1.84 (0.09)</td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td>140</td>
<td>3.47 (0.07)</td>
<td>1.86 (0.04)</td>
</tr>
<tr>
<td>C15A-SB</td>
<td>1%</td>
<td>145</td>
<td>3.10 (0.03)</td>
<td>1.89 (0.09)</td>
</tr>
</tbody>
</table>

With the addition of nanoclay, there is significant decrease in tensile properties for the filaments samples and for spunbond fibers there is less decrease in tensile properties. But there is significant increase in tensile properties of nanoclay added thermally bonded spunbond fabrics. Improvement of tensile properties may be resulted from bond formation and improvement of fiber thermal resistance by addition of nanoclay. Bhat et al. (2008) observed similar tensile properties changes and suggested that it is because fibers with nanoclay additives maintain better integrity during the calendering based on SEM observations. However, we have not observed significant differences in bond point morphology and fibers near bond points between samples with nanoclay samples and polypropylene control (Figure 5.9a-c). Despite no visual difference on bond surfaces, observation of tensile failures still suggested that bond point formation during thermal calendering can be still responsible for improving tensile properties.
Few studies (Warner 1989; Dharmadhikary et al., 1999) suggest that fibers with lower strength and higher elongation results in higher strength nonwoven fabric compared to that of higher strength and low elongation fibers. A study on thermal bonded PP nonwovens by Wei et al (1985) conclude that fiber which has less orientation in amorphous region get fused easily under thermal bonding than that of much oriented fibers.

5.3.5 Thermal Properties

5.3.5.1 Thermal degradation of nanomax/PP composite fiber produced with spunbond process

Thermal stability behavior of PP and PP/nanoclay spunbond fiber samples studied using Thermo gravimetric analyzer (TGA) is shown in Figure 5.10 and the values of onset degradation temperature are given in Table 5.8. As shown in Figure 5.10, there is significant improvement in the thermal stability for PP/nanoclay fiber samples compared to pure PP.
Onset degradation temperature is improved up to 100°C with the addition of nanoclay particles. The enhanced thermal stability obtained with clay addition is due to the superior insulating behavior of the clay particles. Also clay particles acts as mass transport barrier to the volatile products generated during decomposition (Ding et al., 2005). Other studies (Marchant et al., 2002; Kato et al., 1997; Chen et al., 2003; Seo et al., 2000) on thermal degradation of clay/polymer matrix suggest that clay intercalation or exfoliation in the polymer matrix contributes to enhanced thermal stability.

**Table 5.8:** Onset degradation temperature of PP and PP-nanoclay spunbond fibers

<table>
<thead>
<tr>
<th>Clay type</th>
<th>Onset degradation temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>345</td>
</tr>
<tr>
<td>Nanomax PP-1%</td>
<td>444</td>
</tr>
<tr>
<td>Nanomax PP-2%</td>
<td>444</td>
</tr>
<tr>
<td>Nanomax PP-3%</td>
<td>447</td>
</tr>
</tbody>
</table>
Figure 5.10: TGA curves of PP and PP-nanoclay spunbond fibers (Heating rate - 10°C/minute)

5.3.5.2 Tensile property retention of spunbond fabrics after heat exposure

The results of change in tensile property after heat treatment are shown in Figure 5.11. It shows that after heat treatment there is up to 8% decrease in peak load for PP nonwoven samples but there is no decrease in peak load is observed for samples based on nanoclay. This further proves that presence of nanoclay acts as heat stabilizing agent. Even though percent decrease in strain at break is higher for nanoclay added samples, the final value of strain at break after heat treatment process is higher than that of PP nonwoven samples.
Figure 5.11: % Loss in mechanical property of thermal bonded spunbond nonwoven fabric (Bonding temperature: 145°C) after aging at 100°C for 36 hours

5.3.6 Dynamic mechanical analysis

Solid-state mechanical properties of the composites such as modulus are one of indirect measure of the extent of dispersion of clay particles in the polymer matrix. Also, this study of visco-elastic properties of polymer nanocomposites is mainly important for load bearing applications where the stress is applied for longer period of time. Dynamic mechanical analysis (DMA) measures the response of the material to a cyclic deformation as a function of the temperature. Three main parameters are obtained from DMA:
The storage modulus (E’) - represents the elastic response to deformation

The loss modulus (E”) – represents the plastic response to deformation

\[ \tan \delta = \frac{E'}{E''} \], for determining the occurrence of molecular mobility transitions such as the glass transition temperature

All 3 parameters are useful to analyze the nature of interaction between the polymer matrix and the clay particles.

Storage moduli of the nonwoven fabrics at the temperature range of from -100 to 150 °C are compared in Figure 5.12. It shows that at all temperature ranges storage modulus of clay added nonwoven samples are higher than that of PP. This shows that presence of nanoclay acts as a reinforcement agent and improves the modulus of the samples. For polymer/nanoclay systems, a marked improvement in storage modulus represents good interaction between polymer chains and the nanoclay particles. When the clay particle intercalates or exfoliates in the polymer matrix, the polymer chains between the clay platelets will have restricted chain mobility and hence there will be increase in storage modulus. Kawasumi et al., (1997) first studied the reinforcement effect of the nanoclay particles on PP matrix.
Figure 5.12: Storage modulus of thermal bonded spunbond nonwoven fabric (Bonding temperature: 145°C)

Table 5.9: Storage modulus of spunbond nonwoven fabric at different temperature range

<table>
<thead>
<tr>
<th>Sample</th>
<th>Storage modulus at different temperature (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
</tr>
<tr>
<td>PP</td>
<td>53</td>
</tr>
<tr>
<td>Nanomax PP-1%</td>
<td>95</td>
</tr>
<tr>
<td>Nanomax PP-2%</td>
<td>143</td>
</tr>
</tbody>
</table>

5.4 CONCLUSIONS

This study shows enhanced mechanical property improvement to spunbond nonwoven fabrics with nanoclay addition at a clay loading of 1 to 3%. Presence of nanoclay particles act as a superior insulator and mass transport barrier to the volatile products during degradation
and helps in improving the thermal stability. This improved thermal stability property can also be a factor in improving the mechanical property of spunbond nonwoven fabric by improving the heat resistance of fibers at bond spots. It has also been found that nanoclay addition alters crystallization kinetics of PP and results in microstructure of nanoclay/PP composite fibers. Higher Avrami constant n, and crystallization rate constant in nanoclay/PP composite fiber suggest that nanoclay particles act as a heterogeneous nucleating agent in the polymer matrix and increase the crystallization rate of the host polymer. Reinforcement effect of the nanoclay is confirmed by increase in storage modulus of nonwoven fabric at a temperature range from -100 to 150°C.

