ABSTRACT

DASDEMIR, MEHMET. Investigating Polymer Interface and Its Influence on Bicomponent Nonwoven Structures for Thermoplastic Composites. (Under the direction of Dr. Behnam Pourdeyhimi, Dr. Benoit Maze, and Dr. Nagendra Anantharamaiah).

Bicomponent fibers are designed to meet requirements of two materials into one single fiber by hosting two components along the fiber length. Conceptually, the structure of these fibers already mimics the fiber-matrix structure of a fiber reinforced composite. In this study, we developed a thermoplastic composite fabrication technique that can allow converting bicomponent nonwovens into composites in a single step by taking advantage of their inherent composite characteristic. This technique not only eliminated the need for any resin or binder usage and post-processing from composite production steps but also provided uniform matrix distribution and excellent wetting capabilities. With using this technique, we successfully produced isotropic thermoplastic composites with polymer combinations of polyethylene terephthalate/polyethylene (PET/PE), polyamide-6/polyethylene (PA6/PE), polyamide-6/polypropylene (PA6/PP), and PP/PE. The effects of processing temperature, fiber volume fraction, and thickness of the preform on the formation and structure of the nonwoven composites were investigated and discussed here. Moreover, the changes on the fine structure of the bicomponent fibers after processing were examined to better explain the mechanics behind the process. We also determined what combination of mechanical properties these novel nonwoven composites can offer.

Polymer interfaces can strongly affect the properties and function of materials. For composite materials, a strong binding at the interface can increase load transfer capabilities and improve mechanical properties. Most of the polymers used in bicomponent fibers are thermodynamically immiscible with each other. Therefore, they are expected to show a weak interface which may cause premature failure. However, the characterization of polymer interfaces and its influence on mechanical properties of bicomponent fibers have not been fully elucidated. In this study, we therefore investigated the influence of polymer type,
composition and interface on the structural and mechanical properties of core/sheath type bicomponent nonwoven fibers to better understand the behavior of these complex systems. After characterizing the polymer interfaces, PP/PE was shown to be the most compatible polymer pairing with the highest interfacial adhesion value. On the other hand, PET/PE was found to be the most incompatible polymer pairings followed by PA6/PP and PA6/PE. Accordingly, the tensile strength values of the bicomponent fibers deviated from the theoretically estimated values depending on the core-sheath compatibility. These results unveiled the direct relation between interface and tensile response of the bicomponent fiber.

The consequences of polymer incompatibility also arose for PET/PE, PA6/PP, and PA6/PE nonwoven composites in which we observed debonding at the fiber-matrix interfaces. We anticipated that this problem would negatively affect the mechanical performance of these composites. Therefore, we also focused our effort on the interface enhancement in PA6/PE and PET/PE nonwoven based composites. For this purpose, we used several reactive compatibilizers at different loading content in the sheath component of bicomponent fiber. Compatibilization temperatures were also varied and the compatibilization efficiency of the compatibilizers was compared. The tensile properties of both PA6/PE and PET/PE nonwoven composites were improved in the presence of compatibilizers. The best performing compatibilizer was found to be styrene-b-ethylene-co-butylene-b-styrene grafted with 2 wt% maleic anhydride. The optimum compatibilizer concentration in terms of tensile properties was the lowest compatibilizer loading of 2 wt%. The characterization of fractured surfaces showed the evidence of adhesion of matrix polymer to reinforcement fiber. As a result, cohesive failure was observed for the composites including compatibilizers. These results show that reactive compatibilization of PA6/PE and PET/PE was achieved during composite fabrication stage and improved the adhesion between two polymers resulting in a higher load transfer and better mechanical properties.
Investigating Polymer Interface and Its Influence on Bicomponent Nonwoven Structures for Thermoplastic Composites

by
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DEDICATION

My family is the most precious asset in my life. This dissertation is therefore dedicated to:

- My daughters Nisa Nur and Yagmur who brought the greatest joy to my life;
- My wife Cigdem who stood by me all the time and helped me in obtaining my dream;
- My parents Nazli and Mustafa Dasdemir who sacrificed their life to raise me;
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I would not have accomplished my dreams without your endless support, encouragement, and most importantly your eternal love.
BIOGRAPHY

Mehmet Dasdemir was born in Turkey June 25th, 1981. He grew up in Gaziantep and graduated from F. N. Tekerekoglu Anatolian High School in 1999. He received his bachelor’s degree in Textile Engineering in 2004 and his master’s degree in Textile Science in 2006, both from University of Gaziantep, Turkey. In 2007 he began pursuing a doctoral degree in Fiber and Polymer Science at North Carolina State University under the supervision of Dr. Behnam Pourdeyhimi, Dr. Benoit Maze, and Dr. Nagendra Anantharamaiah. After finishing his Ph.D., he plans on returning to Turkey and working as an assistant professor in Textile Engineering Department of Engineering Faculty at University of Gaziantep.
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CHAPTER 1

Introduction
1.1 Introduction

Fiber reinforced composites are engineered materials that combine complementary properties of two constituents, fiber and matrix, to create a synergy on the overall properties. They can be separated into two groups according to the type of resin used for the matrix: thermosets or thermoplastics. Even though thermoset resins are dominant in the composite market, there is a great impetus to use thermoplastics instead of thermosets. This is due to the fact that using thermosets in composite applications brings some drawbacks such as limited shelf time, comparatively higher processing costs and longer production time. Additionally, fracture toughness and damage tolerance of the composites can be greatly improved when thermoset matrices such as epoxies, unsaturated polyesters and vinyl esters are replaced by thermoplastics [1]. One of the other advantages of using thermoplastic materials in composite application is the ability to reprocess (reshape) and use it in a post-consumer application [2].

Most of the studies on thermoplastic composite fabrication techniques were conducted on high performance fibers or highly oriented fibers and tapes. In addition, preforms were in the form of unidirectionally arranged filaments, tape or woven fabric. The advantages of nonwoven fabrics for composites compared to other preforms are their low cost, high production rate, and convenience for randomization of fibers [2, 3]. For instance, even though a woven fabric with plain weave has maximum mechanical properties in the two perpendicular directions of fibers (0° and 90°), it has considerably lower mechanical properties in the diagonal and other directions [2].

The process of making thermoplastic composites require several steps including fiber formation, fabric or tape construction, and preparation of polymer melt, wetting, and drying. The main challenge in current methods is to combine two distinct materials. This is due to the fact that the polymer melt has to follow long flow paths through the fibrous reinforcement. Thus, impregnation by the matrix polymer and formation of defects (voids) in the structure are the main drawbacks of conventional thermoplastic composite fabrication techniques. We envisaged that these drawbacks may be overcome by using the bicomponent
structures since they can offer many advantages such as uniform distribution of matrix and excellent wetting. Therefore, in this study, we focused our effort to develop a thermoplastic composite fabrication technique that can allow converting bicomponent nonwovens into composites.

Bicomponent fibers are designed to meet requirements of two materials into one single fiber by hosting two components along the fiber length. Conceptually, the structure of these fibers already mimics the fiber-matrix structure of fiber reinforced composites. Therefore, they are also known as “composite”, “conjugate” and “hetero” fibers. Natural counterpart of a bicomponent fiber is wool which consists of hydrophobic outer layer (scales) and strong, oriented fibrous structures inside. Formation of typical melt spun bicomponent fibers or filaments involve coextruding two polymers from a single spinneret with a desired cross-sectional arrangement.

Polymer interfaces can strongly affect the properties and function of materials. For composite materials, a strong binding at the interface can increase load transfer and improve mechanical properties. Most of the polymers used in bicomponent fibers are thermodynamically immiscible with each other. Therefore, they generally show a weak interface which can cause premature failure in certain cases. Previous studies on bicomponent fibers have mainly focused on the structure and physical properties of bicomponent fibers at high-speed melt spinning [4-10]. In these studies, several polymer combinations have been investigated to observe the effect of interaction of two components on the structure of each component in the fiber. However, the influence of the interface on mechanical properties of bicomponent fibers has not been fully elucidated. Also, most of the studies were conducted for high-speed melt spun fibers [4-10] and very limited literature [11] is available for bicomponent nonwoven fibers. In this study, we investigated the influence of polymer type, composition and interface on the structural and mechanical properties of bicomponent nonwoven fibers.

Interfacial behaviour alters the bulk property of the system. It is affected by adhesion, miscibility, compatibilization, surface wetting and morphology at the interface. Phase
separation occurs when two incompatible polymers come into contact [12]. The interface also determines the overall efficiency of the composite. Dissimilar materials for fiber and matrix are usually used in the composites [13]. When these materials are thermodynamically immiscible, they show high interfacial tension which can lead to poor adhesion or even phase separation at the interface. For this reason, the load transfer between fiber and matrix in the composite is not expected to be efficient. As a result of this interface issue, the mechanical performance of the composite will be negatively affected.

The interface issue has been addressed for polymer blends by using compatibilization approach [14-30]. In this approach, compatibility is promoted through either block or functional graft copolymers that can provide interaction and reaction between the components at the interface [12]. These compatibilization agents are known as “compatibilizers”. When the compatibilizer with functional group is added during the blending, this process is often called “reactive compatibilization” [31].

Even though the interface issue has been extensively addressed for polymer blends, there has been very limited effort made for bicomponent fibers [32, 33] and composites [34, 35]. For composites, the reactive compatibilization approach was typically used to improve the adhesion between natural reinforcement fiber and a thermoplastic matrix [34, 35]. The compatibilization process for this type of short fiber reinforced composite involves blending all components in single step and is very similar to the compatibilization process used for polymer blends. For long fiber reinforced composites this compatibilization route cannot be followed since the process of making these composites does not involve combining all components in a blender. Also, the reactive compatibilization of the polymers during the bicomponent fiber production or nonwoven composite formation stages is different from that of blending in terms of the time and temperature allowed for the reaction and the geometry obtained or defined for the end product. In this regard, the present work also focused on the reactive compatibilization of bicomponent fibers and composites made from them.
The overall objectives of this study are to:

(i) Develop novel thermoplastic composites using bicomponent nonwovens as a precursor and explore what combination of physical properties these composites can offer;

(ii) Investigate the influence of polymer type, composition and interface on structural and mechanical properties of core/sheath (c/s) type bicomponent nonwoven fibers;

(iii) Tailor polymer interface to improve the mechanical performance of nonwoven composites.

In this regard, Chapter 3 introduces a new technique to make thermoplastic composites from bicomponent nonwovens in a single step. The investigation of the effects of polymer type, composition and interface on the structure and mechanical properties of bicomponent nonwoven fibers are given in Chapter 4. The application of reactive compatibilization approach to tailor polymer interfaces in PA6/PE and PET/PE nonwoven based thermoplastic composites are discussed in Chapter 5 and Chapter 6, respectively.
1.2 References


CHAPTER 2

Literature Review
2.1 Bicomponent Fibers

Bicomponent fibers are designed to meet requirements of two materials into one single fiber by hosting two components along the fiber length. Therefore, they are also known as “composite”, “conjugate” and “hetero” fibers in the literature. Natural counterpart of a bicomponent fiber is wool which consists of hydrophobic outer layer (scales) and strong, oriented fibrous structures inside. Formation of typical melt spun bicomponent fibers or filaments includes coextruding two polymers from a single spinneret with designed cross-sectional arrangement. Since it is possible to produce special fibers by selecting cross-sectional designs depending on the end-use application, bicomponent fibers have gained great commercial interest.

Although the first patent for bicomponent fibers was issued in 1937 by Germany’s I.G. Farben for side-by-side viscose fibers to achieve wool-like crimp [1], the first commercial bicomponent fiber was introduced in 1960s by DuPont. It was designed for hosiery application in which bicomponent monofilament had self-crimping properties imparted by using side-by-side arrangement of two types of nylon. It was followed by the introduction of polyamide 6.6/polyamide 6 (core/sheath) bicomponent staple fibers by ICI. In the 1970s, Japanese producer Chisso entered the market with a commercially successful product: a core/sheath polypropylene/polyethylene bicomponent fiber for diapers. The historical development of bicomponent fibers is summarized in Table 2.1.

Bicomponent fibers are mainly produced in Japan, China, South Korea, Taiwan, and the U.S. The global production capacity was estimated to be around 236,000 tons a year in 2007 [1]. Asia is the leading producer with 161,000 tons followed by the U.S (40,000 tons) and Europe (35,000 tons). In the Asia, Japan, with its 80,000 tons production, plays an important role in the market. One of the biggest producers in the world is the Japanese company Chisso with a capacity of 37,000 tons a year. In Europe, ES FiberVisions and Trevira are two important producers.
<table>
<thead>
<tr>
<th>Date</th>
<th>Product Name</th>
<th>Manufacturer</th>
<th>Polymers</th>
<th>Type</th>
<th>Major End Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>1960s</td>
<td>Cantrece</td>
<td>DuPont</td>
<td>Polyamide (Nylon)</td>
<td>Side-by-side</td>
<td>Hosiery-Stretch</td>
</tr>
<tr>
<td></td>
<td>Cambrelle</td>
<td>ICI</td>
<td>Polyamide 6.6/ Polyamide 6</td>
<td>Core/Sheath</td>
<td>Shoe Linings</td>
</tr>
<tr>
<td></td>
<td>Mirafi/Terram</td>
<td>Celanese/ICI</td>
<td>Various</td>
<td>Core/Sheath</td>
<td>Geotextiles</td>
</tr>
<tr>
<td>1970s</td>
<td>Monvelle</td>
<td>Monsanto</td>
<td>Polyamide 6/ Polyurethane</td>
<td>Eccentric Core/Sheath</td>
<td>Hosiery-Stretch</td>
</tr>
<tr>
<td></td>
<td>Fiber ES</td>
<td>Chisso</td>
<td>Polypropylene/ Polyethylene</td>
<td>Core/Sheath</td>
<td>Diapers-Coverstock</td>
</tr>
<tr>
<td>1980s</td>
<td>Melty</td>
<td>Nippon Ester</td>
<td>Polyester/Copolyester or Polyolefin</td>
<td>Core/Sheath</td>
<td>Nonwovens-Thermally Bonded</td>
</tr>
<tr>
<td></td>
<td>Colback (Spunbond)</td>
<td>BASF</td>
<td>Polyester/Polyolefin</td>
<td>Core/Sheath</td>
<td>Nonwovens-Thermally Bonded</td>
</tr>
<tr>
<td>1990s</td>
<td>Celbond</td>
<td>Hoechst Celanese</td>
<td>Polyester/Copolyester or Copolyolefin</td>
<td>Concentric Core/Sheath</td>
<td>Nonwovens-Thermally Bonded</td>
</tr>
</tbody>
</table>

### 2.1.1 Types of Bicomponent Fibers

Bicomponent fibers can be classified according to the distribution of each component within cross-sectional area. The main cross-section configurations includes side-by-side, core/sheath, islands-in-the-sea, alternating segments, citrus and tipped cross-section types (see Figure 2.1).

#### 2.1.1.1 Side-by-side

Side-by-side bicomponent fibers were the first bicomponent fibers developed. They have cross sectional arrangement of two fiber components located next to one another (see Figure 2.1a) along the fiber length. They are typically used in self-crimping applications in which they provide helical crimp. It is due to the difference in the shrinkage or expansion properties
between each component, which creates the crimp in the fiber. The crimp can be either developed by fiber itself (latent crimp) right after the production or imparted by a subsequent heat treatment in a relaxed state or other heat treatments such as water quenching and a hot knife edge method [3]. When they are used in a fabric, they can increase bulkiness and resiliency [3, 4]. The amount of bulk that could be gained is a function of the geometrical distribution, strain properties and elastic modulus of each component in the fiber [5]. Typical polymer combinations for side-by-side configuration are Polyethylene/Polypropylene and Copolyester/Polyester [4].

![Figure 2.1 Types of bicomponent fiber cross-sections: (a) side-by-side, (b) core/sheath with concentric and (c) eccentric configuration, (d) islands-in-the-sea, (e) alternating segments with stripes and (f) pies, (g) citrus, and (h) tipped trilobal](image)

For nonwoven applications, side-by-side bicomponent fibers with self–crimping property can provide extra loftiness in the web and improve stretch/recovery properties. Therefore they are being currently used or have potential for several application areas such as apparel, sleeping bags, furniture, pillows, automotive, and shoe interlinings [3, 4].
2.1.1.2 Core/sheath

In the core/sheath bicomponent fiber structure, one of the components (sheath) functions as a shell and surrounds the second component (core). Depending on the location of the core component these fibers can be either concentric where the core is at the center (see Figure 2.1b) or eccentric (see Figure 2.1c). The eccentric configuration is used for providing self-crimping properties. On the other hand, if the fiber and fabric strength is mostly desired, concentric configuration can be chosen. It is also possible to take advantage of two important characteristics of the components where they are needed (surface and core). For instance, we can use high-strength component for the core while using a component that can provide resistance to environmental conditions for the sheath. Other important properties that can be gained for the surface without sacrificing strength of the fiber are luster, dyeability, adhesion, water absorbency and soil resistance. In addition to these advantages, the cost of the fiber can also be reduced by using low cost material for the core when only surface characteristic is main concern. Commonly used polymer combinations are listed in Table 2.2.

Table 2.2 Core/sheath polymer combinations

<table>
<thead>
<tr>
<th>Most Common (Core/Sheath)</th>
<th>Others (Core/sheath)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene/Polyethylene</td>
<td>Polyamide 6 or 6.6/Polyethylene</td>
</tr>
<tr>
<td>Polyester/Polyethylene</td>
<td>Polyester/Polyamide 6</td>
</tr>
<tr>
<td>Polyester/Polyamide 6</td>
<td>Polyester/Copolyester</td>
</tr>
<tr>
<td>Polyester/Copolyester</td>
<td>Poly(lactic acid)/Polyamide 6</td>
</tr>
</tbody>
</table>

Most of the bicomponent fibers commercially produced today have core/sheath structures. Major application areas of these fibers are nonwovens. There are several purposes of using these materials in a nonwoven product. These include but not limited to the following: bonding (self-bonding) improvement in thermally bonded nonwovens, strength and flexibility increase, cost reduction, and surface property enhancement.
One of the major usages of the core/sheath (mostly concentric) bicomponent fibers in nonwovens is “self-bonding” application [3, 6-8]. In this application, the sheath component of the bicomponent fiber which has lower melting point than the core is used as a natural binder in nonwovens. So, when a bicomponent nonwoven web is heated to a temperature that is enough to melt the sheath but not the core, sheath polymer melts and flows to the nearest adjacent fiber contact in the web. Upon cooling, molten sheath component solidifies at points of contact between adjacent fibers. This basically provides good bonding at fiber intersections due to the better control and placement of the binder sheath component. In this application, core/sheath bicomponent fibers allow using lower bonding temperatures than a typical thermal bonding application in nonwovens. At the same time, depending on the heating method (through-air bonding or calendering), fabrics with high loft and bulk (through-air bonding) or improved strength and flexibility (calendering) can be produced.

Important processing parameter for thermal bonding includes temperature and time. Temperature and time should be adjusted to allow sufficient melt viscosity and time for the sheath component to flow to the adjacent fiber contact. Another important material related property is the melting temperature difference between components. It was suggested that the melting temperature difference should be at least around 40 °C to achieve good bonding [3].