5.5 REFERENCES

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16. Loo S.L., Gleason K.K., Polymer, 2004, 45, 5933-5939


CHAPTER 6

STRUCTURE AND PROPERTIES OF NANOCLAY ADDED BICOMPONENT SPUNBOND FIBERS AND NONWOVENS
Structure and Properties of Nanoclay added Bicomponent Spunbond Fibers and Nonwovens

ABSTRACT

Bicomponent spunbond fibers of nanoclay-PP were produced and subsequently the webs were thermal bonded to produce spunbond fabrics with a basis weight of 50gsm. Bicomponent fibers and nonwoven fabrics were characterized for their structure and mechanical properties. It was found that with the addition of nanoclay there is up to 25% increase in maximum stress and up to 60% increase in breaking strain was obtained for nonwoven samples. Tensile property of spunbond thermal bonded nonwoven samples doesn’t not change with position of the nanoclay and the properties are comparable at lower nanoclay loading, while at higher nanoclay loading mechanical properties of samples where nanoclay is located in sheath was found to be higher. Also, shift in the optimum bonding temperature to lower temperature was observed for both the samples, with the effect was more pronounced when nanoclay is located in sheath. The improvement in tensile property in nonwoven fabric is attributed to the changes in the bonding mechanism and improved thermal stability caused by presence of nanoclay. Thermal degradation kinetic studies using TGA shows thermal stability is increased up to 100°C with the addition of nanoclay and the effect is more pronounced when nanoclay particles are distributed in the sheath of the fiber.

6.1 INTRODUCTION

Nanocomposites based on nanoclay additive found great interest because of their low cost, ready availability and improvement in mechanical, thermal, and barrier properties (Ton-That
et al., 2004). The composites based on nanoclay (layered silicates) are generally termed as polymer layered silicate nanocomposites (Giannelis, 1996). Most of the research based on nanoclay additives has found much interest when Toyota research group successfully prepared polyamide based nanocomposites by in-situ polymerization technique (Usuki et al., 1993a, 1993b; Kojima et al., 1993). After that many studies were carried out in different polymer systems to understand the nature of interaction between nanoclay and polymer matrix and the property improvement imparted because of the presence of nanoclay. As the silicate particles are polar in nature, it has good compatibility with polar polymer like Nylon. Therefore in these cases, even without surface modification and presence of compatibilizer nanocomposite structures can be obtained. Many studies on Nylon nanocomposites showed greater improvement in the material properties because of its good compatibility with silicate particles (Li et al., 2006; Loo et al., 2004; Fornes et al., 2001; Mehrabzadeh et al., 2002; Zhang et al., 2006). Silicate particles exhibit incompatibility with non-polar polymers like polypropylene (PP) and polyethylene (PE). Studies on surface modification of nanoclay found to improve the compatibility with non-polar polymers. This can be done by exchange of the cations in the interlayer with cationic surfactants like alkylammonium or alkylphosphonium ions. This process lowers the surface energy of the clay and renders the nanoclay organophilic. The surface modified clay is thus called as organoclay and is compatible with organic polymers. Usuki et al (1993) first reported the organically modified clay by replacing the sodium ions present in the interlayer with ammonium cations of ω-amino acids.
For PP based nanoclay composites, organoclay still could not provide enough nanoclay-polymer interaction to produce high degree of dispersion. Kawasumi et al. (1997) first used maleic anhydride grafted PP as a compatibilizer for PP/nanoclay composites. In this they found that presence of compatibilizer improves the interaction between PP and organically modified clay with stearyl ammonium. Intercalation arises because of the formation of hydrogen bond between maleic anhydride group and the oxygen groups of the silicate. Many studies were carried out later (Chen et al., 2003; Lertwimolnum et al., 2005; Wenyi et al., 2006) based on maleic anhydride-modified PP and found improvement in clay dispersion and mechanical properties.

Compared to films, fiber based systems are known to provide many beneficial characteristics because of their high surface areas, so a combination of nanocomposite technology and fiber formation is highly sought after. However, melt spinning is a more complex process, where fiber fine structure development is determined by polymer-chain responses to tension, temperature, and shear deformation in the spin line. It has been reported that nanoclay incorporation alters the polymer melt rheology and crystallization kinetics (Ma et. al. 2002; Zhang et. al., 2004; Seo et. al, 2000; Varga and Karger-Kocsis 1995), which are the key factors affecting microstructure formation during the fiber melt spinning. Although there were some studies carried on nanoclay modified fibers (Wenyi et. al. 2006; Joshi et. al. 2006; Svoboda et. al., 2002, and nonwoven webs (Bhat et al., 2008), there were no reported studies on the effect of distribution of nanoclay on the fibers. In this study, nanoclay particles are
incorporated in core and sheath of bicomponent spunbond fibers and their effect on structure and mechanical properties were analyzed.

6.2 EXPERIMENTAL

6.2.1 Materials

PP pellet (PP CP360H), which has an average melt flow rate of 35g/10 minute was obtained from Sunoco chemicals. Commercially available pre-compounded montmorillonite based organo-clay/PP- Nanomax® PP was purchased from Nanocor (Arlington Heights, IL, US) and used for the study. Nanomax® PP contains about 50% Nanomer® Nanoclay that is surface modified montmorillonite clays, PP, and maleic anhydride modified polyolefin compatibilizer and is prepared by melt compounding to produce intercalated structures based on patented technology (Qian et al. 2002, Qian et. al., 2003).

6.2.2 Nonwoven production

Even Nanomax® PP precompounded masterbatch pellet containing PP, nanoclay and compatibilizer and good processability was reported in various plastic processing equipment, our initial attempt to spin composite fibers by direct mixing Nanomax PP and PP and extrusion in fiber spinning equipments cause a series of spinning problems including melt fractures, filter blockages, spinline breakages and large agglomeration of clay particles. Therefore nanomax® PP and PP were melt compounded further to reduce clay loading to 5% in the final masterbatch product. Masterbatch preparation was carried out with the help of
Techmer (Clinton, TN). Master batch samples were produced at a temperature of 205°C with a screw speed of 225 rpm.

Spunbond nonwoven fabrics were produced in Hill’s spunbond line at Nonwoven Institute’s pilot lab as shown in Figure 6.1. In this process, nonwoven fabrics are directly produced in a single step. Spunbond nonwoven fabrics with clay additive Nanomax PP were produced. The extrusion temperature was set at 240°C and a throughput of 0.8 g/hole/minute was maintained. The web basis weight was maintained at 50 g/m².

![Diagram of Spunbond process](image)

**Figure 6.1:** Schematic of Spunbond process (Fedorova, 2006)
In order to analyze the effect of distribution of nanoclay particle on the properties of spunbond fabric, 2 different types of spunbond fibers were produced as shown in Figure 6.2. In type 1, nanoclay particles are only present in the sheath of fiber structure and in type 2, nanoclay particles are present in the core of fiber structure. The ratio between core and sheath in both the structures is maintained at 50 wt%/50wt%. Table 6.1 shows the details of produced spunbond fabrics. Spunbond fibers were also collected for characterization.

Figure 6.2: Schematic of nanoclay location in different spunbond fibers

Table 6.1: Spunbond nonwoven fabric details

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Concentration of clay, wt%</th>
<th>Average fiber denier</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Core</td>
<td>Sheath</td>
</tr>
<tr>
<td>PP</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>1.0</td>
</tr>
<tr>
<td>NPP-SB1</td>
<td>---</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>---</td>
</tr>
<tr>
<td>NPP-SB2</td>
<td>2.0</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>---</td>
</tr>
</tbody>
</table>

SB – represents Spunbond
The produced spunbond fabrics were thermal calendared at different temperatures of 135, 140, 145, 150, 155 and 160°C.

6.2.3 Crystallization and Fiber Fine Structures Analysis

6.2.3.1 Melting and crystallization behavior and crystallinity

Melting and crystallization behavior of the composite was analyzed using Perkin-Elmer differential scanning calorimeter (DSC). 4.5 ± 0.5mg of nanoclay/PP composite fibers were heated in a nitrogen atmosphere from 25 to 190°C. In all cases the heating/cooling rate was maintained at 10°C/min.

The crystallinity of the samples was calculated using the following formula:

$$\text{% Crystallinity} = \frac{\Delta H}{\Delta H_{PP}^0} \times 100$$

(6. 1)

where, $\Delta H$ is the enthalpy of fusion of the sample (J/g) and $\Delta H_{PP}^0$ is the enthalpy of fusion of completely crystalline PP (~ 207 J/g) (Karger-Kocsis, 1995).

6.2.3.2 Wide angle X-ray Scattering

Crystalline orientation in spunbond fibers is analyzed using Wide angle X-ray Scattering facility at Brookhaven National Laboratory in beam X10A. The distance between the source and sample is kept at 100.6cm and the diffraction pattern obtained is used for analysis of crystalline orientation of the fibers. Wavelength of X-ray used for the study is 1.095 Å.
6.2.4 Thermal degradation

Thermal degradation of the samples was analyzed using Perkin-Elmer diamond Thermo-gravimetric analyzer. Samples of weight (5-10mg) were placed in the sample pan and heated from 25°C to 600°C in N₂ atmosphere. Onset degradation temperature (T_{onset}) was measured at a temperature where 10% degradation of the sample occurs.

6.2.5 Tensile Properties

Tensile properties of fabrics were measured according to ASTM standard D3035, in Instron tensile tester using 45.36 kg load cell. The gauge length used was 7.62 cm and the fabrics were extended at a rate of 300 mm/minute. Five specimens per sample of width 2.54cm and 15.24cm wide were cut in both machine and cross direction of the thermal bonded nonwoven fabric. The average force required to break the nonwoven fabric and elongation at break are reported.

6.3 RESULTS AND DISCUSSIONS

6.3.1 The Effect of Nanoclay on Crystallization and Fine Structures of nanoclay/PP Composite Fibers

6.3.1.1 Melting and crystallization of nanomax/PP composite fibers

The melting endotherm of spunbond fibers with nanoclay particles added in the sheath and core are shown in Figure 6.3. Unlike the melting endotherm of PP spunbond fibers, the melting endotherm of nanoclay added spunbond fiber when nanoclay is located in sheath is
narrower and the first melting peak is more prominent. This shows that the crystal sizes are much narrower when nanoclay particles are present in sheath. Also, changes in shape of melting endotherm implicate possible alteration of fiber microstructure as the result of nanoclay addition; even there are little changes in overall crystallinity (Table 6.2). Whereas, melting endotherm of nanoclay samples when nanoclay is located in core shows two distinct melting peaks as that of PP with shift in the second melting peak to lower temperature. There is no significant difference in melting behavior was observed for nanoclay added samples based on nanoclay location.

**Table 6.2: Melting and % crystallinity of nanoclay-PP spunbond fibers**

<table>
<thead>
<tr>
<th>% Nanoclay loading</th>
<th>On-set Melting Temp (°C)</th>
<th>1st Peak, Melting temperature Tm, (°C)</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>160.3</td>
<td>162.4</td>
<td>44</td>
</tr>
<tr>
<td>Nanoclay in Sheath</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0%</td>
<td>159.1</td>
<td>163.2</td>
<td>46</td>
</tr>
<tr>
<td>2.0%</td>
<td>159.0</td>
<td>164.0</td>
<td>44</td>
</tr>
<tr>
<td>Nanoclay in Core</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0%</td>
<td>159.7</td>
<td>163.0</td>
<td>46</td>
</tr>
<tr>
<td>2.0%</td>
<td>159.7</td>
<td>163.0</td>
<td>46</td>
</tr>
</tbody>
</table>
Figure 6.3: DSC Heating thermogram of nanoclay-PP spunbond fibers with nanoclay located in (a) Sheath (b) Core
6.3.1.2 Analysis of Crystalline Orientation

Crystalline orientation of nanoclay added spunbond fibers were analyzed from the diffraction pattern of wide angle x-ray scattering as shown in Figure 6.4. Figure 6.4a shows the diffraction pattern of PP spunbond fibers corresponds to slightly oriented monoclinic crystal form of PP [Jinan et al., 1989]. After addition of nanoclay particles, the crystal orientation is improved and results in formation of highly oriented monoclinic crystal form with all types of nanoclay addition with nanoclay location in both core and sheath. [Figure 6.4b-e].
Figure 6.4: Wide angle X-ray Scattering patterns of Spunbond fibers