Polypropylene/Polyethylene (PP/PE), Polyester/Polyethylene (PET/PE), and Polyester/Copolyester (PET/CoPET) core/sheath bicomponent fibers are typically used for nonwoven applications. PP/PE fibers are usually blended with cellulose fibers or superabsorbent particles such as fluff pulp for disposable diaper and sanitary coverstock nonwoven applications while PET/CoPET fibers are typically used for bedding, insulated apparel, medical applications, and furniture [3]. Other end use applications of bicomponent nonwovens include automotive carpets and roofing. In these particular applications, these nonwovens provide thermoforming ability, flexibility, and strength.
It is also possible to reduce the cost of homocomponent fiber made from expensive polymers or additives by switching to core/sheath bicomponent fiber. For instance, a recycled or less expensive polymer is used in the core component while an expensive polymer or additives which impart surface characteristics such as luster, adhesion, absorbency, etc. is used for sheath polymer [6]. Similarly, if electrical properties (conduction) are desired, core component can be chosen to add conductive particles. Thus, the amount of the expensive polymer or additive required to be added in the fiber can be reduced.

2.1.1.3 Islands in the Sea

In islands in the sea bicomponent fiber, islands refer to the fibers aligned longitudinally along the fiber length while the sea component is the matrix that surrounds these fibers. Fiber cross-section for this type of bicomponent fibers is shown in Figure 2.1d. The maximum number of islands can be as much as 300. These fibers are usually used to make nonwovens having very fine fibers. These fine fibers are typically obtained by removing the sea component with a subsequent process involving solvent, chemical or heat treatment [3]. Another method to achieve such fine fibers is hydroentangling in which some degree of mechanical splitting of components is achieved with use of high energy water jets. The resultant fibers have very small diameter and high surface area. Therefore the nonwoven fabrics have good hand and excellent elastic recovery. They can also provide better insulation and absorption properties [3]. Thus, they can be used in apparel, synthetic leather, wipes, and filtration application.

Polyester/Polyamide 6 (PET/PA6; islands/sea), Polyester/Polypropylene (PET/PP), Polypropylene/Polyvinyl alcohol (PP/PVA) are some of the common polymer combinations for islands in the sea bicomponent fibers.
2.1.1.4 Alternating Segments

Bicomponent fibers with alternating segment cross-section include several stripes (see Figure 2.1e) or pies (see Figure 2.1f) of two major components that are arranged next to one another. Like islands in the sea fibers, this type of bicomponent fibers is used to obtain fine fibers by splitting the two components. Similarly, splitting can be achieved by chemical, mechanical or heat treatment. These fibers are typically used in wipes, synthetic leathers, and insulation application.

PET/PA6 is one of the most common polymer combinations used in alternating segment type of bicomponent fibers and nonwovens. One particular product that utilizes this polymer combination is the Freudenberg’s Evolon. It is a revolutionary nonwoven product composed of segmented pie spunbonded filaments which are split and entangled by hydroentangling. The resultant nonwoven fabric is durable, launderable, breathable, and flexible [9].

2.1.1.5 Citrus

As the name implies, the citrus type of bicomponent fiber has a cross-section (see Figure 2.1g) similar to that of a citrus fruit. This type of bicomponent fiber is also used to make fine fibers by splitting components.

2.1.1.6 Tipped Trilobal

Tipped trilobal bicomponent fiber (see Figure 2.1h) is a three sided fiber in which the tip of each side includes a second component. This fiber cross-section is typically chosen to facilitate the spinning process or to provide functionality on the tips. The grooves on the trilobal section may introduce more surface area and can be useful for particle capture in filtration application.
2.1.2 Bicomponent Fiber Production

There are two major methods of producing bicomponent fibers: (i) co-extrusion (melt spun) and (ii) coating spun fiber with another polymer solution. The former method is more common due to the fact that it can provide several advantages such as being environmentally friendly (no solvent usage), cost effective and versatile (ability to configure fiber cross-section). In co-extrusion method, two separate molten polymer streams meet in a location called the spinneret counterbore which is very close to spinneret orifice and then they are co-extruded as a single filament. Bicomponent fiber production techniques which use this approach vary with cross-section type and arrangement of each component. For instance, in order to obtain a side-by-side cross-section, two molten polymer streams (A and B in Figure 2.2) are split by a knife edge or septum before the spinneret counterbore (see Figure 2.2a). For a core/sheath cross-section, there could be multiple arrangements of the spinneret in which core polymer is usually supplied via a different orifice or channel (see Figure 2.2b). After the core polymer (A) leaves the feeding channel, it is immediately surrounded by the sheath polymer (B) and then they travel in core/sheath form at the spinneret counterbore and exit from the spinneret orifice.

![Figure 2.2 Examples of polymer flow arrangement in the spinneret for side-by-side (a) and core/sheath (b) bicomponent fibers](image)

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In 1992, Hills [10] issued a patent which explains methods for making a wide variety of bicomponent fibers using a unique spinneret design and arrangement. This patent also covers the historical development of bicomponent spinning process by citing 106 patents related to bicomponent fibers and spinning. In this patent, they claimed that their new spinneret design could reduce cost, increase the density of the orifices, and improve fiber uniformity. Figure 2.3 shows a perspective view of this new spin pack assembly which is composed of several plates: a top plate (11), a screen support plate (12), a metering plate (13), an etched distributor plate (14), and a spinneret plate (15) hosting several orifices called spinneret counterbore (41). What is unique about this spin pack assembly is that distributor plates are etched to distribute polymer melts. Using etching technique instead of drilling or milling allows obtaining several very small distribution paths which can facilitate guiding many polymer component streams to several spinneret orifices or counterbores. Thus, the density of the orifices could be increased.

Figure 2.3 Hills’ spin pack assembly [10]
After two polymer components, A and B, are molten, they enter the spin pack separately at two locations 17 and 18, respectively. They are then filtered and spread across the width of the spin pack by means of screen filters (22 and 23) and flow through metering plate (13). Two main polymer streams are distributed by means of distributor plate (14) and enter the spinneret counterbores (41). After entering the spinneret counterbore, they are coextruded by exiting from the spinning orifice (40). The spinneret counterbore is the location where the two polymer streams meet and take the final cross-section form therefore it is important to focus on this section. Figure 2.4 shows the side view of this section. Interactions between two components and any arrangement of polymer melts start to occur in the spinneret counterbore and continue until they are solidified.

![Figure 2.4 Side view of spinneret counterbore](image)

Figure 2.4 Side view of spinneret counterbore
In order to determine the residence time \( t \) of the two components in the spinneret counterbore, the total volume \( V \) of this section and the flow rate per orifice \( Q \) should be calculated. The volume calculations are given by Equations 2.1-2.5:

\[
V = V_1 + V_2 + V_3
\]  
\[
V_1 = \frac{1}{4} L_4 \pi D_1^2
\]  
\[
V_2 = \frac{1}{4} L_2 \pi D_2^2
\]  
\[
L_3 = \left( \frac{D_1 - D_2}{2} \right) \tan Q
\]  
\[
V_3 = \frac{1}{12} L_3 \pi \left( D_1^2 + D_1 D_2 + D_2^2 \right)
\]

where \( D_1 \) is the counterbore diameter; \( D_2 \) is the orifice diameter; \( L_1 \) is the counter length; \( L_2 \) is the capillary length; \( L_3 \) is the length of the merging orifice; \( L_4 \) is the length of the upper counter section; \( Q \) is the angle for the merging orifice. Volume flow rate per each orifice can be calculated using following Equations 2.6-2.8:

\[
Q = \frac{\dot{m}_T}{\rho_T n}
\]  
\[
\rho_T = f_A \rho_A + (1 - f_A) \rho_B
\]
\[ f_A = \frac{w_A/\rho_A}{w_A/\rho_A + w_B/\rho_B} \]  \hspace{1cm} (2.8)

where \( \dot{m}_r \) is the overall mass flow rate; \( \rho_T \) is the overall melt density of two polymers; \( n \) is the number of orifices in the spinneret; \( f_A \) is the volume fraction of the component A; \( \rho_A \) is the melt density of the component A; \( \rho_B \) is the melt density of the component B; \( w_A \) is the weight ratio of component A; \( w_B \) is the weight ratio of the component B. After calculating the volume and flow rate, residence time can be evaluated by taking their ratio (Equation 2.9).

\[ t = \frac{V}{Q} \]  \hspace{1cm} (2.9)

Melt viscosities (\( \mu \)) of the components have a great impact on the processing and formation of the desired cross-section, particularly for side-by-side type of bicomponent fiber. First, individual viscosities of each component at the spin pack temperature should be high enough to avoid turbulence at the exit of the spinning orifice [3]. Second, viscosities of both components at the spin pack temperature should be comparable to obtain desired cross-section (see Figure 2.5a) [3, 7]. If the viscosity of component A is lower than that of component B under the spinning condition, component A will tend to encapsulate component B (see Figure 2.5b). This is due to the fact that friction between the spinneret counterbore wall and the polymer stream of component B (high viscosity component) is higher than that of between the wall and component A. Therefore, component B loses more momentum than component A during flowing and they try to rearrange themselves to create the least amount of resistance to flow. For this reason, the component A moves towards the wall to reduce shear in the flow and tries to encapsulate component B [11]. Thus, distortion of the cross-section occurs.
In the case of a very high difference in viscosity (e.g. $\mu_A << \mu_B$ in Figure 2.5c), component A tends to fully surround component B. In such cases, some spinning problems arise and extrusion becomes unstable. One of the commonly encountered problems is the formation of extrudate dogleg [7]. It occurs when there is a considerable difference between the velocity profiles of two components in the spinneret counterbore. Because of the shear, the component A travels faster than component B in the counterbore. At the exit of the spinneret, the component A will have a higher velocity. However, since the shear on polymers is removed, the extrudate will tend to have a flat velocity profile. Therefore, component A will push component B at the exit of the orifice where the extrudate bends towards the component B to attain a flat velocity profile. Spinning becomes impossible if the degree of bending is too high.

In addition to polymer viscosities, rates of cooling and surface tensions of the two components are critical for the formation and properties of bicomponent fibers [7, 8]. Rates of cooling determine the orientation of each component while the surface tensions determine the adhesion between two components in the resultant bicomponent fiber. Adhesion between two components can also be affected by the applied drawing ratio. If a drawing ratio which is higher than the natural drawing ratio of one component is applied, it may lead to splitting of components [3].
2.1.3 Bicomponent Nonwoven Production Using Spunbonding Process

In 2000’s, a new era in bicomponent fiber production and end-use products started with the introduction of bicomponent spunbond and meltblown spinlines using Hills’ technology by Reifenhauser and Nordson. These new equipment and development in the process reduced the cost and complexity of the process and increased production rates. Thus, it led to a rapid growth in the development and commercialization of bicomponent products. Most of these new products were made by using bicomponent spunbond technology rather than bicomponent meltblown. This is due to the fact that bicomponent spunbond offers better control and versatility than bicomponent meltblown.

The spunbonding process is a method of producing fabrics directly from polymers in a single step. It combines filament extrusion, quenching, drawing (attenuation), deposition, bonding, and winding. Therefore, it is one of the most cost effective and fastest methods of making a fabric. As a comparison, the relative production rates range between 1 and 6 for weaving; 3 and 16 for knitting, whereas it is between 200 and 2000 for spunbonding [12].

Major components of a typical spunbond spinline are polymer feeding unit (polymer hopper), extruder, filter, metering pump, spin pack, quench air chambers, attenuation and deposition system, collecting and forming belt, compaction roll, bonding unit (calendar if thermally bonded), and winder (see Figure 2.6).

In a typical spunbonding process, polymer pellets bearing moisture are dried before the spinning to avoid degradation of polymers under thermal and mechanical actions. After conditioning (if necessary), polymer pellets are fed to an extruder by means of auxiliary feeding unit. Stabilizers, additives, color master-batch, resin modifiers or other additives can also be added using side feeders or by simply mixing with main polymer at desired ratios. In the extruder, polymer pellets or mixture melt progressively with the application of heat and friction. The molten polymer is then conveyed from the extruder to a filter where foreign
particles such as metals or any solid polymer particulates are filtered to prevent unstable fiber extrusion and clogging in the spin pack.

![Diagram of spinning process](image)

**Figure 2.6** Schematic drawing of open spunbonding process [13]

After filtering, the polymer stream is transferred with the help of metering pump. The metering pump adjusts the volumetric flow rate of the molten polymer and provides high pressure for the spin pack. The molten polymer then enters the spin beam. In the spin beam, it first goes to the feed distribution system in which a uniform flow of polymer is maintained for the spin pack. Before the molten polymer reaches to the spinneret, it is distributed uniformly along the width of the die by means of distributor plates. At the same time, temperature and residence time of the molten polymer is maintained constant in the spin pack for a uniform polymer flow. Several molten polymer streams then enter spinneret capillaries from where they are extruded to form several filaments. These extruded filaments first pass
through a quenching zone. In this zone, cool air is blown onto molten filaments to facilitate cooling and solidification. The degree of cooling is a function of blown air temperature, flow rate, and humidity. These parameters should be adjusted to provide sufficient cooling and/or solidification. Otherwise, some critical problems such as fiber roping and inability of the fibers to form a web arise [13].

After passing the quenching zone, the filaments go into a tapered conduit by means of high velocity air which provides acceleration and attenuation of the filaments. The degree of attenuation is very important because it determines the fiber diameter and most importantly the molecular orientation of the polymer chains in the filament [14]. Even though attenuation of filaments by high velocity air jets is the most common and least expensive method, it causes some variations in the fiber diameter distribution. Other alternative methods for attenuation are the use of drawing roll and the application of electrostatic field. The former method is expensive but provides a very narrow diameter and yields fully drawn filaments [13].

Before filaments are deposited on a collecting conveyor belt, they must be separated to form a web with high uniformity and cover. In order to achieve that, an electrostatic charge could be applied to filaments to provide spreading and separation. After these filaments are separated they are laid down on the moving collection belt. At the same time, processing air used during attenuation is vacuumed with the help of suction under the belt. The fiber orientation of the laid web can also be adjusted by means of mechanical oscillation, electrostatic charging, air foils and so on [14]. Generally, spunbond webs attain random fiber orientation with some degree of tendency to the machine direction. The collected spunbond web then travels through the compaction rolls where the initial web integrity is provided. This compaction process also facilitates the handling of the web in subsequent processes. After the spunbond web passes through the compaction rolls bonding, finishing (if necessary), and slitting are applied to form final nonwoven fabric. Finally, the nonwoven fabric is wound onto roll.
Several techniques could be used for bonding spunbond webs. Most commonly used techniques include hydroentangling, needlepunching, calendaring, through air thermal bonding, and chemical bonding. Among these techniques calendaring is one of the most common and cost effective way of bonding spunbond webs. It makes use of heat and pressure to provide fiber fusions.

The major difference between a typical spunbonding and bicomponent spunbonding processes is that the later has the ability to process two separate polymers to form bicomponent nonwovens. In order to achieve that, the bicomponent spunbonding spinline (see Figure 2.7) accommodates two polymer feeding units, two extruders and a different spin pack. In this process, two separate polymers are first fed to different extruders. After extrusion of these polymers, two molten polymer streams are carried by following two identical but separate paths. Along this path they pass through the filters, the metering pumps, and the spin beam. When they enter the spin pack, they are distributed separately and finally meet in the spinneret counterbore. At that stage, they become a conjugate polymer stream and exit from the spinneret. Further steps in the process are exactly same as homocomponent spunbonding explained above.
Figure 2.7 Schematic drawing of the bicomponent spunbonding process at NWI, NCSU [15]

2.2 Fiber Reinforced Thermoplastic Composites

Fiber reinforced composites are engineered materials that combine complementary properties of two constituents, fiber and matrix, to create a synergy on the overall properties. They can be separated into two groups according to the type of the matrix resin used. These are thermosets and thermoplastics. Even though thermoset resins are dominant in the composite market, there is a great impetus to use thermoplastics instead of thermosets. This is due to the fact that using thermosets in composite applications brings some drawbacks such as limited shelf time, comparatively higher processing costs and longer production time. Additionally,
fracture toughness and damage tolerance of the composites can be greatly improved when thermoset matrices such as epoxies, unsaturated polyesters and vinyl esters are replaced with thermoplastics [16]. One of the other advantages of using thermoplastic materials in composite application is the ability to reprocess (reshape) and use it in a post-consumer application [17].

Conventional thermoplastic composite fabrication techniques are pultrusion and injection molding. These techniques can be used for short-fiber reinforced thermoplastics such as glass fiber reinforced composites. For long fibers, thermoplastic composites are made by wetting out the reinforcement components (in the form of aligned fiber, tape, and woven fabric) with polymer melt. The methods of making these composites require several steps including fiber formation, fabric or tape construction, and preparation of polymer melt, wetting, and drying. The main challenge in current methods is to combine two distinct materials. This is due to the fact that the polymer melt has to follow long flow paths through the fibrous reinforcement. Therefore, impregnation by the matrix polymer and formation of defects (voids) in the structure are the main drawbacks of conventional thermoplastic composite fabrication techniques.

### 2.2.1 Single Polymer Composites

A new concept of thermoplastic composite fabrication was first introduced in 1975 by Capiati and Porter [18]. In this approach, fiber component has aligned and extended chains, therefore it has thermodynamically more stable crystals and higher melting point than conventionally crystallized matrix polymer. Thus, the difference in melting points between these two chemically identical components can be utilized to obtain a single polymer thermoplastic composite. Capiati and Porter [18] particularly studied all polyethylene composite and observed a partial melting of the fiber surface and a transcrystalline region at the interface. To evaluate the interfacial shear strength they performed single fiber pull-out test and found a high interfacial strength which was granted by the epitaxial bonding between two components.
Single polymer composites also known as self-reinforced or all-polymer or matrix-less composites then gained much attention due to the fact that they can provide good interfacial adhesion and enhanced recyclability. Several techniques have been developed: film stacking [19, 20], hot compaction [21-24], solution impregnation [25], wet powder impregnation [26], and co-extrusion [27-29]. Among these techniques, film stacking, hot compaction, and recently co-extrusion are the most popular due to advantages such as strong fiber-matrix interface and high delamination resistance they can provide.

In the film stacking technique, polymer films with a lower melting point than the reinforcement fibers are placed in between preforms. Upon heating, these films melt and form the matrix. Even though interlayer films can improve delamination strength and allow a wide processing temperature window, penetration of polymer melt through fibers can still be problematic [19].

Hot compaction technique was first introduced in 1993 by Ward and his research team [21]. In this technique, a small fraction of the surface of each oriented fiber is melted by carefully controlling the temperature. At the same time, with the help of pressure, the molten polymer flows and fills the gap between remaining reinforcement fibers. Upon cooling, molten polymer epitaxially crystallizes on the initial fibers and forms the matrix phase (see Figure 2.8). Initial research on the hot compaction was mostly done on melt spun polyethylene (PE) fibers [21, 30, 31]. After successful experimentation with melt spun PE, their research was extended to other highly and partially oriented thermoplastic fibers: polyethylene terephthalate (PET) [32], polypropylene (PP) [33-35], gel spun PE [24], and polyamide 6-6 (PA6-6) [36]. These fibers were either unidirectionally arranged [21, 24, 30-33] or in the form of woven fabric [34-37]. In addition to fibers, unidirectionally arranged [38] or woven [34, 38-41] thin flat tapes were also used as starting material for hot compaction.