(a) PP

(b) Sheath - 2%

(c) Sheath - 3%

(d) Core - 2%

(e) Core - 3%
6.3.2 Thermal degradation

Thermal stability behavior of PP and PP/nanoclay spunbond fiber samples studied using Thermo gravimetric analyzer (TGA) is shown in Figure 6.5 and the values of onset degradation temperature are given in Table 6.3. As shown in Figure 6.5, there is significant improvement in the thermal stability for PP/nanoclay fiber samples compared to pure PP. Onset degradation temperature is improved up to 100°C with the addition of nanoclay particles. Thermal degradation temperature of fiber samples with nanoclay located in core of a fiber is found to be less when compared to sample which contain nanoclay in sheath. This is because absence of nanoclay particles in the fiber sheath results in earlier degradation. The mechanism of influence of nanoclay on thermal stability is further explained in Chapter 7.

![TGA curves of PP and nanoclay-PP spunbond fibers at 1% nanoclay loading (Heating rate -10°C/minute)](image)

**Figure 6.5:** TGA curves of PP and nanoclay-PP spunbond fibers at 1% nanoclay loading (Heating rate -10°C/minute)
Table 6.3: Onset degradation temperature of PP and PP-nanoclay spunbond fibers at 1\% nanoclay loading

<table>
<thead>
<tr>
<th>Nanoclay location</th>
<th>Onset degradation temperature $T_{\text{onset}}{^{\circ}\text{C}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>345</td>
</tr>
<tr>
<td>Sheath</td>
<td>444</td>
</tr>
<tr>
<td>Core</td>
<td>447</td>
</tr>
</tbody>
</table>

6.3.3 **Tensile properties of thermal bonded nonwoven fabrics**

Thermal bonded nonwoven fabrics with nanoclay additives showed significant increases both in breaking strength and strain at break. Table 6.4 shows the value of average maximum stress of the nonwoven fabrics at different thermal bonding temperature. At all thermal bonding temperature, breaking stress value is higher for nanoclay added samples irrespective of nanoclay locations. At lower nanoclay loading, there was no significant difference observed between samples where nanoclay is distributed either in sheath or core, but at 3\% nanoclay loading significant difference between the samples is observed.
Table 6.4: Comparison of effect of nanoclay location on breaking stress of PP/nanoclay spunbond thermal bonded nonwoven fabrics along machine direction

<table>
<thead>
<tr>
<th>Bonding temperature (°C)</th>
<th>PP</th>
<th>Maximum stress (N/mm)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1%</td>
<td>2%</td>
<td>3%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sheath</td>
<td>Core</td>
<td>Sheath</td>
<td>Core</td>
<td>Sheath</td>
<td>Core</td>
</tr>
<tr>
<td>135</td>
<td></td>
<td>1.00 (0.02)</td>
<td>1.51 (0.10)</td>
<td>1.48 (0.04)</td>
<td>1.99 (0.04)</td>
<td>1.98 (0.07)</td>
<td>2.47 (0.16)</td>
<td>1.93 (0.09)</td>
</tr>
<tr>
<td>140</td>
<td></td>
<td>1.24 (0.04)</td>
<td>1.89 (0.09)</td>
<td>1.84 (0.07)</td>
<td>2.33 (0.12)</td>
<td>2.26 (0.06)</td>
<td>2.34 (0.15)</td>
<td>2.16 (0.11)</td>
</tr>
<tr>
<td>145</td>
<td></td>
<td>1.71 (0.07)</td>
<td>2.28 (0.13)</td>
<td>2.18 (0.13)</td>
<td>2.09 (0.05)</td>
<td>2.14 (0.07)</td>
<td>2.22 (0.12)</td>
<td>1.96 (0.06)</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td>1.30 (0.06)</td>
<td>2.12 (0.11)</td>
<td>2.09 (0.13)</td>
<td>1.88 (0.11)</td>
<td>2.08 (0.04)</td>
<td>1.79 (0.07)</td>
<td>1.61 (0.15)</td>
</tr>
</tbody>
</table>
Table 6.5: Mechanical properties of PP and PP/nanoclay spunbond thermal bonded nonwoven fabrics at optimum bonding temperature

<table>
<thead>
<tr>
<th>Nanoclay Location</th>
<th>Conc. %</th>
<th>Optimum Bonding Temp. (°C)</th>
<th>Breaking Stress (N/mm)</th>
<th>Breaking Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>MD</td>
<td>CD</td>
</tr>
<tr>
<td>PP</td>
<td>--</td>
<td>145</td>
<td>1.71 (0.07)</td>
<td>1.12 (0.02)</td>
</tr>
<tr>
<td>Sheath 1%</td>
<td>1%</td>
<td>145</td>
<td>2.28 (0.13)</td>
<td>1.24 (0.05)</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>140</td>
<td>2.33 (0.12)</td>
<td>1.28 (0.07)</td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td>135</td>
<td>2.47 (0.16)</td>
<td>1.05 (0.07)</td>
</tr>
<tr>
<td>Core 1%</td>
<td>1%</td>
<td>145</td>
<td>2.18 (0.13)</td>
<td>1.42 (0.03)</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>140</td>
<td>2.26 (0.06)</td>
<td>1.51 (0.07)</td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td>140</td>
<td>2.16 (0.11)</td>
<td>1.30 (0.09)</td>
</tr>
</tbody>
</table>

Figure 6.6 and Figure 6.7 shows the effect of breaking stress on bonding temperature for spunbond nonwoven fabric when nanoclay particle is present respectively in sheath and core of fiber. Increase in breaking stress was observed both in machine and cross direction. It is observed that with increase in clay loading optimum bonding temperature found to shift to lower bonding temperature. Table 6.5 shows tensile properties of nonwoven fabrics at their optimum bonding temperature both in machine and cross direction. It can be noticed from Table 6.5 that for PP and nanoclay added PP spunbond nonwoven samples, optimum bonding temperature is 145°C at lower clay loading levels. But with increase in clay loading levels, it can be observed that there is shift in optimum bonding temperature for both the samples whether nanoclay is either distributed in sheath or core. This effect is more pronounced when nanoclay is distributed in sheath, where there is continuous shift in the bonding temperature with increase in clay loading was observed. This is explained from the
results of thermal degradation study that the presence of nanoclay in the sheath helps in absorbing the heat energy and helps in preventing fiber degradation.