Among the above mentioned materials, hot compacted PP was found to be the most promising candidate with potential for commercial development due to the fact that it can
provide a good cost/performance balance for several applications [23]. It is now commercially available under the trade name of Curv® from Propex Fabrics. Regarding the structure of the preform, woven filaments or tapes were suggested to be the most useful structures because of the advantage of providing greater surface area [23]. This is important for sufficient contact and adhesion between layers.

![Figure 2.8](image_url) Transverse sections of hot compacted samples: (a) transmission electron micrograph of etched melt spun PE [22]; (b) etched PET fibers [32]

The most critical processing parameter in hot compaction is the temperature. It determines the amount of matrix and the mechanical performance of the resultant composite (see Figure 2.9). An optimum compaction temperature approximately ranges between the onset and peak melting temperatures of the polymer. The major challenge here is to perform compaction in such a very narrow optimum window. In order to address this issue, Hine et al. [42] combined two techniques: hot compaction and film stacking. In order to use lower compaction temperature, they placed the films in between compacted preforms where the matrix material is mostly required. Thus, they did not only widen the processing temperature
window but also improved the inter-layer strength. Overall, hot compaction technique can offer high modulus and strength thermoplastic composites with small loss of the original fiber properties and provide strong fiber-matrix interface.

![Original Fiber Modulus](image)

**Figure 2.9** Effect of compaction temperature on mechanical performance of hot compacted melt spun PE fibers [23]

Another alternative method of making thermoplastic composite is using coextruded tapes. This technique was developed by Peijs et al. [27, 28] to produce all-PP composites. In their studies, two grades of PP with different melting temperatures were coextruded and then cold drawn to improve the mechanical properties. The coextruded tape is composed of a highly oriented PP in the core and a copolymer PP in the skin. The temperature difference in the melting points of these two polymers allows the melting of the matrix component (skin) while keeping the reinforcement component (core) intact. The schematic drawing of this technique is shown in Figure 2.10. Due to the several advantages that this technology
presents: large processing temperature window (20-40 °C for PP), reduced risk of fiber orientation, and high fiber volume fraction (~90%), it was commercialized by Lankhorst-Indutech in the Netherlands under the trade name PURE® and also by its licensee Milliken in the USA under the trade name Tegris®.

![Coextrusion Process](image)

**Figure 2.10** Schematic drawing of the coextrusion technique [27]

Although coextrusion technique brings several advantages, the incompatibility between the two components used could lead to interface issue. Therefore, interface strength between fiber and matrix could be lower for this type of composites compared to other all-polymer composites where an identical polymer is involved in both the fiber and matrix.

In a recent study, Zhang and Peijs [29] used bicomponent yarns instead of tapes. Unidirectionally aligned PET multifilament bicomponent yarns with core/sheath structure in which low melting temperature co-PET was used in the sheath, were consolidated by heat and pressure to obtain all-PET composite. They investigated the effects of consolidation temperature and pressure and found that the pressure values used had almost no impact on tensile properties. On the other hand, while longitudinal modulus and strength varies with temperature, transverse strength increases up to an optimum reached at a processing temperature of 220 °C. The examination of fracture surfaces revealed that tensile failure mode actually shifts from ductile to fragile when processing temperature was increased. It was attributed to an improvement in interfacial adhesion between matrix and fiber at comparatively higher consolidation temperature.
2.2.2 Nonwovens for Composites

The advantages of nonwoven fabrics for composites compared to other preforms are their low cost, high production rate, and convenience for randomization of fibers [17, 43]. For instance, even though a woven fabric with plain weave has maximum mechanical properties in the two perpendicular directions of fibers (0° and 90°), it has considerably lower mechanical properties in the diagonal and other directions [17]. In addition to the benefits that can be gained from nonwovens, using the bicomponent structures in thermoplastic composite fabrication offer many advantages such as uniform distribution of matrix and excellent wetting.

The patent literature [44, 45] includes some examples of composite molded parts made using nonwovens. For instance, Ernst et al. [45] described a method for producing molded parts from a nonwoven containing a bonding agent. The bonding agent is either in the form of powder or fiber. This agent could be thermoplastic or thermoset and premixed and prebonded with other fibers in nonwoven. Its function is to provide intersections between fibers and required hardening like a matrix after the formation of the part. When a thermoplastic bonding agent is used, the nonwoven preform is heated until the bonding agent softens. It is then inserted into an open or closed compression mold. The mold is then closed and the preform is compressed. If the closed mold is used, the air trapped inside the mold is sucked out. After the bonding agent is cooled, the molded part is removed. The schematic drawing of above explained process is shown in Figure 2.11.

Formation of three-dimensional (3-D) structures from nonwovens was studied by Grissett [46]. In this study, the patented SpaceNet® thermoforming system [47, 48] was used to produce 3-D deep-draw structures from nonwoven substrate. This system utilizes a thermo-mechanical deformation instead of using a second component such as a binder to shape the nonwoven substrate. Initially, thermal energy is applied to the substrate to soften the fibers and provide sufficient fiber strains. Afterwards, the substrate is pressed in between either a matching (male-female) or interdigitated mold (see Figure 2.12). The degree of applied
mechanical deformation during this stage does not introduce any considerable damage to mechanical characteristics. Finally, it is removed from the press and cooled. The resultant structure is a semi-rigid 3-D nonwoven with increased surface area. It is also claimed to be resilient, lightweight, air and water permeable, and supportive [49]. Therefore, it is now commercially available under the trade name of Novolon™ and being used in outdoor & protection applications, consumer matresses, medical beddings, and geo-textiles (see Figure 2.13).

**Figure 2.11** Schematic drawing of molded composite part production from nonwovens [45]
Figure 2.12 Formation of 3-D structures from nonwovens using SpaceNet® [46]

Figure 2.13 Applications of 3-D nonwoven structures [49]
2.3 Thermodynamics of Polymer Blends

The Gibb’s free energy of mixing can be used to describe mixing behavior for polymer blends with following thermodynamic equation:

\[ \Delta G_m = \Delta H_m - T \Delta S_m \] (2.10)

where \( \Delta G_m \) is the free mixing energy; \( \Delta H_m \) is the mixing enthalpy; \( T \) is the temperature and \( \Delta S_m \) is the mixing entropy.

The thermodynamic condition of miscibility is same as that of a molecular mixture in which the free mixing energy must be lower than zero (\( \Delta G_m < 0 \)). According to Flory and Huggins [50], the mixing enthalpy and entropy can be expressed by following formulas

\[ \Delta H_m = RT \chi_{12} \phi_1 \phi_2 \] (2.11)

\[ \Delta S_m = -R \left( \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 \right) \] (2.12)

where \( R \) is the gas constant; \( \chi_{12} \) is the Flory-Huggins parameter describing the interaction between polymer segments 1 and 2; \( \Phi_1 \) and \( \Phi_2 \) are the volume fractions and \( N_1 \) and \( N_2 \) are the degrees of polymerization of polymer 1 and 2, respectively.

The entropic part is related to the motion of the center of the mass of the polymer molecules. It is therefore called translational entropy. Although this component of the free mixing energy contributes to the mixing, it is usually very small due to the large molecular weights of the polymer. Therefore, the enthalpic part usually dominates the mixing behavior. It can
be either positive or negative depending on the compatibility of the two polymers. Since most polymers are incompatible with each other, their interaction parameter is large and the enthalpy of mixing is positive. So, the free mixing energy becomes positive and leads to phase separation.

The calculation of the free mixing energy based on the Flory-Huggins theory does not account any intermolecular interactions which can range from purely dispersive forces to very strong hydrogen bonds. Coleman et al. [51, 52] developed a modified version of the Flory-Huggins equation in which a free energy term ($\Delta G_H$) is added to original equation to take into account the presence of strong, specific intermolecular interactions such as hydrogen bonding.

\[
\Delta G_m = RT \chi_{12} \phi_1\phi_2 + RT \left( \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 \right) + \Delta G_H
\]  

(2.13)

2.3.1 Calculation of Polymer Interaction Parameter

The estimation of Flory-Huggins polymer interaction parameter ($\chi$) is useful to predict the degree of miscibility of a polymer blend. It can be calculated using solubility parameters, as in Equation 2.14:

\[
\chi_{12} = \frac{<V>(\delta_i - \delta_j)^2}{RT}
\]

(2.14)

where $<V>$ is the mean molar volume and $\delta_i$ is the solubility parameter for polymer i.

The solubility parameter for a low molecular weight compound can be calculated from heat of vaporization measurement. However this measurement cannot be performed for polymers
since they degrade before the evaporation. In order to calculate the solubility parameters for polymers, either experimental or theoretical methods must be used. Both of these techniques are indirect methods. The experimental method results in large errors [51, 52] during the estimation of the polymer miscibility. Therefore, the theoretical method is commonly preferred.

The solubility parameters for polymers can be estimated via the use of group contribution methods (GCMs) which account for each group present in the repeat unit of the polymer. That is to say that GCMs consider the contribution of each functionality to the solubility. The calculations of solubility parameter via the use of GCMs are given by Equations 2.15-18

\[
\delta = \frac{\sum n_i E_{coh_i}}{\sum n_i V_i} \tag{2.15}
\]

\[
F_i = \sqrt{E_{coh_i} V_i} \tag{2.16}
\]

\[
\delta = \frac{\sum F_i}{V} \tag{2.17}
\]

\[
V = \frac{M}{\rho} \tag{2.18}
\]

where \(n_i\) is the number of group \(i\); \(E_{coh_i}\) is the cohesive energy of group \(i\); \(V_i\) is the molar volume of group \(i\); \(F_i\) is the molar attraction constant of group \(i\); \(V\) is the total molar volume; \(M\) is the molecular weight of the repeat unit; \(\rho\) is the density of the polymer.
Values of F for different groups were determined by regression analysis for various common structural groups in low-molecular-weight compounds and reported by several researchers [51, 53-55]. Tables 2.3 and 2.4 list F and V values for unassociated and weakly associated groups, respectively [51].

**Table 2.3** Molar attraction constants and volumes for unassociated groups [51]

<table>
<thead>
<tr>
<th>Group</th>
<th>V (cm$^3$ mole$^{-1}$)</th>
<th>F ((cal.cm$^3$)$^{0.5}$ mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_3$</td>
<td>31.8</td>
<td>218</td>
</tr>
<tr>
<td>-CH$_2$-</td>
<td>16.5</td>
<td>132</td>
</tr>
<tr>
<td>&gt;CH-</td>
<td>1.9</td>
<td>23</td>
</tr>
<tr>
<td>&gt;C&lt;</td>
<td>-14.8</td>
<td>-97</td>
</tr>
<tr>
<td>C$_6$H$_3$</td>
<td>41.4</td>
<td>562</td>
</tr>
<tr>
<td>C$_6$H$_4$</td>
<td>58.8</td>
<td>652</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>75.5</td>
<td>735</td>
</tr>
<tr>
<td>CH$_2$=</td>
<td>29.7</td>
<td>203</td>
</tr>
<tr>
<td>-CH=</td>
<td>13.7</td>
<td>113</td>
</tr>
<tr>
<td>&gt;C=</td>
<td>-2.4</td>
<td>18</td>
</tr>
<tr>
<td>-OCO-</td>
<td>19.6</td>
<td>298</td>
</tr>
<tr>
<td>-CO-</td>
<td>10.7</td>
<td>262</td>
</tr>
<tr>
<td>-O-</td>
<td>5.1</td>
<td>95</td>
</tr>
<tr>
<td>&gt;N-</td>
<td>-5.0</td>
<td>-3</td>
</tr>
</tbody>
</table>

**Table 2.4** Molar attraction constants and volumes for weakly associated groups [51]

<table>
<thead>
<tr>
<th>Group</th>
<th>V (cm$^3$ mole$^{-1}$)</th>
<th>F ((cal.cm$^3$)$^{0.5}$ mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-Cl</td>
<td>23.9</td>
<td>264</td>
</tr>
<tr>
<td>-CN</td>
<td>23.6</td>
<td>426</td>
</tr>
<tr>
<td>-NH$_2$</td>
<td>18.6</td>
<td>275</td>
</tr>
<tr>
<td>&gt;NH</td>
<td>8.5</td>
<td>143</td>
</tr>
</tbody>
</table>
According to Coleman’s model (Equation 2.13), repulsive “physical” forces and attractive “favorable” forces are separated. The repulsive forces are taken into account in $\chi$ whereas the attractive forces are handled with the addition of the extra term “$\Delta G_H$” to the free mixing energy. Therefore, the estimation of the non-hydrogen bonded solubility parameters of strongly self-associated polymers (i.e. polyamides) is required. This can be achieved by following two methods. First, hydrogen bonding molecules are chosen from compounds that are not strongly self-associated. Second, an analogous hypothetical molecule in which the proton is eliminated is used for calculations. The application of these two methods were explained for the estimation of the non-hydrogen bonded solubility parameter for polyamides which can strongly self-associate through hydrogen bonding of -CO- and >NH groups [51]. In the first method, -CO- and >N-H group contributions from compounds that are not strongly self-associated were used to construct a non-hydrogen bonded contribution for the amide (-CO-NH-). In the second method, instead of the >N-H group contribution >N- group contribution was used with -CO- to calculate the contribution for the amide group.

In contrast to Coleman’s method, Hansen [56] accounted for hydrogen bonding interactions by extending the solubility parameter. The total solubility parameter ($\delta_t$) is calculated taking the geometric mean of three parameters:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

(2.19)

where $\delta_d$ is the dispersion (nonpolar) component; $\delta_p$ is the electrostatic (polar) component; $\delta_h$ is the hydrogen bond component of the $\delta_t$. For polymers these parameters are experimentally calculated from the swelling experiments of a self-associated polymer with solvents of known solubility parameter [57]. However, Coleman [51] argued that there is an inherent error in the determination of the solubility parameter by means of this experimental method.
### 2.4 Polymer Interfaces

The interface is defined to be a region where composition and energy vary from one bulk phase to the other [58]. It usually has a thickness less than 0.1 µm. Polymer interfaces can be categorized in four groups in terms of constituent forming the material (see Table 2.5).

**Table 2.5 Classification of polymer interfaces [59]**

<table>
<thead>
<tr>
<th>Symmetric (X/X) polymer-polymer interfaces</th>
<th>Asymmetric (X/Y) polymer-polymer interfaces</th>
<th>Asymmetric polymer-nonpolymer interfaces</th>
<th>Multicomponent polymer interfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous materials</td>
<td>Amorphous materials</td>
<td>Polymer-metal interfaces</td>
<td>Blends</td>
</tr>
<tr>
<td>Semi-crystalline materials</td>
<td>Structurally asymmetric</td>
<td>Polymer-ceramic interfaces</td>
<td>Compatibilizers</td>
</tr>
<tr>
<td>Liquid materials</td>
<td>Dissimilar compatible</td>
<td>Polymer-biological interfaces</td>
<td>Interactive components</td>
</tr>
<tr>
<td></td>
<td>Dissimilar incompatible</td>
<td></td>
<td>Non interactive components</td>
</tr>
<tr>
<td>Semi-crystalline materials</td>
<td>Similar</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dissimilar</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In symmetric interfaces, the same polymer exists on both side of the interface, whereas in asymmetric interfaces two different polymers meet at the interface. Asymmetric polymer-nonpolymer interfaces consist of a polymer and a non-polymer material such as metal and ceramic. They form when two polymers are immiscible (incompatible) with each other. Multicomponent polymer interfaces are formed with more than two polymeric materials and may include some compatibilizers or interactive and non-interactive components. For
instance; a blend of two polymers containing a compatibilizer is assumed to have a multicomponent polymer interface.

Interface width between two polymers is of great interest in interfacial studies. It ranges from 1 to 50 nm for most incompatible polymers. During the mixing of incompatible polymers, penetration of polymer chains into the interface can occur at temperatures above the glass transition temperature. The interfacial width generally increases with time and reaches an equilibrium value. The equilibrium state is determined by the Flory-Huggins interaction parameter (χ) which describes the interactions between two different polymer segments. It is also possible to correlate interface width to χ. The typical property profile of an interface for two polymer system is shown in Figure 2.14 [60].

![Figure 2.14 Property profile of an interface and determination of the interface width](image)

**Figure 2.14** Property profile of an interface and determination of the interface width
The distance is measured from the interface normal which is perpendicular to the polymer-polymer interface (see Figure 2.14). The interface width can be obtained by simply following the deviation from the measured property on the curve. The interface width generally depends on the volume fraction of each component. The interfacial width can also be calculated by using following Equation 2.20:

\[
a = \frac{2b}{\sqrt{6} \chi}
\]  

(2.20)

where \(a\) is the interfacial width and \(b\) is the characteristic segment length.

As shown in above equation, the interface width decreases with increasing \(\chi\) value. That is to mean that incompatibility reduces the interface width. After the interfacial width is obtained, it is also possible to calculate volume fraction profile along the interface between two polymers (see Equation 2.21) according to the mean field theory [60].

\[
\phi(z) = \frac{1}{2} \left(1 + \tanh \left(\frac{2z}{a}\right)\right)
\]  

(2.21)

where \(\phi\) is the volume fraction and \(z\) is the coordinate perpendicular to the interface.

2.4.1 Effect of the Interface on Mechanical Properties

Interfacial behaviour determines the bulk property of a composite system. It is affected by adhesion, miscibility, compatibilization, surface wetting and morphology at the interface. In this regard, mechanical properties of polymer mixtures mainly depend on the nature of the interfaces, i.e. their thickness and mechanical strength [60].
The composition of polymers and their compatibility determine the resulting property of a polymer blend. In Figure 2.15, curve $a$ represents miscible polymer blend in which combined property can be obtained according to additivity. Compatible polymer blend can also show a synergy in combined property as shown in curve $b$. But it is rarely observed. In most cases, polymer blends are immiscible. Their resulting property (curve $c$) is lower than each component’s property and goes through a minimum. It is mainly due to the poor interfacial adhesion between each component in the polymer blend. The interface width for this type of polymer blends is assumed to be very thin, typically in the range of 2-3 nm. In addition, if the polymers are not mixed, they tend to minimize their interface width. In most cases, demixing causes phase separation in immiscible polymer blends in which the phase separation can range between 0.1 nm and several hundreds of micrometers. This state is called macrophase separation [60].

**Figure 2.15** Effect of the composition and compatibility of the components on resultant property: (a) additivity: miscible polymer blend; (b) synergy: compatible polymer blend; (c) immiscible polymer blend: incompatible [60]
The interface also determines the overall efficiency of a composite [61]. In this regard, the role of the perfect interface is to transfer an applied load from matrix to fiber evenly without any loss [62]. However, it is highly challenging to achieve the desired load transfer between components due to the fact that dissimilar materials for fiber and matrix are usually used in the composites. It is therefore important to focus on the fiber matrix interface and interaction.

Zhandarov and Mader [62] divided existing methods for interface characterization for composites into four levels (listed in Table 2.6). First one is the molecular level which deals with chemical bonds, acid-base interactions and van der Waals forces. Micro level is the second one and mainly concentrates on interfacial shear strength and bond strength. The third level is the meso level in which the distribution of the fibers in the matrix is analyzed. Lastly, the macro level comes and focuses on the properties of composite.

**Table 2.6** Classification of structural levels for interface characterization in composites (adapted from reference [62])

<table>
<thead>
<tr>
<th>Level</th>
<th>Area of interest</th>
<th>Measured properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular</td>
<td>Chemical structure of the phases&lt;br&gt;The nature and surface concentration of interfacial bonds and bond energies (e.g. van der Waals forces, acid-base interactions and chemical bonds).</td>
<td>Work of adhesion&lt;br&gt;Strength of interfacial interactions&lt;br&gt;Interface width</td>
</tr>
<tr>
<td>Micro</td>
<td>Interface formation&lt;br&gt;Load transfer through the interface&lt;br&gt;Bond strength&lt;br&gt;Stress transfer efficiency&lt;br&gt;Interfacial failure problem</td>
<td>Interfacial strength&lt;br&gt;Interfacial shear stress&lt;br&gt;Critical energy release rate</td>
</tr>
<tr>
<td>Meso</td>
<td>Structural elements</td>
<td>Distribution of reinforcing fiber in composite</td>
</tr>
<tr>
<td>Macro</td>
<td>Bulk properties of the composite</td>
<td>Tensile and impact properties</td>
</tr>
</tbody>
</table>
In Zhandarov and Mader’s study [62], the authors mainly concentrate on the micro level characterization of the interface. Their approach was to divide the micro level characterization into three stages; (1) identification of interfacial parameters, (2) selection of micromechanical test, (3) development of models for predicting interfacial characteristics. Micromechanical tests and interfacial parameters were then classified in an organized manner. Among six micromechanical tests, micro-bond and pull-out tests were chosen due to their adequacy and accuracy to measure interfacial shear strength between fiber and matrix. Theoretical models of interfacial failure in micromechanical tests were introduced in order to determine ultimate shear strength for debonding of fiber and matrix. These models are stress-controlled debonding, energy-controlled debonding, adhesional pressure and model including imperfect interface. The interfacial parameters were then determined by using all these models for glass fiber–cement and aramid fiber-epoxy pairs.

### 2.5 Rule of Mixture and its Application to Composites

It is important to predict properties of mixtures for practical applications. Factors needed to characterize mixtures include concentration and properties of the components, interaction between the constituents, size and shape of the particles, and form of packing. The basic rule for determining the property of a mixture is called the rule of mixture (ROM) [63].

The upper and lower bound properties of the mixtures can be predicted by using ROM. As shown in Figure 2.16, two materials are glued together and then stretched by a force. The lower and upper bound properties of this mixture are predicted by Equations 2.22 and 2.23, respectively.

\[
P = P_1 \phi_1 + P_2 \phi_2
\]  
\[\frac{1}{P} = \frac{\phi_1}{P_1} + \frac{\phi_2}{P_2}\]  

\[P = P_1 \phi_1 + P_2 \phi_2\]  
\[\frac{1}{P} = \frac{\phi_1}{P_1} + \frac{\phi_2}{P_2}\]  

\[\frac{1}{P} = \frac{\phi_1}{P_1} + \frac{\phi_2}{P_2}\]  

\[\frac{1}{P} = \frac{\phi_1}{P_1} + \frac{\phi_2}{P_2}\]
where $P$ is the property of the mixture; $P_1$ and $P_2$ are the corresponding property for components 1 and 2; $\phi_1$ and $\phi_2$ are the concentrations of the components which may be weight fractions, volume fractions, or mole fractions depending upon the type of property being measured.

**Figure 2.16** Properties of the mixture: (a) upper, and (b) lower bound

In order to make accurate predictions, the nature of the mixture should be known. There are two types of mixtures: single phase and two-phase. In the single phase systems, components are miscible or soluble in each other such as miscible copolymers. Properties of this type of mixture can be predicted by using Equation 2.24. On the other hand, in the two phase systems, components are immiscible or partially miscible in each other such as composites. The two phase system is divided into two groups in terms of the nature of the phases. The first one is the two phase system with one continuous phase which includes a continuous phase and a dispersed or discontinuous phase, e.g. filled polymers. The second type is the two phase systems with two continuous phases, e.g. laminates and block copolymers. The mixture rule for this type of systems is given in Equation 2.25 and may be applicable to miscible mixtures.
\[ P = P_1 \phi_1 + P_2 \phi_2 + I \phi_1 \phi_2 \]  

\text{Equation 2.24}

where \( I \) is the interaction term which is related to intermolecular interactions and packing. It must be determined empirically from experiment data and can be either positive or negative. If there is no interaction \( I = 0 \).

\[ P^n = P_1^n \phi_1 + P_2^n \phi_2 \]  

\text{(2.25)}

where \( n \) is a constant and determined by the type of the system and kind of the property. It typically ranges from -1 to 1. When \( n = 0 \), the resulting equation becomes logarithmic rule of mixture:

\[ \log P = \phi_1 \log P_1 + \phi_2 \log P_2 \]  

\text{(2.26)}

The logarithmic rule of mixture can be used to predict elastic modulus of polymer blends which form a continuous phase [63].

The basic ROM is a simple and useful tool to predict some properties of the composite materials. For instance, micromechanical behavior of unidirectionally aligned long-fiber composite can be predicted this way. Application of the rule of mixture to the long-fiber composite is based on some basic assumptions [64]. They are:

- Fibers are uniformly distributed throughout the matrix,
- Perfect bonding exists between fibers and matrix.
- No void presents in the composite.
- The applied force is parallel to the fiber direction.
- Both fibers and matrix behave as linearly elastic material.
The aligned long-fiber composite can be treated as if it were composed of parallel two pieces. These two pieces are the constituents bonded together, with relative thickness in proportion to the corresponding areas or volume fractions of matrix and fiber. This is illustrated in Figure 2.17.

Figure 2.17 Schematic illustration of a representation of a composite as bonded two pieces of matrix and fiber (F is the applied load; A is the cross-sectional area; f is the fiber volume fraction; m and f subscripts represent matrix and fiber respectively)

A load applied in the fiber direction is shared between fiber and matrix:

\[ F = F_f + F_m \]  \hspace{1cm} (2.27)

The stresses depend on the areas of fiber and matrix:

\[ \sigma A = \sigma_f A_f + \sigma_m A_m \]  \hspace{1cm} (2.28)
2.6 Compatibilization

The compatibilization of two immiscible polymers can be achieved by following two methods [60]. First, a block copolymer having at least two blocks in which one block is compatible with one component in the composite and the second block is compatible with another component is added as a binding agent. This type of copolymers helps reducing interfacial tension and the size scale of phase separation at the interface [65]. Second, a polymer with functional group is used to provide interaction and reaction between the components at the interface. These agents are known as “compatibilizers”. When the compatibilizer with functional group is added during the production stage, this process is often called “in-situ or reactive compatibilization” [66].

2.6.1 Compatibilization of PA6/PE Blends

Several compatibilizers listed in Table 2.7 have been extensively used for compatibilizing the PA6/PE blends. It has been shown that adding the compatibilizers into the blends lowers the interfacial tension [67] and enhances the adhesion at the interface [68]. The performance of these compatibilizers has also been compared by many researchers [67-76].

Jiang et al. [69] studied the effectiveness of LDPE-g-MA and HDPE-g-MA on the compatibilization of PA6/LDPE blends and compared their effectiveness with that of previously reported E-AA copolymer [68]. They found that maleic anhydride (MA) functionalized PE can react faster with PA6 than E-AA. However, due to the high miscibility between LDPE-g-MA and LDPE, there was less amount of PE-g-MA available at the interfacial region where reaction with PA6 is expected to occur. On the other hand using HDPE-g-MA which is comparatively less miscible with LDPE yielded better migration to PA6-LDPE interface and was shown to be more effective compatibilizer than E-AA and LDPE-g-MA. In addition to above mentioned compatibilizers, GMA bearing compatibilizers such as E-GMA [70, 74, 75, 77], LDPE-g-GMA [74] and SEBS-g-GMA [71, 74] were also employed. Even though epoxy functional group on glycidyl methacrylate (GMA) offers the
highest reactivity towards to end groups of PA6, these compatibilizers showed comparable performance with E-AA and lower performance than HDPE-g-MA [70]. This was mainly attributed to cross-linking resulting from reactions of the epoxy with both the amine and the carboxyl end groups of PA6 [71]. MA functionalized thermoplastic elastomers such as SEP-g-MA [72] and SEBS-g-MA [67, 71, 72, 75, 76] were also used as compatibilization precursors for PA6/PE blends and shown to be the most effective compatibilizers among compatibilizers listed in Table 2.7. They do not only improve minor phase dispersion but also enhance the mechanical properties of the PA6/PE blends.

**Table 2.7** Compatibilizers used in the compatibilization of PA6/PE blends

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Polymer</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-AA</td>
<td>Ethylene-(b)-Acrylic Acid</td>
<td>[67, 68, 73, 75]</td>
</tr>
<tr>
<td>E-AA-Zinc</td>
<td>Ethylene-(b)-Acrylic Acid with Zinc ionomer</td>
<td>[67, 68]</td>
</tr>
<tr>
<td>E-AA-PBO</td>
<td>Ethylene-(b)-Acrylic Acid combined with a low molar mass bis-oxazoline compound</td>
<td>[73]</td>
</tr>
<tr>
<td>PE-g-MA</td>
<td>Polyethylene grafted with Maleic Anhydride</td>
<td>[76]</td>
</tr>
<tr>
<td>LDPE-g-MA</td>
<td>Low Density Polyethylene grafted with Maleic Anhydride</td>
<td>[69, 78]</td>
</tr>
<tr>
<td>HDPE-g-MA</td>
<td>High Density Polyethylene grafted with Maleic Anhydride</td>
<td>[69, 72]</td>
</tr>
<tr>
<td>SEBS</td>
<td>Styrene-(b)-Ethylene-(co)-Butylene-(b)-Styrene</td>
<td>[67, 71]</td>
</tr>
<tr>
<td>SEBS-g-MA</td>
<td>Styrene-(b)-Ethylene-(co)-Butylene-(b)-Styrene grafted with Maleic Anhydride</td>
<td>[67, 71, 72, 75, 76]</td>
</tr>
<tr>
<td>SEP-g-MA</td>
<td>Styrene-(b)-Ethylene-(co)-Propylene grafted with Maleic Anhydride</td>
<td>[72]</td>
</tr>
<tr>
<td>E-GMA</td>
<td>Ethylene-(b)-Glycidyl MethAcrylate</td>
<td>[70, 74, 75, 77]</td>
</tr>
<tr>
<td>LDPE-g-GMA</td>
<td>Low Density Polyethylene grafted with Glycidyl MethAcrylate</td>
<td>[74]</td>
</tr>
<tr>
<td>SEBS-g-GMA</td>
<td>Styrene-(b)-Ethylene-(co)-Butylene-(b)-Styrene grafted with Glycidyl MethAcrylate</td>
<td>[71, 74]</td>
</tr>
</tbody>
</table>

In addition to the type of compatibilizer, its molecular architecture [69, 71], the functional group content [68, 69, 71, 74, 76], its content in the blend [67-70, 74, 75], and composition of the blend polymers [68, 71, 72, 74] were other factors that can influence the
compatibilization of PA6/PE blend. It was reported that compatibilization effectiveness of HDPE-g-MA increased with decreasing the molar mass of PE backbone and using uniformly distributed MA groups along the chains [69]. On the other hand, for MA-grafted elastomers molecular characteristics did not play important role on the level of compatibilization achieved [71]. The effectiveness of the compatibilizer (E-AA) was shown to increase with an increase of the functional group content [68]. The saturation point of the compatibilizer added in the blend varied with blend composition and compatibilizer type [67-70, 74, 75].

2.6.2 Compatibilization of PET/PE Blends

Several compatibilizers have been used for compatibilizing the PET/PE blends (see Table 2.8). The performance of some of these compatibilizers has been studied by many researchers [79-84]. It was reported that SEBS-g-MA performs better than HDPE-g-MA and SEBS in the PET/HDPE blend, and improves the toughness of the blend with a considerable increase in elongation at break [79]. The effectiveness of diethyl maleate (DEM) functionalized SEBS and LDPE as a compatibilizer in the PET/LDPE blend was also investigated [80]. It was speculated that the SEBS-g-DEM could lower the interfacial tension more than the LDPE-g-DEM and promote co-continuous phase in the blend.

Kalfoglou et al. [81] also conducted morphological analysis and tensile testing on PET/HDPE blends and showed that SEBS-g-MA performs better than E-EA-g-MA. However, the compatibilizers having GMA as a functional group such as E-EA-GMA and E-GMA were found to be more effective than the compatibilizers functionalized with MA [80, 81, 84]. It is due to the fact that the reactivity of the GMA functionality is higher than that of MA [81]. Coltelli et al. [80] also reviewed that the GMA functionalized polyolefins perform better than MA functionalized polyolefins in terms of tensile and impact properties. On the other hand other studies found that E-GMA and SEBS-g-MA showed comparable compatibilization effectiveness in the PET/HDPE blend [82].
### Table 2.8 Compatibilizers used in the compatibilization of PET/PE blends

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Polymer</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-AA</td>
<td>Ethylene-\textit{b}-Acrylic Acid</td>
<td>[84]</td>
</tr>
<tr>
<td>PE-g-MA</td>
<td>Polyethylene grafted with Maleic Anhydride</td>
<td>[85]</td>
</tr>
<tr>
<td>HDPE-g-MA</td>
<td>High Density Polyethylene grafted with Maleic Anhydride</td>
<td>[79, 82, 84]</td>
</tr>
<tr>
<td>EPR-g-MA</td>
<td>Ethylene-\textit{b}-Propylene grafted with Maleic Anhydride</td>
<td>[84]</td>
</tr>
<tr>
<td>E-MeA-g-MA</td>
<td>Ethylene-\textit{b}-Methyl Acrylate grafted with Maleic Anhydride</td>
<td>[81, 83]</td>
</tr>
<tr>
<td>SEBS</td>
<td>Styrene-\textit{b}-Ethylene-\textit{co}-Butylene-\textit{b} Styrène</td>
<td>[79, 86]</td>
</tr>
<tr>
<td>SEBS-g-MA</td>
<td>Styrene-\textit{b}-Ethylene-\textit{co}-Butylene-\textit{b} Styrène grafted with Maleic Anhydride</td>
<td>[79, 81, 82, 84, 87]</td>
</tr>
<tr>
<td>E-GMA</td>
<td>Ethylene-\textit{b}-Glycidyl MethAcrylate</td>
<td>[81-84]</td>
</tr>
<tr>
<td>E-EA-GMA</td>
<td>Ethylene-\textit{b}-Ethylene Acrylate-\textit{b}-Glycidyl MethAcrylate</td>
<td>[81, 83]</td>
</tr>
<tr>
<td>ULDPE-g-DEM</td>
<td>Ultra Low Density Polyethylene grafted with Diethyl Maleate</td>
<td>[80]</td>
</tr>
<tr>
<td>SEBS-g-DEM</td>
<td>Styrene-\textit{b}-Ethylene-\textit{co}-Butylene-\textit{b} Styrène grafted with Diethyl Maleate</td>
<td>[80]</td>
</tr>
</tbody>
</table>

In addition to the type of the compatibilizer [80, 82-84, 86], blend composition [80, 83, 84], the functional group content [81, 83], the molecular weight of the PET [85], and the molecular weight of the PE [87] are other factors that can influence the compatibilization.
2.7 References


CHAPTER 3

Formation of Novel Thermoplastic Composites Using Bicomponent Nonwovens as a Precursor

This chapter is essentially a manuscript by Dasdemir M, Maze B, Anantharamaiah N, and Pourdeyhimi B, and has been published in Journal of Materials Science, 46: 3269-3281 (2011).
Formation of Novel Thermoplastic Composites Using Bicomponent Nonwovens as a Precursor

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Abstract

This study focuses on a novel technique to produce thermoplastic composites directly from bicomponent nonwovens without using any resins or binders. Conceptually, the structure of the bicomponent fibers making up these nonwovens already mimics the fiber-matrix structure of fiber reinforced composites. By using this approach, we successfully produced isotropic thermoplastic composites with polymer combinations of polyethylene terephthalate/polyethylene (PET/PE), polyamide-6/polyethylene (PA6/PE), polyamide-6/polypropylene (PA6/PP), and PP/PE. The effects of processing temperature, fiber volume fraction, and thickness of the preform on the formation and structure of the nonwoven composites were discussed. Processing temperatures of 130 and 165 °C for PE and PP matrices respectively resulted in intact composite structures with fewer defects, for fiber volume fraction values of up to 51%. Moreover, an insight into the changes on the fine structure of the bicomponent fibers after processing was provided to better explain the mechanics behind the process. It is hypothesized that the composite fabrication process can result in annealing and increases the degree of crystallinity and melting temperature of polymers by thickening lamellae and/or removing imperfections. One of the other outcomes of this study is to establish what combination of mechanical properties (tensile and impact) nonwoven composites can offer. Our results showed that compared to glass mat reinforced thermoplastic composites, these novel isotropic nonwoven composites offer high specific strength (97 MPa/g.cm⁻³ for PA6/PE), very high strain to failure (152% for PP/PE) and superior impact strength (147 kJ/m² for PA6/PP) which can be desirable in many critical applications.

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3.1 Introduction

Fiber reinforced composites are engineered materials that combine complementary properties of two constituents, fiber and matrix, to create a synergy on the overall properties. They can be separated into two groups according to the type of the matrix resin used. These are thermosets and thermoplastics. Even though thermoset resins are dominant in the composite market, there is a great impetus to use thermoplastics instead of thermosets. This is due to the fact that using thermosets in composite applications brings some drawbacks such as limited shelf time, comparatively higher processing costs and longer production time. Additionally, fracture toughness and damage tolerance of the composites can be greatly improved when thermoset matrices such as epoxies, unsaturated polyesters and vinyl esters were replaced with thermoplastics [1]. One of the other advantages of using thermoplastic materials in composite application is the ability to reprocess (reshape) and use it in a post-consumer application [2].

Conventional thermoplastic composite fabrication techniques are pultrusion and injection molding. These techniques can be used for short-fiber reinforced thermoplastics such as glass fiber reinforced composites. For long fibers, thermoplastic composites are made by wetting out the reinforcement components (in the form of aligned fiber, tape, and woven fabric) with polymer melt. The methods of making these composites require several steps including fiber formation, fabric or tape construction, and preparation of polymer melt, wetting, and drying. The main challenge in current methods is to combine two distinct materials. This is due to the fact that the polymer melt has to follow long flow paths through the fibrous reinforcement. Therefore, impregnation by the matrix polymer and formation of defects (voids) in the structure are the main drawbacks of conventional thermoplastic composite fabrication techniques.
3.1.1 Matrix-less Composites

A new concept of thermoplastic composite fabrication was first introduced in 1975 by Capiati and Porter [3]. In this approach, fiber component has aligned and extended chains, therefore it has thermodynamically more stable crystals and higher melting point than conventionally crystallized matrix polymer. Thus, the difference in melting points between these two chemically identical components can be utilized to obtain a single polymer thermoplastic composite. Capiati and Porter [3] particularly studied all polyethylene composite and observed a partial melting of the fiber surface and a transcrystalline region at the interface. To evaluate the interfacial shear strength they performed single fiber pull-out test and found a high interfacial strength which was granted by the epitaxial bonding between two components.