**Figure 6.6:** Effect of nanoclay addition on breaking stress of thermal bonded spunbond nonwovens with nanoclay location in sheath (a) machine direction (b) cross direction
Figure 6.7: Effect of nanoclay addition on breaking stress of thermal bonded spunbond nonwovens with nanoclay location in core (a) machine direction (b) cross direction
\textbf{Figure 6.8:} Effect of nanoclay location on breaking stress (thermal bonded spunbond nonwovens (along machine direction) for 3\% nanoclay loading

\textbf{Figure 6.9:} Effect of nanoclay location on strain at break (thermal bonded spunbond nonwovens (along machine direction) for 3\% nanoclay loading
Figure 6.8 compares effect of nanoclay position on the breaking stress of thermal bonded spunbond nonwoven fabric at 3% nanoclay loading. It is found that irrespective of the position of clay, breaking stress is found to increase and the increment is similar in both the cases. Table 6.4 compares the breaking stress of samples based on nanoclay position at different bonding temperatures and nanoclay loading. It can be noticed that at lower nanoclay loading, there is no effect on location of nanoclay on the breaking stress, but at 3% nanoclay loading, breaking stress was found out be higher when nanoclay is located is sheath. This might be because of the higher thermal stability for samples when nanoclay is located in sheath compared to when nanoclay is located in core. Figure 6.9 shows the effect of nanoclay location on the breaking strain of spunbond nonwoven fabric along machine direction at 3% nanoclay loading. With the addition of nanoclay particles, breaking strain is found to increase at different bonding temperatures. Improvement of tensile properties may be resulted from bond formation and improvement of fiber thermal resistance by addition of nanoclay.

6.4 CONCLUSIONS

This study shows enhanced mechanical property improvement to spunbond nonwoven fabrics with nanoclay addition at a clay loading of 1 to 3%. Irrespective of the position of nanoclay, mechanical property of spunbond thermal bonded nonwoven fabric is found to increase with nanoclay addition. Presence of nanoclay particles act as a superior insulator and mass transport barrier to the volatile products during degradation and helps in improving the thermal stability. This improved thermal stability property can also be factor in improving the mechanical property of spunbond nonwoven fabric by improving the heat resistance of
fibers at bond spots. It has also been found that the presence of nanoclay increases the crystalline orientation in PP.

6.5 REFERENCES


15. Loo S.L., Gleason K.K., Polymer, 2004, 45, 5933-5939


CHAPTER 7

THERMAL DEGRADATION KINETICS OF
NANOCLAY-PP FIBERS PRODUCED BY MELT SPINNING
Thermal Degradation Kinetics of Nanoclay-PP Fibers Produced by Melt Spinning

Abstract
Nanocomposite fibers of polypropylene and montmorillonite-based organoclay were produced by melt-spinning process, and their thermal degradation properties were studied. The addition of nanoclay has significant effect on the increase in the thermal degradation of polypropylene fibers. Thermal degradation kinetic study carried out using Ozawa-Flynn-Wall method shows presence of nanoclay increases the activation energy required for degradation.

7.1 INTRODUCTION
Owing to the low density nature, polypropylene is one of the most widely used thermoplastic materials in many different applications. But it has its own disadvantages such as low toughness, low service temperature. Many different studies were carried by many researchers to enhance the thermal degradation and thermal stability of polypropylene. One of the most widely used methods to improve the thermal stability in recent times is addition of nanofillers to produce polymer nanocomposites. Different types of fillers such as talc, carbon nanotubes were tried with polypropylene to improve its thermal stability. Layered silicates are one type of nanofiller which is widely used to improve the thermal behavior of polymers. Improved thermal stability based on nanoclay composite was first reported by Blumstein [1965] on
intercalated PMMA/clay composites. PMMA/clay composites found to have 40-50°C higher decomposition temperature. Improved thermal stability is attributed to the intercalation or exfoliation of the clay particles. Later on many different studies were carried out using differed types of layered silicates on different polymer matrix systems.

The main factors which influence the thermal stability are degree of clay dispersion nanoclay loading. The improvement in thermal stability is directly related to the degree of clay dispersion. Higher degree of exfoliation results in enhancement of thermal degradation and stability (Srivastava et.al., 2006; Riva et.al., 2002; Guo et al., 2004). Liu et al., [2003] in their study observed that improvement in thermal stability is much more significant in exfoliated nanocomposite than in intercalated nanocomposite. Improvement in thermal stability is not directly related to concentration of nanoclay. Agglomeration of nanoclay at higher nanoclay concentration will have negative influence on the thermal stability of polymers (Lim et al., 2002; Paul et al., 2003). Apart from nanoclay dispersion and concentration, method of preparation of nanocomposite also found to influence the thermal stability. Zheng and White [2003] observed that increase in thermal stability is significant in melt blending process compared to that of in situ polymerization method. Although different studies were carried on thermal stability of nanoclay on different polymer systems, the exact mechanism behind the thermal stability improvement caused by nanoclay is not fully understood. The most commonly accepted reason is the presence of nanoclay helps in enhancing the performance of char layer, which hinders the diffusion of volatile decomposition products (Zhu et al., 2001; Gilman, 199; Alexandre et al., 2000; Kotsilkova et al., 2001; Giannelis and Burnside,
Also the exfoliated clay particles act as an insulator and the formation of tortuous path also hinders the passage of volatile decomposition products (Wang et al., 2004). Blumstein [1965] proposes that the enhanced thermal stability is result of the restricted thermal motion of polymer chains between the clay layers. In all the reported studies, the major factor which influences the thermal behavior is distribution of the layered silicates in the polymer matrix. Nanocomposite structures with intercalated or exfoliated structures found to have improved thermal behavior.

In this study, using melt intercalation technique nanocomposite fibers of PP and montmorillonite based organoclay were produced and their thermal behavior and kinetics of thermal degradation were carried out.

7.2 EXPERIMENTAL

7.2.1 Materials

Spunbond grade PP (PP CP360H) with an average melt flow rate of 35g/10 minute was supplied by Sunoco Chemicals (Philadelphia, PA). A commercially available, precompounded, montmorillonite-based organoclay-PP (Nanomax PP) was purchased from Nanocor (Arlington Heights, IL). Nanomax PP contained about 50% Nanomer nanoclay (i.e., surface-modified montmorillonite clays), PP, and a maleic anhydride modified polyolefin compatibilizer and was prepared by melt compounding, on the basis of patented technology, to produce intercalated structures (Qian et al. 2002, Qian et. al., 2003).
7.2.2 Preparation of masterbatch

Even Nanomax PP precompounded masterbatch pellets containing PP, nanoclay, and compatibilizer and good processability were reported in various plastic processing equipment, our initial attempt to spin the composite fibers by the direct mixing of Nanomax PP and PP and extrusion in fiber-spinning equipment caused a series of spinning problems, including melt fractures, filter blockages, spin-line breakages, and large agglomeration of the clay particles. Therefore, Nanomax PP and PP were melt compounded further to reduce the clay loading. Nanoclay–PP composite pellets with nanoclay loadings of 5 wt % were prepared by melt compounding at 205°C in a TechmerPM (Clinton, TN).

7.2.3 Melting spinning of nanoclay-PP composite fibers

The produced masterbatch samples were then mixed and extruded with PP to produce nanoclay/PP composite fibers with the Hills Spunbond line in the Nonwovens Institute, North Carolina State University (Raleigh, NC, USA). Spinning speed was maintained approximately at 3500 m/m and extrusion temperature was 240°C. A melt throughput of 0.8 g hole⁻¹ minute⁻¹ was maintained. As a control, PP without nanoclay was melt extruded at the same condition. Fiber sizes of all samples were about 2 denier.

In order to analyze the effect of distribution of nanoclay particle on thermal degradation, core-sheath (50wt%-50wt %) bicomponent fibers were produced shown in Figure 7.1. In type 1, nanoclay particles are distributed in the whole of fiber cross-section, in type 2, nanoclay
particles are only present in the sheath of the fiber and in type 3, and they are located only in the core of the fiber. Nanoclay-PP fibers as given in Table 7.1 were produced.

![Diagram showing nanoclay location in different fibers]

**Figure 7.1:** Schematic of nanoclay location in different fibers

<table>
<thead>
<tr>
<th>Fiber type</th>
<th>Concentration of clay, wt%</th>
<th>Average fiber denier</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>---</td>
<td>2.0</td>
</tr>
<tr>
<td>Type 1</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Type 2</td>
<td>2.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Type 3</td>
<td>3.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Type 2</td>
<td>1.0</td>
<td>2.7</td>
</tr>
<tr>
<td>Type 3</td>
<td>1.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

**Table 7.1:** Spunbond fiber details
7.2.4 Thermal degradation
Thermal degradation of the samples was analyzed using Perkin-Elmer diamond Thermo gravimetric analyzer. Samples of weight (5-10mg) were placed in the sample pan and heated from 25°C to 600°C in N₂ atmosphere. Onset degradation temperature was measured at a temperature where 10% degradation of the sample occurs.

7.2.5 Kinetics of thermal degradation
For the kinetic study, the samples were heated at different heating rates of 10, 20 and 30°C/minute. The samples were heated at these heating rates to find the activation energy of the fiber samples at different weight loss %.

7.3 RESULTS AND DISCUSSION
7.3.1 Effect of nanoclay loading
Thermal stability behavior of PP and PP/nanoclay fibers studied using Thermo gravimetric analyzer (TGA) is shown in Figure 7.2 and the values of onset degradation temperature are given in Table 7.1. As shown in Figure 7.2, there is significant improvement in the thermal stability for PP/nanoclay fiber samples compared to pure PP. Onset degradation temperature is improved up to 100°C with the addition of nanoclay particles. Figure 7.3 shows the derivative thermogravimetric curves for the PP and PP/nanoclay spunbond fiber samples. From the derivative thermogravimetric curves, the temperature correspond to maximum rate of weight loss is denoted as peak temperature (T_{peak}). It can be observed that presence of nanoclay in fiber samples increases the peak temperature of degradation. It can also be
observed that increase in nanoclay loading has little or no effect on both the onset and peak temperature.

The enhanced thermal stability obtained with nanoclay addition is due to the superior insulating behavior of the clay particles. Also clay particles acts as mass transport barrier to the volatile products generated during decomposition (Ding et al., 2005). Other studies (Marchant et al., 2002; Kato et al., 1997; Chen et al., 2003; Seo et al., 2000) on thermal degradation of clay/polymer matrix suggest that clay intercalation or exfoliation in the polymer matrix contributes to enhanced thermal stability. It was hypothesized that char formation during degradation hinders the diffusion of volatile decomposition produces and helps in increasing the thermal stability.

The difference between peak temperature of degradation and onset temperature is given in Table 7.2 as degradation temperature range. It can be noticed that range where degradation occurs is higher for PP fiber sample compared to that of nanoclay fiber samples. This phenomenon is also noticed from Figure 1, which shows steep decrease in weight loss % in a narrower range of temperature for nanoclay added fiber samples. As the nanoclay particles are highly inorganic in nature, they absorb the heat energy during initial stages of degradation and contribute to increase in thermal stability. But with rise in temperature, when nanoclay particles start to degrade, apart from the heat energy supplied during the degradation process the already stored energy in nanoclay particles also contributes to the
nanoclay degradation. This causes degradation of nanoclay containing fiber samples at a narrower range after the initial thermal stability caused by presence of nanoclay.