Single polymer composites also known as self-reinforced or all-polymer or matrix-less composites then gained much attention due to the fact that they can provide good interfacial adhesion and enhanced recyclability. Several techniques have been developed: film stacking [4, 5], hot compaction [6-9], solution impregnation [10], wet powder impregnation [11], and co-extrusion [12-14]. Among these techniques, film stacking, hot compaction, and recently co-extrusion are the most popular due to the advantages such as strong fiber-matrix interface and high delamination resistance they can provide.

In the film stacking technique, polymer films with a lower melting point than the reinforcement fibers are placed in between preforms. Upon heating, these films melt and form the matrix. Even though interlayer films can improve delamination strength and allow a wide processing temperature window, penetration of polymer melt through fibers can still be problematic [4].

Hot compaction technique was first introduced in 1993 by Ward and his research team [6]. In this technique, a small fraction of the surface of each oriented fiber is melted by carefully controlling the temperature. At the same time, with the help of pressure, the molten polymer flows and fills the gap between remaining reinforcement fibers. Upon cooling, molten
polymer epitaxially crystallizes on the initial fibers and forms the matrix phase. Initial research on the hot compaction was mostly done on melt spun polyethylene (PE) fibers [6, 15, 16]. After successful experimentation with melt spun PE, their research was extended to other highly and partially oriented thermoplastic fibers: polyethylene terephthalate (PET) [17], polypropylene (PP) [18-20], gel spun PE [9], and polyamide 6.6 (PA6.6) [21]. These fibers were either unidirectionally arranged [6, 9, 15-18] or in the form of woven fabric [19-22]. In addition to fibers, unidirectionally arranged [23] or woven [19, 23-26] thin flat tapes were also used as starting material structure for hot compaction.

Among above mentioned materials, hot compacted PP was found to be the most promising candidate with potential for commercial development due to the fact that it can provide cost/performance balance for several applications [8]. It is now commercially available under the trade name of Curv® from Propex Fabrics. Regarding the structure of the preform, woven filaments or tapes were suggested to be the most useful structures because of the advantage of providing greater surface area [8]. This is important for sufficient contact and adhesion between layers.

The most critical processing parameter in hot compaction is the temperature. It determines the amount of matrix and the mechanical performance of the resultant composite. An optimum compaction temperature approximately ranges between onset and peak melting temperatures of the polymer. The major challenge here is to perform compaction in such a very narrow optimum window. In order to address this issue, Hine et al. [27] combined two techniques: hot compaction and film stacking. In order to use lower compaction temperature, they placed the films in between compacted preforms where the matrix material is mostly required. Thus, they did not only widen the processing temperature window but also improve the inter-layer strength. Overall, hot compaction technique can offer high modulus and strength thermoplastic composites with small loss of original fiber properties and provide strong fiber-matrix interface.
Another alternative method of making thermoplastic composite is using coextruded tapes. This technique was developed by Peijs et al. [12, 13] to produce all-PP composites. In their studies, two grades of PP with different melting temperatures were coextruded and then cold drawn to improve the mechanical properties. The coextruded tape composed of a highly oriented PP in the core and a copolymer PP in the skin. The temperature difference in the melting points of these two polymers allows melting the matrix component (skin) while keeping the reinforcement component (core) intact. Due to the several advantages that this technology presents: large processing temperature window (20-40 °C for PP), reduced risk of fiber orientation, and high fiber volume fraction (~90%), it was commercialized by Lankhorst-Indutech in the Netherlands under the trade name PURE® and also by its licensee Milliken in the USA under the trade name Tegris®.

Although coextrusion technique brings several advantages, incompatibility of two components used could lead to interface issue. Therefore, interface strength between fiber and matrix could be lower for this type of composites compared to other all-polymer composites where an identical polymer is involved in both the fiber and matrix.

In a recent study, Zhang and Peijs [14] used bicomponent yarns instead of tapes. Unidirectionally aligned PET multifilament bicomponent yarns with core/sheath structure in which low melting temperature co-PET was used in the sheath, were consolidated by heat and pressure to obtain all-PET composite. They investigated the effects of consolidation temperature and pressure and found that the pressure values used had almost no impact on tensile properties. On the other hand, while longitudinal modulus and strength varies with temperature, transverse strength increases up to an optimum reached at a processing temperature of 220 °C. The examination of fracture surfaces revealed that tensile failure mode actually shifts from ductile to fragile when processing temperature was increased. It was attributed to an improvement in interfacial adhesion between matrix and fiber at comparatively higher consolidation temperature.
3.1.2 Nonwovens as Preforms

Most of the above mentioned studies on thermoplastic composite fabrication techniques were conducted on high performance fibers or highly oriented fibers and tapes. In addition, preforms were in the form of unidirectionally arranged filaments, tape or woven fabric. In this study, we used bicomponent nonwoven fabrics with different polymer pairings and contents as a precursor to produce thermoplastic composites from conventional textile materials without using any resin or binder. The advantages of nonwoven fabrics for composites compared to other preforms are their low cost, high production rate, and convenience for randomization of fibers [2, 28]. For instance, even though a woven fabric with plain weave has maximum mechanical properties in the two perpendicular directions of fibers (0° and 90°), it has considerably lower mechanical properties in the diagonal and other directions [2]. In addition to the benefits that we gain from nonwovens, using the bicomponent structures in thermoplastic composite fabrication offer many advantages such as uniform distribution of matrix and excellent wetting.

We have examined the viability of a process which is similar to the co-extrusion approach proposed by Peijs et al [12-14]. This process allows the production of composites directly from bicomponent nonwovens. Conceptually, the structure of the bicomponent fibers making up these nonwoven already mimics the fiber-matrix structure of fiber reinforced composites. The matrix polymer (sheath) usually has a lower melting point than the core or reinforced polymer, thereby if a temperature that is close to the melting temperature of the matrix is chosen, the applied heat to the preform will allow matrix polymer to soften. Afterwards, by the means of pressure and heat, the matrix polymer flows and fills the inter-fibrillar spaces; therefore, consolidation can be achieved. On the other hand, the core polymer will retain its mechanical properties. Upon cooling, we can obtain either flat or shaped composites (or even be reshaped) depending on the type of mold used. This way, thermoplastic composites and laminates can be produced by using only the bicomponent nonwoven webs or fabrics. Conceptual description of above mentioned process is illustrated in Figure 3.1. This process eliminates the need for any resin or binder usage and post-processing from composite
production steps. The resultant composites are inexpensive and 100% thermoplastic, so that it is lightweight and reusable. Depending on the polymer combinations chosen, these novel nonwoven composites can combine the desired mechanical properties for many application areas. In this regard, one of the outcomes of this paper is to establish what combination of mechanical properties these materials can offer.

![Figure 3.1 Schematic representation of nonwoven composite making process](image)

### 3.2 Materials

Commercial fiber grades of PET, PA6, and PP were used as the core (reinforcement) polymer. Linear low density PE and PP were used as the sheath (matrix) polymer. Some of the basic properties and suppliers of these polymers are listed in Table 3.1.
Table 3.1 Properties and suppliers of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Trade Name</th>
<th>Supplier</th>
<th>Density $\rho$, g/cm$^3$</th>
<th>Melting Temperature $T_m$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>F-61HC</td>
<td>Eastman Chemical Co.</td>
<td>1.41</td>
<td>250</td>
</tr>
<tr>
<td>PA6</td>
<td>Ultramid BS-</td>
<td>BASF</td>
<td>1.13</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>2702</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>CP-360H</td>
<td>Sunoco</td>
<td>0.905</td>
<td>166</td>
</tr>
<tr>
<td>PE</td>
<td>Aspun 6850A</td>
<td>Dow Chemical Co.</td>
<td>0.955</td>
<td>129</td>
</tr>
</tbody>
</table>

1 The density values of PA6, PP, and PE were obtained from corresponding polymer data sheet supplied by the producer. PET density value was taken from the reference [29].

2 The melting temperatures of all polymers were peak melting temperatures and measured by means of a differential scanning calorimeter at a heating rate of 10°C/min.

3.3 Methods

3.3.1 Production of Bicomponent Fibers and Nonwovens

Bicomponent nonwoven fibers and nonwovens were produced using the bicomponent spunbonding process (see Figure 3.2) at the Nonwovens Cooperative Research Center’s pilot facility (NC State University, Raleigh, NC, USA).

The spunbonding process is a method of producing fabrics directly from polymers in a single step. It combines filament extrusion, drawing (attenuation), deposition, bonding, and winding (see Figure 3.2). Therefore, it is one of the most cost effective and fastest methods of making a fabric. As a comparison, the relative production rate ranges between 1 and 6 for weaving; 3 and 16 for knitting, whereas it is between 200 and 2000 for spunbonding [30].

The bicomponent fiber cross-section chosen was a sheath-core structure (see Figure 3.3) in which one component (core) is fully surrounded by the second component (sheath). Two polymer ratios used were 50 wt%/ 50 wt% and 75 wt%/25 wt% (core/sheath). Attenuated fiber samples which are continuous oriented filaments were collected before the deposition
on the forming belt during the process for investigation. Spunbond nonwoven fabrics with 250 g/m² basis weight were also produced using unheated calendaring rolls which can provide sufficient web integrity for handling at subsequent composite fabrication stages.

Figure 3.2 Schematic drawing of the bicomponent spunbonding process at NCSU [31]
3.3.2 Fabrication of Nonwoven Composites

Nonwoven fabrics were cut to 20 cm x 20 cm dimensions. Single layer nonwoven fabrics were stacked on top of one another. Four different thicknesses were obtained by using 2, 4, 8, and 16 layers of nonwoven fabrics. Each layer of these nonwoven fabrics had the dominant orientation in the machine direction. In order to get balanced structures, fiber orientation in these laminates was configured by simply rotating each layer with respect to its dominant orientation and placing it on top of the previous layer. A hot press was used to produce nonwoven composite. The cross-layered fabrics were then placed between Teflon® sheets to prevent fabrics from sticking on the hot surfaces of the press.

Direct composite fabrication from nonwoven fabrics comprises three stages: i) preheating, ii) compacting (consolidation), and iii) cooling (see Figure 3.1). In the first stage, the preform is heated to soften the matrix polymer under a comparatively low pressure ($P_r$) of 0.5 MPa. In this stage, residence time ($t_r$) and temperature ($T_r$) required for softening depends on the type of the matrix used and the thickness of the preform (see Table 3.2). In the second stage, the preheated preform is pressed between two heated plates and held for some time. Thus, matrix polymer flows and fills the gap between reinforcement fibers. At the same time, consolidation of the structure facilitates the removal of the unwanted voids that could weaken the resultant composite. In order to consolidate the structure, a high pressure ($P_c$) of 12 MPa
was used. In this stage, consolidation time ($t_c$) and temperature ($T_c$) are variables that can affect the structure of the resultant composite. In the last stage, composite samples are quenched in between two metal plates at room temperature. Time-temperature and time-pressure profile during nonwoven composite fabrication can also be seen in Figure 3.4. Solid line represents the change on the sample temperature, while the dotted line shows the profile of the applied pressure on the sample. $T_r$ and $T_c$ were kept same for all samples which makes the process flow easier in the hot press. The pressure was increased appreciably after the preheating stage to achieve a better consolidation.

### Table 3.2 Processing parameters

<table>
<thead>
<tr>
<th>Matrix Polymer</th>
<th>Number of Layers</th>
<th>Residence Temperature, $T_r$ ($^\circ$C)</th>
<th>Residence Time, $t_r$ (sec)</th>
<th>Consolidation Temperature, $T_c$ ($^\circ$C)</th>
<th>Consolidation Time, $t_c$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>2</td>
<td>130</td>
<td>30</td>
<td>130</td>
<td>30</td>
</tr>
<tr>
<td>PE</td>
<td>4</td>
<td>130</td>
<td>60</td>
<td>130</td>
<td>60</td>
</tr>
<tr>
<td>PE</td>
<td>8</td>
<td>130</td>
<td>120</td>
<td>130</td>
<td>60</td>
</tr>
<tr>
<td>PE</td>
<td>16</td>
<td>130</td>
<td>240</td>
<td>130</td>
<td>90</td>
</tr>
<tr>
<td>PP</td>
<td>2</td>
<td>165</td>
<td>30</td>
<td>165</td>
<td>30</td>
</tr>
<tr>
<td>PP</td>
<td>4</td>
<td>165</td>
<td>60</td>
<td>165</td>
<td>60</td>
</tr>
<tr>
<td>PP</td>
<td>8</td>
<td>165</td>
<td>120</td>
<td>165</td>
<td>60</td>
</tr>
<tr>
<td>PP</td>
<td>16</td>
<td>165</td>
<td>240</td>
<td>165</td>
<td>90</td>
</tr>
</tbody>
</table>

#### 3.3.3 Tensile Testing of Nonwoven Composites

Composite tensile testing was performed to determine the tensile strength of the composites formed with 2, 4, and 8 plies of nonwoven fabrics. Slippage in the grips was prevented by using diamond grip faces, while the sample fracture at the grip were prevented by using dog bone shaped specimens as specified in the ASTM Standard D 638-08. MTS Q-Test machine with 90 kN load cell was used for the test. The crosshead speed was adjusted to 51 mm/min. Mechanical parameters: initial modulus, tensile strength, strain at break and tensile energy to break were measured.
3.3.4 Izod Impact Testing

The notched izod impact test specimens were machined from a nonwoven composite sample which was made from 16 plies of nonwoven fabrics and had around 4 mm thickness. Six specimens were prepared for each sample and conditioned 48 hours before the test. Samples were tested in the Tinius Olsen Model 92T impact testing machine according to the ASTM Standard D256-06 Method A. Testing conditions were reported as 23°C and 50% relative humidity. All specimens have a dimension of 12.7±0.2 mm X 63.5±2 mm and a notch depth of 2±0.2 mm. Impact strength and impact resistance values were noted and averaged for each sample.
3.3.5 Wide Angle X-Ray
An Omni instrumental wide angle X-ray diffractometer (WAXD) was used to determine the crystallite dimensions for each of the components in the bicomponent nonwoven fibers and composites. The instrument was operated at 30 kV and 20 mA with a Be-filtered CuKα radiation source (λ=1.54 Å). The fibers were manually wound around a sample holder which was then perpendicularly positioned to the x-ray beam. They were scanned at a rate of 0.1 sec⁻¹ from 5° to 40° (2θ). The nonwoven composite specimens were mounted onto the sample holder. They were scanned at a rate of 0.05 sec⁻¹ from 10° to 40°.

3.3.6 Differential Scanning Calorimetry
Thermal analysis was carried out for bicomponent fibers and nonwoven composites by means of differential scanning calorimetry (DSC). Perkin Elmer Diamond DSC calorimeter and Pyriss Series Diamond DSC software were used for the thermal analysis of all the samples. The samples weighed between 3 and 5 mg. The samples were scanned at the heating rate of 10°C/min in the temperature ranges from 25 °C to 270 °C.

3.3.7 Scanning Electron Microscopy
Scanning electron microscope (SEM) images were taken for nonwoven composites. In order to take a clear cross-section image, samples were embedded into liquid nitrogen in which they freeze, and then fractured using a razor blade. SEM analysis was performed on the samples after they were coated with a layer of AuPd at a 5kV accelerating voltage and 40 nA beam current in a Hitachi S-3200 SEM.
3.4 Results and Discussions

3.4.1 Microstructural Analysis

3.4.1.1 Effect of Processing Temperature

Processing temperature is one of the most important parameters that can affect the final composite microstructure. In order to investigate the effect of temperature, we used series of temperatures ranging from 125 °C to 150 °C with increments of 5 °C for PE matrix samples. In the case of processing at 125 °C which is slightly lower than the peak melting temperature of the PE component (127 °C) in the fiber, the matrix polymer did not melt enough to flow and fill the gaps in the composite structure. This situation is depicted in Figure 3.5a. It was shown that insufficient heat could cause defects such as voids in the structure and delamination easily occurs for this structure due to the lack of adhesion between layers. On the other hand, processing at temperatures equal or greater than 135 °C led to over-softening the molten matrix polymer. Combined with the effect of high pressure, the molten polymer was squeezed out from structure and therefore the composite structure lost its integrity (see Figure 3.5b). When 130 °C (± 2 °C) was used, the molten matrix polymer was able to reach a melt viscosity level allowing the polymer to flow and fill the interstices between fibers (see Figure 3.6). Thus, a composite structure with fewer defects could be produced.
**Figure 3.5** PP/PE (50 wt%/50 wt%) nonwoven composites processed at (a) 125 °C and (b) 135 °C

**Figure 3.6** SEM picture of PA6/PE (50 wt%/50 wt%) nonwoven composite processed at 130°C
3.4.1.2 Effect of Reinforcement Volume Fraction

Reinforcement volume fraction determines the packing density of the composite. In most practical applications, a higher reinforcement volume fraction is desired. However, some limitations exist due to the distribution of the fibers in the structure. A random fiber distribution reduces the possible reinforcement volume fraction values. PA6/PE nonwoven composite with high reinforcement volume fraction ratio of 0.72 (achieved at polymer weight ratio of 75/25) is shown in Figure 3.7. When this structure was examined, some matrix-free regions were observed. This is mainly due to the random fiber orientation in nonwoven structures which does not allow close packing. On the other hand, when the reinforcement volume fraction was reduced to values between 0.4 and 0.5 (achieved at polymer ratio of 50/50), nonwoven composites could be produced with far fewer defects in the structure. Some examples of these composites are shown in Figure 3.8.

![Figure 3.7 SEM pictures of PA6/PE (75 wt%/25 wt%) nonwoven composite processed at 129 °C with a fiber volume fraction ratio of 0.72: (a) cross-section, (b) surface](image-url)

Figure 3.7 SEM pictures of PA6/PE (75 wt%/25 wt%) nonwoven composite processed at 129 °C with a fiber volume fraction ratio of 0.72: (a) cross-section, (b) surface
3.4.2. Characterization of Bicomponent Fibers and Nonwoven Composites

3.4.2.1 Thermal Properties

In order to show process-structure relationship, thermal analysis was carried out. Melting and crystallization temperatures for bicomponent fibers and composites were determined by analyzing DSC traces for both bicomponent fibers and nonwoven composites made thereof and listed in Table 3.3.
Table 3.3 Melting and crystallization temperatures of bicomponent fibers and nonwoven composites

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Bicomponent Fiber</th>
<th>Nonwoven Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Core</td>
<td>Sheath</td>
</tr>
<tr>
<td></td>
<td>Core</td>
<td>Sheath</td>
</tr>
<tr>
<td></td>
<td>$T_m$ (°C)</td>
<td>$T_c$ (°C)</td>
</tr>
<tr>
<td>PET/PE</td>
<td>250</td>
<td>206</td>
</tr>
<tr>
<td>PA6/PE</td>
<td>216</td>
<td>191</td>
</tr>
<tr>
<td>PA6/PP</td>
<td>216</td>
<td>189</td>
</tr>
<tr>
<td>PP/PE</td>
<td>162</td>
<td>122</td>
</tr>
</tbody>
</table>

Results given in Table 3.3 were obtained from the first melting endotherms and cooling exotherms. It’s important to point out that these results include the thermal history of the material being tested. Results show that the melting temperatures of both sheath and core polymers increased after going through the composite fabrication process. The increase in the melting points of the polymers can be explained by means of the Gibbs free energy theory (Equation 3.1). According to this theory, the change in the Gibbs free energy ($\Delta G$) per unit mass upon melting is zero. Hence, the melting temperature ($T_m$) is the ratio of the change of enthalpy ($\Delta H$) to entropy ($\Delta S$) from the crystalline state to the melt (Equation 3.2).

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (3.1)

$$T_m = \Delta H / \Delta S$$  \hspace{1cm} (3.2)

Based on this theory, it is possible to increase the melting point of a polymer by changing $\Delta H$ or $\Delta S$ of the system. For polymer systems, $\Delta H$ is determined by the specific interactions between polymer chains. It can be affected by the degree of the chain regularity, perfection of the crystals, and size of the crystallites. During nonwoven composite fabrication process,
sheath component in the bicomponent fiber underwent partial or complete melting with the loss of the microstructure associated with it. After partial or complete melting of the initial lamellae, new lamellae were formed during recrystallization. Because of the long consolidation time, high temperature and pressure, an annealing effect can be achieved. Thus, the thickness of the new lamellae became larger than that of initial lamellae [32]. This leads to an increase in the enthalpy required to melt crystallites; and therefore an increase in the melting point of the sheath polymer was observed.

In addition to an increase in the $\Delta H$, a reduction in the $\Delta S$ which is determined by the orientational and conformational entropies of polymer chains could be observed for polymeric materials heated under constrained conditions [33]. Typically, polymers will try to relax by restoring their preferential isotropic structure, when they are heated. This leads to a transition to more disordered phase with an increase in the entropy. However, it is possible to avoid this relaxation by heating and melting polymers under constrained condition. Thus, polymer chains will have very limited freedom to switch to more disordered phase. During preheating and consolidation stages, bicomponent fibers were constrained between hot plates under high pressure and therefore polymer chains in sheath polymer were prevented from any structural relaxation. At the same time, a melt orientation was introduced. Therefore, a reduction in the orientational and conformational entropies of polymer chains which could cause an increase in the melting point of sheath polymer was achieved. Similarly, the melting temperature shifts for constrained fibers were also reported in the literature [14, 17, 33].

Figure 3.9 presents the DSC endotherms of bicomponent fibers and nonwoven composites. In this figure, dark curves show the DSC endotherms of nonwoven composites while the lighter curves show those of bicomponent fibers. In each curve, there are two melting endotherms where the melting endotherms at higher temperatures belong to core or reinforcement polymers. For example, PA6/PP bicomponent fiber showed two melting endotherms at 166 °C and 216 °C in which the later belongs to PA6 (core) polymer. When the melting behaviors of the core polymers were analyzed, two consecutive endothermal melting peaks were observed. For instance, PA6 component in PA6/PP fiber had two consecutive peaks at 216
84 °C and 222 °C. In this type of broad endotherm for a core polymer, the lower temperature melting peak corresponds to crystallites with imperfections while the higher temperature melting peak represents the more perfect crystallites. It was found that for bicomponent fibers, the lower temperature melting peaks were more dominant than the higher one. However, after composite fabrication process, the intensity of the lower temperature melting peak reduced substantially with an increase in the intensity of the higher temperature melting peak. This indicates that the distribution of crystal sizes was narrowed and imperfections in the former crystallites were reduced during composite fabrication. It can be attributed to the annealing effect brought by the composite fabrication. Therefore, the melting temperatures of the core polymers shift to higher temperatures after formation of the composite.

Figure 3.9 DSC endotherms of bicomponent fibers and nonwoven composites
Contrary to melting temperature, a change in crystallization temperature was not observed for core polymers except PP. However, there is a slight decrease in the crystallization temperatures of sheath polymers. When we compare cooling behavior of sheath polymer in the fiber with that of matrix polymer, it can be expected from sheath polymer to cool faster during fiber formation than the formation of matrix phase in composite. This is due to the fact that fibers have larger surface area to volume ratio than composites. Therefore, they can crystallize at higher temperatures compared to bulk matrix material in the composite. For PP/PE nonwoven composites, this situation is more complicated because these polymers have close crystallization temperatures. For this reason, any change attributed by heat treatment could affect the behavior of the second component.

### 3.4.2.2 Crystallinity and Crystalline Structure

The degree of crystallinity of each polymer in the bicomponent fibers and composites was calculated using Equation 3.3 [34]:

$$X = \frac{\Delta H_f - \Delta H_c}{w \times \Delta H_f^0}$$  \hspace{1cm} (3.3)

where $X$ is the degree of crystallinity of a material; $\Delta H_f$ is the heat of fusion of a polymer (measured from area under melting peak curve of DSC); $\Delta H_c$ heat of cold crystallization of the polymer; $\Delta H_f^0$ is the theoretical heat of fusion for perfectly crystalline polymer (obtained from literature); $w$ is the weight fraction of the polymer in bicomponent or composite structure.

The theoretical heats of fusion for homopolymers were assumed to be 230 J/g [35], 293 J/g [35], 140 J/g [36], 209 J/g [37] for PA6, PE, PET and PP respectively. Cold crystallization peak was not observed for polymers in both bicomponent fibers and composites. Results from the degree of crystallinity calculation are shown in Table 3.4. A significant increase in
the crystallinity values of sheath polymer was observed for all polymer pairs when they were converted to the composite.

Table 3.4 Degree of crystallinity values for bicomponent fibers and nonwoven composites

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Bicomponent Fiber</th>
<th>Nonwoven Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core/Sheath or Fiber/Matrix</td>
<td>Core $X_c$</td>
<td>Sheath $X_s$</td>
</tr>
<tr>
<td>PET/PE</td>
<td>0.332</td>
<td>0.473</td>
</tr>
<tr>
<td>PA6/PE</td>
<td>0.290</td>
<td>0.467</td>
</tr>
<tr>
<td>PA6/PP</td>
<td>0.309</td>
<td>0.395</td>
</tr>
<tr>
<td>PP/PE</td>
<td>0.417</td>
<td>0.518</td>
</tr>
</tbody>
</table>

The crystalline structures for bicomponent fibers and nonwoven composites were examined by using x-ray diffractions (see Figure 3.10 and Table 3.5). General trend for matrix polymers is more sharpened and better resolved peaks. For instance, the intensity of reflections at angular position $2\theta$ of $22^\circ$ which corresponds to 110 plane of PE increased appreciably for composite samples. It suggests that size and/or perfection of crystallites that is perpendicular to this plane increased. Moreover, reflections around angular position $2\theta$ of $25^\circ$ corresponding to 200 plane of PE appeared for composite samples suggesting a crystal growth in the direction perpendicular to this plane. Similarly, characteristic peaks for PP matrix in PA6/PP at $15^\circ$ (110), $17.8^\circ$ (040), and $19.4^\circ$ (130) also showed up for composite samples indicating a crystal growth.

Crystal sizes for PET/PE and PP/PE samples were also calculated using Scherrer formula (Equation 3.4) and summarized in Table 3.6. Results clearly show that crystal sizes (thickness of the lamellae) of PE have considerably improved during composite fabrication. This explains why significant increases in the crystallinity values of sheath polymers were obtained. It also justifies the melting point increase in these polymers after the conversion to composite.
where \( w \) is the width of crystallite (Å) which is the mean size of the crystallites (the ratio of the root-mean-fourth-power to the root-mean-square value of the thickness); \( \lambda \) is the wavelength (Å) (Cu K\( \alpha \) (\( \lambda = 1.54 \) Å) was used); \( \beta \) is the full width at half maximum intensity (radians); and \( \theta \) is the Bragg’s angle (radians).

$$w = \frac{0.94 \times \lambda}{\beta \times \cos \theta}$$  \hspace{1cm} (3.4)

Figure 3.10 WAXD patterns for bicomponent fibers and nonwoven composites
Table 3.5 Observed peak positions for each polymer in bicomponent fibers and nonwoven composites

<table>
<thead>
<tr>
<th>Polymer</th>
<th>1&lt;sup&gt;st&lt;/sup&gt; Peak Position</th>
<th>2&lt;sup&gt;nd&lt;/sup&gt; Peak Position</th>
<th>3&lt;sup&gt;rd&lt;/sup&gt; Peak Position</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 (degree)</td>
<td>Crystallographic Plane (hkl)</td>
<td>20 (degree)</td>
</tr>
<tr>
<td>PET</td>
<td>18.4</td>
<td>(010)</td>
<td>26.3-26.5</td>
</tr>
<tr>
<td>PA6</td>
<td>21.7-22.1</td>
<td>(200)</td>
<td>-</td>
</tr>
<tr>
<td>PP</td>
<td>14.6-15</td>
<td>(110)</td>
<td>17.5-17.8</td>
</tr>
<tr>
<td>PE</td>
<td>22-22.3</td>
<td>(110)</td>
<td>24.6-25</td>
</tr>
</tbody>
</table>
Table 3.6 Crystal sizes of PE in plane (110) for PET/PE and PP/PE

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Sample</th>
<th>2θ (degree)</th>
<th>Crystal Width (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/PE</td>
<td>Fiber</td>
<td>22.3</td>
<td>45</td>
</tr>
<tr>
<td>PET/PE</td>
<td>Composite</td>
<td>22.2</td>
<td>167</td>
</tr>
<tr>
<td>PP/PE</td>
<td>Fiber</td>
<td>22.0</td>
<td>123</td>
</tr>
<tr>
<td>PP/PE</td>
<td>Composite</td>
<td>22.3</td>
<td>212</td>
</tr>
</tbody>
</table>

Overlay of diffraction patterns for PP/PE samples also revealed a slight shift in the diffraction peak positions to higher angles accompanied by increased peak intensity. It suggests that location of the lattice plane changed and unit cell distance (d-spacing) became smaller. It can be attributed to the combination of high pressure and annealing effects on the crystal structures. At the same time crystallite sizes increased so that crystallinity of PP component in the PP/PE composite increased from 41.7% to 44.9%.

We also observed an increase in the crystallinity of PET component in PET/PE samples after composite fabrication. When the x-ray diffraction patterns of these samples were investigated, better resolved peaks for PET at 18.4° (010) and 26.5° (100) in composite sample were obtained. It indicates that the processing temperature of 128 °C accompanied with high pressure induced an improvement on crystal size distribution and perfections. On the other hand, although the degree of crystallinity for PA6 did not undergo appreciable change after the formation of composites, an intensity increase with better resolved peak at 22.1° (200) in PA6/PP composite sample suggests a crystal perfection effect brought about by annealing.
3.4.3 Mechanical Properties

3.4.3.1. Comparison of Tensile and Impact Properties

One of the important outcomes of this study was to evaluate the mechanical properties (tensile and impact) of nonwoven composites and establish how the mechanical properties compared to other conventional and widely used thermoplastic composites such as glass fiber reinforced thermoplastic composites. Therefore, tensile and impact properties of nonwoven composites were measured and compared with a glass mat reinforced polypropylene thermoplastic composite (GMT) having 40% reinforcement glass fiber which can be comparable to the reinforcement fiber percentages (40-51%) of nonwoven composites. Another reason for choosing this structure is the fact that glass fiber mat is one of the closest structure to the bicomponent nonwoven preform in terms of fiber orientation. In this regard, Table 3.7 summarizes results obtained for nonwoven composites and compares with GMT composite. Results showed that in general nonwoven composites yielded higher specific strength values up to 97 MPa/g.cm\(^{-3}\) obtained for PA6/PE nonwoven composite. Thus, nonwoven composites except PP/PE nonwoven composite outperform the GMT in terms of specific stress. One of the other outstanding performances of nonwoven composites compared to GMT composite in terms of the tensile properties is the high strain at break values. Especially, PP/PE nonwoven composites showed tremendous strain at break value of 152% with a standard deviation (\(\sigma\)) of 8% and therefore they were able to absorb high tensile energy (65 MJ/m\(^3\), \(\sigma=5\)).

Notched izod impact strength values of nonwoven composites and GMT composite are also presented in Table 3.7. All nonwoven composite samples showed non-break type of failure described in ASTM standard D256. Among the tested composite samples, PA6/PP nonwoven composite performed best with an average value of 147 kJ/m\(^2\) (\(\sigma=6\)). This value is almost 15 times higher than that of GMT composite. High impact strength values observed for all nonwoven composites suggest that they can be a good candidate for applications where high impact energy absorption is required.
### Table 3.7 Comparison of mechanical properties of thermoplastic composites (standard errors are given in parentheses)

<table>
<thead>
<tr>
<th></th>
<th>PET/PE</th>
<th>PA6/PE</th>
<th>PA6/PP</th>
<th>PP/PE</th>
<th>GMT&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Curv&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Pure&lt;sup&gt;3&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reinforcement Component (%)</strong></td>
<td>40</td>
<td>46</td>
<td>44</td>
<td>51</td>
<td>40</td>
<td>78</td>
<td>90</td>
</tr>
<tr>
<td><strong>Overall Density (g/cm³)</strong></td>
<td>1.14</td>
<td>1.04</td>
<td>1.01</td>
<td>0.93</td>
<td>1.19</td>
<td>0.93</td>
<td>0.77</td>
</tr>
<tr>
<td><strong>Tensile Modulus (GPa)</strong></td>
<td>2.2 (±0.05)</td>
<td>1.7 (±0.02)</td>
<td>1.6 (±0.08)</td>
<td>1.5 (±0.04)</td>
<td>5.8</td>
<td>3.0</td>
<td>1.5-13</td>
</tr>
<tr>
<td><strong>Specific Modulus (GPa/g.cm³)</strong></td>
<td>1.9 (±0.04)</td>
<td>1.6 (±0.02)</td>
<td>1.6 (±0.08)</td>
<td>1.6 (±0.04)</td>
<td>4.9</td>
<td>3.2</td>
<td>1.9-17</td>
</tr>
<tr>
<td><strong>Tensile Strength (MPa)</strong></td>
<td>83 (±0.7)</td>
<td>100 (±1.6)</td>
<td>73 (±0.9)</td>
<td>52 (±1.1)</td>
<td>77</td>
<td>60</td>
<td>4.5-385</td>
</tr>
<tr>
<td><strong>Specific Strength (MPa/g.cm³)</strong></td>
<td>73 (±0.6)</td>
<td>97 (±1.6)</td>
<td>72 (±0.9)</td>
<td>56 (±1.2)</td>
<td>65</td>
<td>64</td>
<td>5.8-500</td>
</tr>
<tr>
<td><strong>Strain at Break (%)</strong></td>
<td>68 (±0.6)</td>
<td>86 (±0.8)</td>
<td>71 (±1.2)</td>
<td>152 (±4.1)</td>
<td>4</td>
<td>27</td>
<td>1-7</td>
</tr>
<tr>
<td><strong>Tensile Energy to Break (MJ/m³)</strong></td>
<td>41 (±0.5)</td>
<td>55 (±1.5)</td>
<td>34 (±0.6)</td>
<td>65 (±2.6)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Notched Izod Impact Test (kJ/m³)</strong></td>
<td>76 (±1)</td>
<td>133 (±1.2)</td>
<td>147 (±2.8)</td>
<td>48 (±1.6)</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1. Glass mat reinforced thermoplastic PP composite [38]
2. Hot compacted woven PP tape thermoplastic composite [18, 19]
Although nonwoven composites offered higher specific strength (except PP/PE nonwoven composite), strain at break and impact strength compared to GMT, they showed lower tensile modulus values. Results showed that the highest tensile modulus of 2.2 GPa (σ=0.3 GPa) was obtained for the PET/PE nonwoven composite. This value is almost two times lower than that of GMT composite (4.9 GPa). It is due to the fact that glass fiber is a high stiffness fiber compared to conventionally produced thermoplastic textile fibers.

In order to give a broad perspective to readers, we also compared nonwoven composites with two new all-polymer composites (Curv® and Pure®) in Table 3.7. However, it is important to point out that these all-polymer composites do not have comparable reinforcement fiber percentages (78% for Curv® [19] and 90% for Pure® [13]) and preform structures with nonwoven composites (<51%). As an example to Curv®, a hot compacted woven (plain) PP tape thermoplastic composite [18, 19] was chosen. Since only unidirectionally arranged structure exists for Pure® Technology in the current literature, we present a coextruded unidirectional PP tape thermoplastic composite properties [13] in Table 3.7. When mechanical properties are compared, nonwoven composites yielded comparable or higher specific strength and strain at break than Curv® and Pure® (except the longitudinal specific strength of Pure®). On the other hand, they generally showed lower specific modulus. It is due to the fact that reinforcement tape in two all-polymer composites are highly oriented structures compared to bicomponent fibers. At the same time the reinforcement component percentages for these two all-polymer composites are higher than nonwoven composites.

One of the important parameter that could have negatively affected the mechanical responses of nonwoven composites is the fiber-matrix interface. When we investigate the microstructure of nonwoven composites (see Figure 3.8), noticeable fiber-matrix debonding for PET/PE, PA6/PP, and PA6/PE can be observed. This debonding issue could lead to weak fiber-matrix strength and lower the mechanical properties. The question remains whether or not it is possible to improve interface and obtain even stronger nonwoven composites by modifying the process and using some interface compatibilization agents. This part of the study is out of the scope of this article and will be addressed in a subsequent article.
3.4.3.2 Effect of Number of Layers (Lamina) on Tensile Properties

Nonwoven composites composed of 2, 4, and 8 layers of nonwoven fabrics with each having 250 g/m² basis weight were produced to determine the effect of number of layers on tensile properties of the composites. In this regard, the tensile properties of nonwoven composites with varying number of layers are presented in Figure 3.11 and 3.12. Results shown in Figure 3.11 indicate that there is no difference between the tensile strength values of composites having different number of layers. Similarly, as the number of layers in the composites increase, the strain value for the composite does not change (see Figure 3.12). These results suggest that tensile properties of the nonwoven composites are not dependent on the thickness of the composites studied.

![Figure 3.11 Tensile strength values of nonwoven composites](image)
The interface in between layers was also investigated by morphological analysis. In order to find the location where two layers came into contact, preferred fiber distributions in the cross-section of nonwoven composite were tracked. Since cross-layering of nonwoven fabrics during composite fabrication enables to get two preferential directions of fiber distribution: along the production direction of nonwoven fabric known as machine direction (MD) and across the width of the fabric which is cross-direction (CD). Thus, we were able to determine the intersection of two layers during morphological examination. One of the examples of this is illustrated in Figure 3.13 which shows the cross-sectional SEM image of a PA6/PE nonwoven composite. From this image, it is clearly seen that there is a smooth transition from one layer to another layer without any matrix free region indicating an intact composite structure.
3.5 Conclusions

In this work, we introduced a new technique to produce engineering thermoplastic composites from bicomponent nonwovens without using any additional resin or binder. Inherent composite structure of the bicomponent fibers enabled to obtain fiber reinforced thermoplastic composites in which PET, PA6, and PP were the reinforcement while PP and PE were the matrix. The effects of temperature and fiber volume fraction on the structure of nonwoven composites were studied by using microstructural analysis. Processing temperatures of 130 °C for PE matrix and 165 °C for PP matrix were found to be the most favorable conditions for producing nonwoven composites with the fewer amount of defects under high pressure. Combination of two factors: (i) random distribution of the fibers and (ii) cross-layering limited to achieve high reinforcement volume fraction (e.g. f=0.72 for PA6/PE) in the resultant composite. However nonwoven composites (PET/PE, PA6/PE, PA6/PP, and PP/PE) with $f \leq 0.51$ were successfully produced.