**Table 7.2:** Onset degradation temperature of PP and PP-nanoclay Type 1 fibers

<table>
<thead>
<tr>
<th>Nanoclay type</th>
<th>Concentration of clay, wt%</th>
<th>Onset degradation temperature</th>
<th>Peak degradation temperature</th>
<th>Degradation temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>--</td>
<td>345°C</td>
<td>421°C</td>
<td>76°C</td>
</tr>
<tr>
<td>Nanomax</td>
<td>1.0</td>
<td>444°C</td>
<td>476°C</td>
<td>32°C</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>444°C</td>
<td>479°C</td>
<td>35°C</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>447°C</td>
<td>479°C</td>
<td>32°C</td>
</tr>
</tbody>
</table>

**Figure 7.2:** TGA curves of PP and PP-nanoclay Type-1 fibers (Heating rate -10°C/minute)
To further understand how the presence of nanoclay affects the kinetics of degradation, nonisothermal degradation is carried out for fiber samples at different heating rates of 10, 20, 30°C/minute. The effect of increase in heating rate on TGA plots for fiber samples are given in Figure 7.4 – 7.5. It can be observed that with increase in heating rate, both onset and peak temperature increases for all the fiber samples. This is because shorter time available for samples at higher heating rates.
Figure 7.4: TGA curves of Type 1 fibers at different heating rates for (a) PP (b) 1% Nanoclay
Figure 7.5: TGA curves of Type 1 fibers at different heating rates for (c) 2% Nanoclay (d) 3% Nanoclay
Kinetics of degradation of fiber samples can be analyzed by calculating the activation energy of the samples. The activation energy can be calculated using various methods. A method by Ozawa, Flynn and Wall is given by (Flynn and Wall, 1966),

\[
\ln(\beta) = \ln\left[A f(\alpha) \left(\frac{d\alpha}{dT}\right)\right] - \frac{E}{RT}
\]

(1)

Where \(\beta\) – heating rate, \(\alpha\) – degree of conversion of mass loss, \(A\) the pre-exponential factor, \(E\) the activation energy (kJ/mol) and \(R\) is the gas constant.

A plot of \(\ln(\beta)\) at different heating rates vs \(1/T\) (temperature corresponds to particular mass loss) should give a straight line fit. The slope of the straight line is directly proportional to the activation energy \((-E/R)\).
Figure 7.6: Plot of ln (heating rate) vs 1/T at different % weight loss for Type 1 fibers with

(a) 1% nanoclay (b) 2% nanoclay
Figure 7.6 shows the plot of ln (β) vs 1/T of spunbond fiber samples at different nanoclay loading. From the slope of the lines activation energy is calculated. Figure 7.7 shows dependence of activation energy at different % weight loss for PP and nanoclay-PP fiber samples. Table 7.3 shows activation energy of samples at different weight loss percentage.

![Graph showing activation energy vs weight loss for PP and Nanomax PP](image.png)

**Figure 7.7:** Dependence of activation energy with % weight loss for Type 1 fibers
### Table 7.3: Activation energy of PP and nanoclay-PP samples

<table>
<thead>
<tr>
<th>Concentration of nanoclay, wt%</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 %</td>
</tr>
<tr>
<td>---</td>
<td>63.2</td>
</tr>
<tr>
<td>1.0</td>
<td>163.1</td>
</tr>
<tr>
<td>2.0</td>
<td>166.7</td>
</tr>
</tbody>
</table>

As shown in the Figure 7.7, the activation energy increases at all the weight percentage for nanoclay added fiber samples. The increase in activation energy suggests that presence of nanoclay particles restricts the flow behavior and hence more energy is required to obtain the same mass loss as in 100% PP and hence improves the thermal stability (Chrissafis et al., 2007, 2009; Wang et al., 2006). The increase in activation energy caused by presence of nanoclay samples can be better explained from Figure 7.8. For PP fiber samples, when the heat energy is applied during the heating process, heat energy is transferred between polymer

![Thermal stability mechanism of nanoclay](image-url)
chains without any hindrances. Presence of nanoclay helps to absorb heat energy, restrict heat/mass transfer between polymer chains and also restricts molecular mobility. As the molecular mobility is the major factor which that contributes to the transport of reactive species within the polymer, presence of nanoclay particles restricts the thermal mobility. All these factors contribute to increase in the thermal degradation of fiber samples.

7.3.3 Effect of nanoclay location

In order to analyze the effect of nanoclay location on thermal behavior, bicomponent fibers with nanoclay particles only in core or sheath of fibers are produced. Figure 7.9 shows the TGA for fiber samples with different nanoclay location. It was observed that there is no difference between samples where nanoclay particles are distributed completely in the fiber matrix and in sheath of fiber. Thermal degradation temperature of fiber samples with nanoclay located in core of a fiber is found to be less than that of other two types. This is because absence of nanoclay particles in the fiber sheath results in earlier degradation. Table 7.4 compares the onset and peak degradation temperature for all the three samples.

<table>
<thead>
<tr>
<th>Nanoclay location</th>
<th>Onset degradation temperature $T_{\text{onset}}$ ($^\circ$C)</th>
<th>Peak degradation temperature $T_{\text{peak}}$ ($^\circ$C)</th>
<th>Degradation temperature range $T_{\text{peak}} - T_{\text{onset}}$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete</td>
<td>444</td>
<td>476</td>
<td>32</td>
</tr>
<tr>
<td>Sheath</td>
<td>447</td>
<td>475</td>
<td>38</td>
</tr>
<tr>
<td>Core</td>
<td>439</td>
<td>461</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 7.4: Onset degradation temperature PP-nanoclay spunbond fibers at 1% nanoclay loading
**Figure 7.9:** TGA curves of PP-nanoclay spunbond fibers at 1% nanoclay loading (Heating rate -10°C/minute)

### 7.4 CONCLUSION

PP/nanoclay nanocomposite fibers were produced by melt spinning process and their thermal degradation properties were studied. Nanoclay addition has significant influence on increase in thermal stability of PP fibers. However increase in nanoclay loading has no effect on the thermal stability. Nonisothermal degradation was carried out to analyze the kinetic of degradation. Activation energy derived from kinetic studies shows presence of nanoclay particles increases the activation energy required for particular mass loss. This increase in activation energy is mainly attributed to restriction of molecular mobility caused by the presence of nanoclay particles.
7.5 REFERENCES


7. Ding C., Jia D., He H., Guo B., Hong H., Polymer testing, 24 (2005), 94-100.


CHAPTER 8

OVERALL CONCLUSIONS AND

RECOMMENDATIONS FOR FUTURE WORK
Overall Conclusions and Recommendation for Future Work

8.1 OVERALL CONCLUSIONS

This research is focused on studying the structure-property relations in polypropylene/layered silicate nanocomposite. Two different commercially available montmorillonite-based organoclay were studied. Nanocomposite fibers and nonwovens of polypropylene and montmorillonite-based organoclay were produced by melt spinning process in presence of polypropylene grafted maleic anhydride as a compatibilizer. Some of the major conclusions are summarized below:

- Nanoclay addition alters crystallization kinetics of PP and result in change in microstructure of nanoclay/PP composite fibers. Higher Avrami constant n, and crystallization rate constant in nanoclay/PP composite fiber suggest that nanoclay particles act as a heterogeneous nucleating agent in the polymer matrix and increase the crystallization rate of the host polymer.

- Nanoclay addition also leads to increases in crystal size as observed in WAXD and DSC analysis. Crystalline orientation is greatly influenced by presence of nanoclay as confirmed by WAXD and WAXS studies. With the presence of nanoclay, mesomorphic form of PP is converted to α-crystalline form, these change in crystalline form suggests nanoclay addition influences the fiber formation process and crystallization behavior.

- Reduction in molecular orientation observed in nanoclay-PP nanocomposite fibers results in significant changes in tensile deformation behavior of fibers. It was also observed that this reduction in fiber is highly dependent on spinning process. Lower
spinning speed (2000m/m) in the multifilament extruder causes higher reduction in fiber orientation, whereas higher spinning speed (3500m/m) in the spunbond process results in comparable fiber orientation or very less decrease in fiber orientation for nanoclay-PP fibers.

- TEM and XRD analysis suggests chances of formation of intercalated/exfoliated nanocomposite morphology. TEM images shows that nanoclay layers are uniformly distributed and the platelets are stacked to the thickness of 10-100nm. Further analysis by XRD reveals that there is increase in the intergallery spacing of the platelets which confirms the intercalation of the nanoclay platelets in the polypropylene matrix.

- Decrease in fiber modulus, tenacity and toughness with increase in strain at break were observed. These observation suggested that nanoclay particles involves fiber formation process and interact with polymer chain, then composite structures created are highly affected by materials and processing parameters both in micro and nano-scale.

- Fiber modulus, tenacity and toughness were greatly influenced by the spinning condition. Lower spinning speed in the multifilament extruder condition results in decrease in fiber modulus, tenacity and toughness with increase in strain at break was observed. Whereas higher spinning speed in the spunbond process results in fiber tensile behavior similar to that of polypropylene fibers. This can be directly related to the change in the fiber orientation at different spinning speed.
Unlike fiber tensile properties, mechanical properties of nanoclay based spunbond thermal bonded fabrics shows greater improvement compared to polypropylene fabrics. This improvement in mechanical property is independent of the location of nanoclay in core or sheath. The improvement in tensile property in nonwoven fabric is attributed to the changes in the bonding mechanism and improved thermal stability caused by presence of nanoclay.

Nanoclay addition has significant influence on increase in thermal stability of PP fibers. Activation energy derived from kinetic studies shows presence of nanoclay particles increases the activation energy required for particular mass loss. This increase in activation energy is mainly attributed to restriction of molecular mobility caused by the presence of nanoclay particles. However increase in nanoclay loading has no effect on the thermal stability, whereas location of nanoclay has an influence on the thermal stability.

8.2 RECOMMENDATIONS FOR FUTURE WORK

Further studies on influence of nanoclay particles on thermal bond formation mechanism can be carried out.

Nanoclay nanocomposite fibers based on polar polymers such as Nylon can be carried out as there is no compatibility issue between the host polymer and the nanoclay.

Theories suggests presence of nanoclay particles creates a tortuous path which might affect the air or oxygen permeability, therefore studies on permeability properties of nanoclay based nanocomposites can be carried out.
APPENDIX A : Mechanical Properties of Spunbond Nonwoven Fabric (100gsm)

Spunbond nonwoven fabrics were produced in Hill’s spunbond line at Nonwoven Institute’s pilot lab. Spunbond nonwoven fabrics with clay additive Nanomax PP and Cloisite 15A were produced. The extrusion temperature was set at 240°C and a throughput of 0.8 g/hole/minute was maintained. The web basis weight was maintained at 100 g/m². The produced spunbond fabrics were thermal calendared at 3 different temperatures of 140, 145 and 150°C.

Table A.1 shows the value of average force required to break the nonwoven fabric and % strain at break for spunbond fabric samples which are thermally bonded at a temperature of 150°C. Figure A.1 shows the stress vs. strain for the PP and PP/nanoclay nonwoven fabric samples.

**Table A.1: Mechanical properties of PP and PP/nanoclay spunbond thermal bonded nonwoven fabric (bonding temperature – 150°C) along machine direction**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak load , lbf</th>
<th>Breaking strain, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>19.9</td>
<td>34.8</td>
</tr>
<tr>
<td>PP+0.5% Nanomax PP</td>
<td>27.9</td>
<td>49.1</td>
</tr>
<tr>
<td>PP+1% Nanomax PP</td>
<td>32.2</td>
<td>57.0</td>
</tr>
<tr>
<td>PP+1% Cloisite 15A/ 2%Epolene</td>
<td>24.7</td>
<td>48.5</td>
</tr>
</tbody>
</table>
It can be noticed that with the addition of clay particle, there is a significant improvement in both peak load and breaking strain. Improvement in peak load is about 60% for PP+1% Nanomax PP samples and up to 24% for PP+1% Cloisite 15A samples. Peak load and breaking strain increases with increase in clay loading for Nanomax type clay samples. Similar trend is observed along machine direction at all the 3 thermal bonding temperatures studied. The greater improvement in peak load in spunbond fabric stage may be caused because of the thermal stability of the fibers at the bond spot or improved frictional behavior between fibers due to the presence of clay particle.
Figure A.2 and Figure A.3 show the behavior of peak load and % strain at break along the nonwoven fabric machine direction at different thermal bonding temperatures studied.

**Figure A.2:** Effect of bonding temperature on peak load of PP and PP/nanoclay spunbond thermal bonded nonwoven fabric along machine direction
The improvement in peak load and breaking strain along cross direction is less than that observed for machine direction. The increase in peak load along cross direction is up to 25%.

**Figure A.3:** Effect of bonding temperature on breaking strain of PP and PP/nanoclay spunbond thermal bonded nonwoven fabric along machine direction

The improvement in peak load and breaking strain along cross direction is less than that observed for machine direction. The increase in peak load along cross direction is up to 25%.

Figure A.4 and A.5 shows the behavior of peak load and % strain at break along the nonwoven fabric cross direction at different thermal bonding temperatures studied.
**Figure A.4:** Effect of bonding temperature on peak load of PP and PP/nanoclay spunbond thermal bonded nonwoven fabric along cross direction

**Figure A.5:** Effect of bonding temperature on breaking strain of PP and PP/nanoclay spunbond thermal bonded nonwoven fabric along cross direction