In order to provide a better insight for the process-structure relationship, thermal properties, crystallinity, and crystal structure of bicomponent nonwovens and nonwoven composites were analyzed and compared. Our findings showed that the melting temperature and degree
of crystallinity of sheath polymers increased when they became matrix. This was attributed to the annealing and constrained fiber effects brought by composite processing. A significant increase in the crystallite sizes for matrix phase achieved after composite fabrication also supports our conclusion. We also observed melting temperature rises for reinforcement fibers. This was also explained to be a result of thermal treatment under pressure which could lead to a better distribution of the crystallite sizes and improved perfections of crystallites.

Mechanical performance of nonwoven composites were also reported and compared with a GMT composite which has a polypropylene matrix and 40% glass fiber content. In general, nonwoven composites showed lower specific modulus but higher specific stress than GMT composite. On the other hand they provided superior strain at break (68-152%) and impact strength (48-147 kJ/m²) values compared to GMT composite (4% and 10 kJ/m², respectively).

Nonwoven composites with different thicknesses achieved with cross-layering 2, 4, and 8 plies of nonwovens having 250 g/m² were also compared in terms of their mechanical (tensile) performance. Our findings showed that tensile properties are not affected by the number of plies in the composite. Moreover, morphological analysis of the intersection of two layers revealed an intact composite structure without any separation or matrix-free region at the interface.

In conclusion, this study shows that thermoplastic nonwoven composites with random fiber distribution can be produced by using only bicomponent nonwovens as a precursor. The resultant composites have isotropic structure with uniform distribution of matrix and high fiber volume fraction at the same level of fiber orientation. From an industrial point of view this technique permits the transformation of an inexpensive preform into an engineered thermoplastic composite in one step with excellent wetting characteristics of matrix polymer.
3.6 References


CHAPTER 4

Influence of Polymer Type, Composition and Interface on the Structural and Mechanical Properties of Core/Sheath Type Bicomponent Nonwoven Fibers

This chapter is essentially a manuscript by Dasdemir M, Maze B, Anantharamaiah N, and Pourderyhimi B, and has been prepared for submission to Journal of Materials Science.
Influence of Polymer Type, Composition and Interface on the Structural and Mechanical Properties of Core/Sheath Type Bicomponent Nonwoven Fibers

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The Nonwovens Institute, North Carolina State University, Raleigh, NC, USA

Abstract

In this study, we investigated the effect of polymer type, composition and interface on the structural and mechanical properties of core-sheath type bicomponent nonwoven fibers. These fibers were produced using poly(ethylene terephthalate)/polyethylene (PET/PE), polyamide 6/polyethylene (PA6/PE), polyamide 6/polypropylene (PA6/PP), polypropylene/polyethylene (PP/PE) polymer configurations at varying compositions. The crystallinity, crystalline structure and thermal behavior of each component in bicomponent fibers were studied and compared with their homocomponent counterparts. We found that the fiber structure of the core component was enhanced in PET/PE, PA6/PE, and PA6/PP whereas that of the sheath component was degraded in all polymer combinations compared to corresponding single component fibers. The degrees of these changes were also shown to be composition dependent. These results were attributed to the mutual interaction between two components and its effect on the thermal and stress histories experienced by polymers during bicomponent fiber spinning. For the interface study, the polymer-polymer compatibility and the interfacial adhesion for the laminates of corresponding polymeric films were determined. It was shown that PP/PE was the most compatible polymer pairing with the highest interfacial adhesion value. On the other hand, PET/PE was found to be the most incompatible polymer pairings followed by PA6/PP and PA6/PE. Accordingly, the tensile strength values of the bicomponent fibers deviated from the theoretically estimated values depending on core-sheath compatibility and interfacial adhesion. These results unveiled the direct relation between interface and tensile response of the bicomponent fiber.

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4.1 Introduction

Bicomponent fibers are designed to meet requirements of two materials into one single fiber by hosting two components along the fiber length. Therefore, they are also known as “composite”, “conjugate” and “hetero” fibers. Natural counterpart of a bicomponent fiber is wool which consists of hydrophobic outer layer (scales) and strong, oriented fibrous structures inside. Formation of typical melt spun bicomponent fibers or filaments involve coextruding two polymers from a single spinneret with a desired cross-sectional arrangement. Since it is possible to produce specialty fibers by selecting cross-sectional designs depending on the end-use application, bicomponent fibers have gained great commercial interest.

Bicomponent fibers can be classified according to the distribution of each component within cross-sectional area. Typical cross-section configurations include side-by-side, core/sheath (c/s), islands-in-the-sea, alternating segments or segmented-pie, citrus and tipped (see Figure 4.1). Most of the bicomponent fibers commercially produced today have c/s structures. In the c/s bicomponent fiber structure, one of the components (sheath) functions as a shell and surrounds the second component (core). Depending on the location of the core component these fibers can be either concentric where the core is at the center (see Figure 4.1b) or eccentric (see Figure 4.1c). The eccentric configuration is used for providing self-crimping properties. On the other hand, if the fiber and fabric strength are mostly desired, concentric configuration can be chosen. Major application areas of these fibers are nonwovens. There are several purposes of using these materials in a nonwoven product. These include but are not limited to the following: bonding (self-bonding) improvement in thermally bonded nonwovens, strength and flexibility increase, cost reduction, and surface property enhancement [1-4]. In addition, bicomponent fibers [5] and nonwovens [6] were recently shown to be a good candidate for the formation of thermoplastic composite structures.
Polymer viscosities, rates of cooling and surface tensions of the two components are critical for the formation and properties of bicomponent fibers [3, 4]. Polymer viscosities of each component should be comparable at the spin pack along with the temperature to obtain desired cross-section [1, 3]. Rates of cooling determine the orientation of each component while the surface tensions determine the adhesion between two components and the final cross-sectional shape in the resultant bicomponent fiber.

Previous studies on bicomponent fibers have mainly focused on the structure and physical properties of bicomponent fibers at high-speed melt spinning [7-13]. In these studies, several polymer combinations (listed in Table 4.1) have been investigated to observe the effect of interaction of two components on the structure of each component in the fiber. The differences in the characteristics of the two polymers in bicomponent fiber including melt (elongational) viscosities and solidification temperatures were some of the major factors affecting the interaction of two components [8]. These factors can influence the spinline
stresses acting on each component and change their thermal histories. As a result, the fiber structure for each component in bicomponent fiber develops under different conditions compared to corresponding single component fiber. For instance, in PET/PP (c/s) bicomponent fiber, PET yields higher orientation and orientation induced crystallization, whereas PP shows lower structure formation than corresponding single component PET and PP fibers [7, 8]. Similar results were also obtained for other polymer combinations listed in Table 4.1 at high-speed melt spinning. Even though major application areas of c/s type bicomponent fibers are nonwovens, all of the above mentioned studies were conducted for high-speed melt spun fibers and very limited literature [14] is available for bicomponent nonwoven fibers.

**Table 4.1** Previous studies on the structure and physical properties of bicomponent fibers at high-speed melt spinning

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Polymer</th>
<th>Configurations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/PP</td>
<td>Poly(ethylene terephthalate)/Polypropylene</td>
<td>c/s</td>
<td>[7, 8]</td>
</tr>
<tr>
<td>PET/PS</td>
<td>PET/Polystyrene</td>
<td>c/s</td>
<td>[7]</td>
</tr>
<tr>
<td>PET/HDPE</td>
<td>PET/High Density Polyethylene</td>
<td>c/s and s/c</td>
<td>[11, 12]</td>
</tr>
<tr>
<td>PET/LLDPE</td>
<td>PET/Linear Low Density Polyethylene</td>
<td>c/s and s/c</td>
<td>[11, 12]</td>
</tr>
<tr>
<td>HMPET/LMPET</td>
<td>High Molecular Weight PET/</td>
<td>c/s and s/c</td>
<td>[9, 10]</td>
</tr>
<tr>
<td></td>
<td>Low Molecular Weight PET Poly(butylene adipate-coterephthalate)/Poly(butylene terephthalate)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBAT/PBT</td>
<td></td>
<td>c/s</td>
<td>[13]</td>
</tr>
</tbody>
</table>

One of the other major factors affecting the interaction is the compatibility of two polymers used in bicomponent fiber. Cho et al. [11, 12] studied PET/LLDPE and PET/HDPE bicomponent melt spun fibers in both c/s and s/c configurations. It was found that using PE in the sheath component yielded interfacial stability which was formed at lower take-up
velocities compared to when it was used in the core component. It was attributed to the
difference in the thermal expansion of each component and their thermal behavior in either
combination. The interfacial instability, in other words phase separation, at the interface was
also observed for PET/ Poly(phenylene sulfide) (PPS) c/s type bicomponent meltspun fibers
[15]. The observation of the phase separation at the interface was attributed to the
incompatibility of these polymers used in bicomponent fibers. On the other hand, when two
compatible polymers were used, strong interfacial adhesion between these two components
could be obtained. For instance using PET with biodegradable aliphatic polyesters such as
poly(butylene succinatek-lactate) (PBSL) or poly(L-lactic acid) (PLLA) in c/s configuration
resulted in physical adhesion of the core and sheath components which was induced by the
interfacial interaction during melt spinning [16]. For these bicomponent fibers, enhanced
mechanical properties compared to a single PET fiber was reported. However, the influence
of the interface on mechanical properties of bicomponent fibers has not been fully elucidated.

In this study, we investigated the effects of polymer type, composition and interface on the
structure and mechanical properties of bicomponent nonwoven fibers. In this regard, typical
c/s type bicomponent nonwoven fibers were produced using PET, polyamide 6 (PA6), PP,
and PE polymers in PET/PE, PA6/PE, PA6/PP, and PP/PE (c/s) polymer configurations at
varying compositions. The structure of each component in bicomponent fibers were studied
and compared with their homocomponent counterparts. Also, tensile properties of
bicomponent fibers and interface between two polymers used in these fibers were
characterized to get a deeper insight into the relation between the mechanical responses of
bicomponent fibers and interface.

4.2 Materials

Commercial fiber grades of Poly (ethylene terephthalate) (PET), Polyamide 6 (PA6),
polypropylene (PP), and linear low density polyethylene (PE) were used for producing fibers
and making films. Some of the basic properties and suppliers of these polymers are listed in
Table 4.2.
Table 4.2 Properties and suppliers of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Trade Name</th>
<th>Supplier</th>
<th>Density $\rho$ (g/cm$^3$)</th>
<th>Melting Temperature $T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>F-61HC</td>
<td>Eastman Chemical Co.</td>
<td>1.41</td>
<td>250</td>
</tr>
<tr>
<td>PA6</td>
<td>Ultramid BS-2702</td>
<td>BASF</td>
<td>1.13</td>
<td>220</td>
</tr>
<tr>
<td>PP</td>
<td>CP-360H</td>
<td>Sunoco</td>
<td>0.905</td>
<td>166</td>
</tr>
<tr>
<td>PE</td>
<td>Aspun 6850A</td>
<td>Dow Chemical Co.</td>
<td>0.955</td>
<td>129</td>
</tr>
</tbody>
</table>

1 The density values of PA6, PP, and PE were obtained from corresponding polymer data sheet supplied by the producer. PET density value was taken from the reference [17].
2 The melting temperatures of all polymers were peak melting temperatures and measured by means of a differential scanning calorimeter at a heating rate of 10 °C/min.

4.3 Methods

4.3.1 Production of Nonwoven Fibers

Homocomponent and bicomponent nonwoven fibers were produced using the spunbonding process (see Figure 4.2) at the Nonwovens Institute’s pilot facility (NC State University, Raleigh, NC, USA). The bicomponent fiber cross-section chosen was a core/sheath structure with different polymer ratios listed in Table 4.3. Overall throughput was adjusted to 0.6 g/min for each hole for an 1162 holes spinneret. Fibers were quenched with quenchers on either side and the quench air temperature was 11 °C. Screw pressures for both extruders were adjusted to 750 psi. Processing temperatures for each polymer are listed in Table 4.4. Drawn fibers with an expected fiber denier value of 1.6 were collected during the process for investigation.
Table 4.3 Polymer combinations and ratios for nonwoven fibers

<table>
<thead>
<tr>
<th>Polymers (core/sheath)</th>
<th>Weight Ratios (wt/wt %)</th>
<th>Volume Ratios (v/v %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/PE</td>
<td>0/100, 50/50, 75/25, 100/0</td>
<td>0/100, 40/60, 67/33, 100/0</td>
</tr>
<tr>
<td>PA6/PE</td>
<td>0/100, 50/50, 75/25, 100/0</td>
<td>0/100, 46/54, 72/28, 100/0</td>
</tr>
<tr>
<td>PA6/PP</td>
<td>0/100, 50/50, 75/25, 100/0</td>
<td>0/100, 44/56, 71/29, 100/0</td>
</tr>
<tr>
<td>PP/PE</td>
<td>0/100, 50/50, 75/25, 100/0</td>
<td>0/100, 51/49, 76/24, 100/0</td>
</tr>
</tbody>
</table>
Table 4.4 Processing conditions for the production of nonwoven fibers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>ProcessingTemperature (°C)</th>
<th>Extruder</th>
<th>Zone 1</th>
<th>Zone 2</th>
<th>Zone 3</th>
<th>Zone 4</th>
<th>Zone 5</th>
<th>Zone 6</th>
<th>Spin Pack</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>260</td>
<td>274</td>
<td>279</td>
<td>285</td>
<td>291</td>
<td>296</td>
<td>296</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA6</td>
<td>232</td>
<td>249</td>
<td>260</td>
<td>266</td>
<td>268</td>
<td>268</td>
<td>268</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>191</td>
<td>204</td>
<td>216</td>
<td>229</td>
<td>235</td>
<td>241</td>
<td>241</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PE</td>
<td>191</td>
<td>204</td>
<td>216</td>
<td>227</td>
<td>227</td>
<td>227</td>
<td>227</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.3.2 Preparation of Films, Laminates and Test Coupons

A heat press was used for the preparation of films. Before making films, PA6 and PET polymer pellets were dried at 80 °C for 24 hours under vacuum while other polymers were used as-received. Processing temperatures were 180 °C for PE, 200 °C for PP, 240 °C for PA6 and 270 °C for PET. The residence time in which polymer pellets melt in a defined geometry without any pressure was set to 5 minutes. The pressure was then applied with 500 psi increment at every 30 seconds until pressure level reached to 5000 psi. Cooling was done under pressure by circulating high pressure air (30 psi) in the system. The cooling rate was noted to be between 8-10 °C/min.

The lamination of PET/PE, PA6/PE, PA6/PP, and PP/PE polymer films was also done in the heat press. Before the lamination, film surfaces were cleaned and films were dried at 80 °C for 6 hours under vacuum. The residence time for all laminates was kept at 5 min in which polymer films reached a certain temperature and melted. The temperature value was maintained at 230 °C for all laminates except PET/PE which was laminated at 270 °C. Lamination time employed was 30 min. The pressure during lamination was kept low (250 psi) to only provide enough contact between two films. The cooling rate was same as that of films (8-10 °C/min).

A reinforced blade and a rotary cutting tool were used to cut specimens from laminates. 50 mm*10 mm coupons were prepared. These coupons were then conditioned at room condition
(22 °C and 50 % relative humidity) for 24 hours before the asymmetric double cantilever beam (ADCB) test.

4.3.3 Tensile Testing of Films

Samples for the film tensile test were prepared using exactly the same condition as the films used in the laminates. Film tensile tests were performed to determine Young’s modulus of films according to ASTM standard D882 under standard test conditions (21±1°C and 65±2 % relative humidity). The polymer films were preconditioned for 24 hours. At least 5 specimens were prepared for each sample set using a dog-bone shaped template. MTS Q-Test machine with 1100 N load cell was used for tensile test. The gauge length for the test was adjusted to 50 mm. Tensile tests were carried out under constant rate of extension with a strain rate of 5 mm/min.

4.3.4 Asymmetric Double Cantilever Beam Test

An asymmetric double cantilever beam (ADCB) tester was designed and built at the Nonwovens Institute (NC State University, Raleigh, USA). This test was performed to determine the strength of interface between two polymers used in bicomponent nonwoven fibers. In this test, an ADCB test coupon (laminate) was mounted on a sample stage. A small crack was initially created between two polymer sheets in the laminate with a razor blade. A moving blade was then inserted into the opening and pushed forward at a constant speed of 3µm/sec. After the crack was stabilized, the length of the opening crack which is an inverse function of the strength of interface between two films was obtained and recorded from several locations along the specimen during the test. This was done by taking the picture of the crack at an interval of 5 min. A total of 34 pictures of the crack were taken for each specimen. The first 10 and last 4 images were omitted and the remaining 20 images were analyzed. From each image, 5 measurements along the crack were done using an image analysis program. Three specimens for each sample were tested in the ADCB tester and a total of around 300 measurements were analyzed for each sample set. Except PET/PE where
PET component was too fragile during crack opening, all polymer interfaces were characterized.

4.3.5 Tensile Testing of Single Fibers

Fiber tensile tests were performed according to ASTM standard D3822-07 under standard test conditions (21±1°C and 65±2 % relative humidity). The fibers were preconditioned for two days. Linear density of the single fibers was measured using the vibroscope method (ASTM D 1577-07) in a Vibromat ME Textechno® test equipment and fiber deniers were noted. Each individual fiber was then pasted on paper cardboards. Great care was taken not to deform the fibers. At least 10 specimens were prepared for each sample set. MTS Q-Test machine with 50 g load cell was used for tensile test. The gauge length for the test was adjusted to 25.4 mm (1 inch). Tensile tests were carried out under constant rate of extension with an extension rate of 15 mm/min.

4.3.6 Wide Angle X-Ray Diffraction

An Omni instrumental wide angle X-ray diffractometer (WAXD) was used to determine the crystallite dimensions of homocomponent nonwoven fibers and each component in the bicomponent nonwoven fibers. The instrument was operated at 30 kV and 20 mA with a Be-filtered CuKα radiation source (λ=1.54 Å). The fibers were manually wound around a sample holder which was then perpendicularly positioned to the x-ray beam. They were scanned at a rate of 0.1 sec⁻¹ from 5° to 40° (20).

4.3.7 Differential Scanning Calorimetry

Thermal analysis was carried out for homocomponent and bicomponent nonwoven fibers by means of differential scanning calorimetry (DSC). Perkin Elmer Diamond DSC calorimeter and Pyriss Series Diamond DSC software were used for thermal analysis of all samples. The sample weights were in the range of 3 to 5 mg. Samples were scanned at the heating rate of 10°C/min with temperature ranging from 25 °C to 270 °C.
4.3.8 Scanning Electron Microscopy

Scanning electron microscope (SEM) images were taken for bicomponent nonwoven fibers. In order to take a clear cross-section image, fibers were dipped into liquid nitrogen in which they freeze, and then fractured using a razor blade. Images of the samples were taken after they were coated with a layer of AuPd at a 5kV accelerating voltage and 40 nA beam current in a Hitachi S-3200 SEM.

4.4 Results and Discussions

4.4.1 Effect of Polymer Type and Composition on Structural Properties

4.4.1.1 Crystallinity and Crystalline Structure

The percent crystallinity of polymers in the homocomponent and bicomponent fibers was calculated using Equation 4.1 [19]:

\[
X = \frac{\Delta H_f - \Delta H_c}{w \times \Delta H_f^0} \times 100
\]  

(4.1)

where \(X\) is the percent crystallinity of a polymer; \(\Delta H_f\) is the heat of fusion of the polymer (measured from the area under the melting peak of the DSC curve); \(\Delta H_c\) heat of cold crystallization of the polymer; \(\Delta H_f^0\) is the theoretical heat of fusion for perfectly crystalline polymer (obtained from literature); \(w\) is the weight fraction of the polymer in bicomponent fiber (for homocomponent fibers \(w = 1\)). The theoretical heats of fusion for homopolymers were assumed to be 230 J/g [20], 293 J/g [20], 140 J/g [21], 209 J/g [22] for PA6, PE, PET and PP respectively. Cold crystallization peak was not observed for polymers in both homocomponent and bicomponent fibers so \(\Delta H_c\) was assumed to be zero.
Figure 4.3a shows the effect of the volume content of sheath component on the crystallinity of the core component. The first noticeable result was an increase in the crystallinity of the core polymers (except PP) when they were spun with sheath component in bicomponent structure. Moreover, increasing the sheath volume fraction increased the crystallinity of the core components. This can be attributed to the difference in thermal and stress histories experienced by core polymer during homocomponent and bicomponent fiber spinning. In PET/PE, PA6/PE, and PA6/PP configurations, the core polymers have much higher solidification temperatures than the sheath polymers. Therefore, during bicomponent fiber spinning, the core components solidify earlier than the sheath polymers. Before the solidification of these core components takes place, they experience spinline stress which induces orientation in this component. In a bicomponent system, a larger portion of this spinline stress at or near the solidification temperature of the polymer typically acts on the component having higher elongational viscosity [7, 8]. It was also previously shown that the spinline stress experienced by the same polymer was higher in bicomponent spinning than the corresponding single fiber spinning [7, 8]. In our case PET and PA6 have much higher elongational viscosities than PP and PE and experienced a great portion of the total spinline stress at solidification temperature of the former polymers. Therefore, the solidification stress experienced by the core polymer in bicomponent system can be expected to be higher than the stress experienced by the same polymer in homocomponent system and increase with increasing the volume content of the sheath polymer. Therefore, it can be postulated that as a result of higher level of solidification stresses, the degrees of orientation induced crystallization were improved for PA6 and PET in bicomponent system as compared to same polymers in homocomponent system. In the PP/PE configuration, the solidification temperatures of two polymers are very close to each other. Therefore, it was not expected from PP to experience a high degree of improved solidification stresses that can increase the crystallinity. Also, due to their similar chemical structure and compatibility, PP and PE may undergo molecular interaction such as inter-diffusion of the chains at their interfacial vicinity. Such molecular interactions may prevent chains from forming crystallites near the
interface. Depending on the composition of two polymers these interactions may also vary. This may be the possible reason for observing a decrease in crystallinity of PP fiber.

**Figure 4.3** Effect of the second component on the crystallinity of (a) core and (b) sheath components

For the sheath polymers, we observed a decrease in the crystallinity in comparison to their homocomponent counterparts (see Figure 4.3b). Also, the percent crystallinity of these polymers gradually decreased with increasing the volume content of the core polymer. This is also closely related to the difference in spinline stresses acting on these polymers during homocomponent and bicomponent fiber spinning. After the solidification of the core polymer takes place, the spinline stress on the sheath polymer suddenly vanishes. This causes a stress relaxation on the sheath polymer. The degree of this stress relaxation increases with
increasing the volume content of core component. As a result orientation induced crystalline formation reduces in the sheath polymers.

The crystalline structure for bicomponent fibers were also investigated using x-ray diffraction technique and compared with their corresponding homocomponent counterparts. In this regard, Figure 4.4 shows the WAXD patterns of homocomponent and bicomponent fibers at four polymer composition ratios: 0/100, 50/50, 75/25, and 100/0 (core wt %/sheath wt %). For guidance to the reader, observed peak positions and their corresponding crystallographic planes for each polymers are also listed in Table 4.5.

When we analyzed WAXD patterns of fibers, we observed that the intensity of crystalline peaks for sheath polymers sharply decreased and, in some instances, they almost disappeared in bicomponent fibers. For instance, in PET/PE bicomponent fibers (see Figure 4.4a), the intensity of reflections at angular position 2θ of 22°, which corresponds to the (110) plane of PE, was significantly reduced as compared to PE homocomponent fiber. At the same time, other peaks at angular positions 2θ of 24° (200) and 37° (020) which appear in homocomponent fibers almost disappeared in PET/PE bicomponent fibers. Moreover, the degree of intensity reduction became more pronounced with increasing the core volume fraction in bicomponent fiber. Similar results were also obtained for other bicomponent fibers (see Figure 4.4b, c, and d). These results suggest that size and/or perfection of crystallites decreased for sheath polymers when they were spun in bicomponent structure. They also support our previous statement on crystallinity decrease for sheath polymers as a result of stress relaxation occurring in bicomponent fiber spinning.
Figure 4.4 WAXD patterns of homocomponent and bicomponent nonwoven fibers: (a) PET/PE, (b) PA6/PE, (c) PA6/PP, and (d) PP/PE
Table 4.5 Observed peak positions for each polymer in homocomponent and bicomponent nonwoven fibers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>1st Peak Position</th>
<th>2nd Peak Position</th>
<th>3rd Peak Position</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2θ (degree)</td>
<td>Crystallographic</td>
<td>2θ (degree)</td>
</tr>
<tr>
<td>PET</td>
<td>18.1-18.4</td>
<td>(010)</td>
<td>26.3-26.5</td>
</tr>
<tr>
<td>PA6</td>
<td>21.7-22.1</td>
<td>(200)</td>
<td>-</td>
</tr>
<tr>
<td>PP</td>
<td>14.4-14.9</td>
<td>(110)</td>
<td>17.2-17.5</td>
</tr>
<tr>
<td>PE</td>
<td>21.9-22.3</td>
<td>(110)</td>
<td>24.2-24.4</td>
</tr>
</tbody>
</table>
The x-ray diffraction patterns for core polymers also showed some difference from their homocomponent counterparts. For instance, in PET/PE bicomponent fibers (see Figure 4.4a), the crystalline peaks for PET at angular positions 2\(^\theta\) of 18° (010) and 26° (100) became more noticeable compared to those for homocomponent PET fiber. Also, increasing the sheath volume content from 25% to 50% in the bicomponent fiber yielded slightly better resolved peak for the core polymer. These results also suggest that the orientation induced crystallization of PET has improved. For other polymer combinations, we observed a slight decrease in peak width which can also be related to change in crystallization behavior.

4.4.1.2 Thermal Behavior

To investigate the changes in thermal behavior of polymers, homocomponent and bicomponent fibers were characterized. Melting and crystallization temperatures of these polymers are listed in Table 4.6. As commonly encountered for most polymers [23], we also observed two endothermic melting peaks for PET, PA6, and PP polymers. Therefore two melting temperatures (\(T_{m1}\) and \(T_{m2}\)) listed in Table 4.6 represent these two peaks. It was found that the melting temperatures of core polymers (except PP) increased in bicomponent fibers when compared to their counterparts in homocomponent fibers. On the other hand, melting temperatures of the sheath polymers was reduced when these polymers were spun in bicomponent structure. Also, crystallization temperatures for these polymers decreased in bicomponent fibers. The melting and crystallization temperatures of the polymers strongly depend on their thermal history [24]. Therefore, these observed results are closely associated with the change in thermal history and crystallization behavior acquired by polymers during bicomponent spinning as opposed to single fiber spinning. They are also in agreement with our previous conclusions on the crystallinity and crystalline structure (see Section 4.4.1.1).
Table 4.6 Melting and crystallization temperatures of homocomponent and bicomponent nonwoven fibers (subscripts c and m refer to crystallization and melting)

<table>
<thead>
<tr>
<th>Polymers (core/sheath)</th>
<th>Polymer Ratios (wt/wt %)</th>
<th>Melting Temperature</th>
<th>Crystallization Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Core T&lt;sub&gt;m1&lt;/sub&gt; (°C)</td>
<td>Core T&lt;sub&gt;m2&lt;/sub&gt; (°C)</td>
</tr>
<tr>
<td>PET/PE</td>
<td>0/100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>250.7</td>
<td>254.5</td>
</tr>
<tr>
<td></td>
<td>75/25</td>
<td>248.7</td>
<td>252.5</td>
</tr>
<tr>
<td></td>
<td>100/0</td>
<td>-</td>
<td>249.7</td>
</tr>
<tr>
<td>PA6/PE</td>
<td>0/100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>216.6</td>
<td>221.8</td>
</tr>
<tr>
<td></td>
<td>75/25</td>
<td>216.4</td>
<td>222.5</td>
</tr>
<tr>
<td></td>
<td>100/0</td>
<td>-</td>
<td>220.8</td>
</tr>
<tr>
<td>PA6/PP</td>
<td>0/100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>216.3</td>
<td>221.2</td>
</tr>
<tr>
<td></td>
<td>75/25</td>
<td>217.7</td>
<td>222.3</td>
</tr>
<tr>
<td></td>
<td>100/0</td>
<td>-</td>
<td>220.8</td>
</tr>
<tr>
<td>PP/PE</td>
<td>0/100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>162.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>75/25</td>
<td>162.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>100/0</td>
<td>162.7</td>
<td>-</td>
</tr>
</tbody>
</table>
4.4.2 Effect of Polymer Type, Composition and Interface on Mechanical Properties

4.4.2.1 Characterization of Interfaces

4.4.2.1.1 Estimation of Flory-Huggins Interaction Parameters

The estimation of Flory-Huggins interaction parameter is useful to predict the degree of miscibility of polymer pairs used in bicomponent fibers. It can be estimated using Equations 4.2 and 4.3:

\[ \chi_{12} = \frac{<V>(\delta_1 - \delta_2)^2}{RT} \]  

(4.2)

where \( \chi_{12} \) is the Flory-Huggins parameter describing the interaction between polymer segments 1 and 2; \( \delta_i \) is the solubility parameter for polymer i; R is the gas constant; T is the temperature; \( <V> \) is the mean molar volume of two polymers

\[ <V> = \sqrt[3]{V_1V_2} \]  

(4.3)

The solubility parameters for polymers were estimated via the use of group contribution methods (GCMs), which account for the contribution of each group present in the repeat unit of the polymer. The calculations of solubility parameter for each polymer via the use of GCMs are given by Equations 4.4 and 4.5.

\[ \delta = \frac{\sum F_i}{V} \]  

(4.4)
\[ V = \frac{M}{\rho} \]  

(4.5)

where \( F_i \) is the molar attraction constant of group \( i \); \( V \) is the total molar volume; \( M \) is the molecular weight of the repeat unit; \( \rho \) is the density of the polymer.

Values of \( F \) were determined by regression analysis for various common structural groups and reported by several researchers [25-29]. In our calculations, we used the most recent \( F \) values reported by Coleman and Painter [29]. The solubility parameters for PET, PA6, PP, and PE were then calculated and found to be 12.4, 10.1, 8, and 7.4 (cal/cm\(^3\))\(^{0.5}\), respectively. It is important to point out that in our calculations, we did not count any inter- and intra-molecular interactions such as hydrogen bonding. After the calculation of solubility parameters, the Flory-Huggins interaction parameters were calculated at spinneret temperatures employed in bicomponent spinning process (296 °C for PET/PE; 268 °C for PA6/PE and PA6/PP; 241 °C for PP/PE). Calculated Flory-Huggins interaction parameters were 1.11, 0.256, 0.523, and 0.014 for PET/PE, PA6/PE, PA6/PP, and PP/PE, respectively. Note that lower the number, the better the polymer-polymer interaction since miscibility increases when the Flory-Huggins interaction parameter approaches zero. Therefore, we can conclude that the most compatible polymer pair studied is PP/PE (0.014). On the other hand, we obtained a large interaction parameter (1.11) for PET/PE suggesting that this polymer pair is highly incompatible in nature.

### 4.4.2.1.2 Interfacial Adhesion

The interfacial adhesion in PA6/PE, PA6/PP, and PP/PE were measured using ADCB test method. Due to the challenges encountered in testing of PET/PE substrate, we could not characterize this polymer pair (see Section 4.3.4). The ADCB test has been widely used to measure the strength of polymer-polymer interfaces by many researchers [30-37]. It has been shown to be a reliable test for studying fracture toughness at the polymer-polymer interfaces.
In this test, the interfacial fracture energy between two rectangular polymer beams is measured by equating the energy needed to generate two new surfaces with the elastic energy stored in these beams [38]. This test also assumes that the released energy only comes from the bending energy of the beam [30] and the critical energy release rate at zero velocity is equal to the measured energy release rate at very low speed [39]. After these two assumptions are made, the interfacial fracture energy can be calculated using the following formula by obtaining the crack length with ADCB method.

\[ G_c = \frac{3\Delta^2 E_i h_i^3 E_2 h_2^3}{8a^4} \times \frac{E_i h_i^3 C_2^2 + E_2 h_2^3 C_1^2}{(E_i h_i^3 C_2^3 + E_2 h_2^3 C_1^3)^2} \]  \hspace{1cm} (4.6)

where \( G_c \) is the interfacial fracture energy; \( \Delta \) is the thickness of the wedge; \( E_i \) is the stiffness (Young’s Modulus) of the beam \( i \); \( h_i \) is the thicknesses of the beam \( i \); \( a \) is the crack length; \( C_i \) is the correction factor:

\[ C_i = 1 + \frac{0.64h_i}{a} \]  \hspace{1cm} (4.7)

The first part of the Equation 4.6 was derived from simple beam theory and can only be applied when \( a/h_i \) is equal or greater than 10 [40]. For small crack lengths, a correction factor (second part of the Equation 4.6) is required to calculate the interfacial fracture energy in the proper limit. PA6/PE and PA6/PP had considerably large cracks (\( a/h>10 \)) in which simple beam theory yields more reliable results.

The interfacial fracture energies of three polymer pairings were compared (see Figure 4.5). Our results show that the interfacial fracture energy of the PA6/PP is the lowest (2.15±0.1
J/m²) and that of PP/PE is the highest (50.6±3.1 J/m²). PA6/PE (4.03±0.43 J/m²) yields higher result than PA6/PP but still much lower than PP/PE. These results are in accordance with our calculations for the Flory-Huggins Interaction parameters for these polymer pairs.

![Interfacial Fracture Energy](image)

**Figure 4.5** Interfacial fracture energies for polymer pairs used in bicomponent nonwoven fibers (error bars show the standard error)

### 4.4.2.2 Tensile Properties

The tensile properties of homocomponent and bicomponent nonwoven fibers were measured using single fiber tensile test. Results are listed in Table 4.7. Maximum stress values and secant modulus at 10% strain for bicomponent fibers ranged between the values obtained for corresponding homocomponent core and sheath fibers. However, strains at break and fiber toughness results for bicomponent fibers (except PP/PE) were much lower than those for corresponding homocomponent core and sheath fibers. This can be ascribed to the weak
interfacial adhesion between two components in bicomponent fibers which can lead to sliding and debonding of the components. Due to this interface issue, load transfer between components may be inefficient and therefore early fracture may occur in one of the component. Thus, early failure may be expected and deterioration on some tensile properties can be observed. Figure 4.6 shows the SEM pictures of bicomponent fiber cross-sections. As seen in Figure 4.6a, b, and c, there is debonding issues in PET/PE, PA6/PP, and PA6/PE which can negatively affect the tensile response of these fibers. On the other hand, PP/PE showed an intact cross-section as a result of good compatibility and high interfacial adhesion of its components. Therefore, we did not observe such large deterioration in strain at break and fiber toughness results for PP/PE bicomponent fibers as compared to others.

4.4.2.2.1 Application of the Rule of Mixture and Modified Rule of Mixture

The basic rule for determining the property of a mixture is called the rule of mixture (ROM) [41]. The simplest form of the ROM equation is given in Equation 4.8.

\[ P = P_1\phi_1 + P_2\phi_2 \]  \hspace{1cm} (4.8)

where \( P \) is the property of the mixture; \( P_i \) is the corresponding property for component \( i \); \( \Phi_i \) is the concentration of the component \( i \) which may be weight fraction, volume fraction, or mole fraction depending upon the type of property being measured.
Table 4.7 Tensile properties of homocomponent and bicomponent nonwoven fibers (standard errors are given in parentheses)

<table>
<thead>
<tr>
<th>Polymers (core/sheath)</th>
<th>Polymer Ratios (wt/wt %)</th>
<th>Fiber Denier</th>
<th>Maximum Stress (MPa)</th>
<th>Strain at Break (%)</th>
<th>Fiber Toughness (MPa)</th>
<th>Secant Modulus at 10% (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/PE</td>
<td>0/100</td>
<td>1.66 (±0.05)</td>
<td>96 (±2)</td>
<td>371 (±11)</td>
<td>367 (±7)</td>
<td>504 (±12)</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>1.65 (±0.05)</td>
<td>169 (±4)</td>
<td>79 (±3)</td>
<td>84 (±3)</td>
<td>546 (±48)</td>
</tr>
<tr>
<td></td>
<td>75/25</td>
<td>1.64 (±0.07)</td>
<td>234 (±9)</td>
<td>85 (±6)</td>
<td>115 (±9)</td>
<td>602 (±66)</td>
</tr>
<tr>
<td></td>
<td>100/0</td>
<td>1.78 (±0.14)</td>
<td>360 (±10)</td>
<td>106 (±6)</td>
<td>200 (±13)</td>
<td>691 (±96)</td>
</tr>
<tr>
<td>PA6/PE</td>
<td>0/100</td>
<td>1.66 (±0.05)</td>
<td>96 (±2)</td>
<td>371 (±11)</td>
<td>367 (±7)</td>
<td>504 (±12)</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>1.63 (±0.05)</td>
<td>262 (±3)</td>
<td>106 (±3)</td>
<td>166 (±6)</td>
<td>573 (±25)</td>
</tr>
<tr>
<td></td>
<td>75/25</td>
<td>1.54 (±0.04)</td>
<td>390 (±4)</td>
<td>115 (±4)</td>
<td>266 (±11)</td>
<td>708 (±43)</td>
</tr>
<tr>
<td></td>
<td>100/0</td>
<td>1.63 (±0.06)</td>
<td>501 (±4)</td>
<td>148 (±6)</td>
<td>414 (±18)</td>
<td>718 (±20)</td>
</tr>
<tr>
<td>PA6/PP</td>
<td>0/100</td>
<td>1.44 (±0.05)</td>
<td>157 (±4)</td>
<td>333 (±15)</td>
<td>362 (±27)</td>
<td>492 (±18)</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>1.72 (±0.03)</td>
<td>274 (±4)</td>
<td>104 (±2)</td>
<td>172 (±3)</td>
<td>566 (±19)</td>
</tr>
<tr>
<td></td>
<td>75/25</td>
<td>1.71 (±0.06)</td>
<td>380 (±7)</td>
<td>119 (±5)</td>
<td>267 (±12)</td>
<td>690 (±11)</td>
</tr>
<tr>
<td></td>
<td>100/0</td>
<td>1.63 (±0.06)</td>
<td>501 (±4)</td>
<td>148 (±6)</td>
<td>414 (±18)</td>
<td>718 (±20)</td>
</tr>
<tr>
<td>PP/PE</td>
<td>0/100</td>
<td>1.66 (±0.05)</td>
<td>96 (±2)</td>
<td>371 (±11)</td>
<td>367 (±7)</td>
<td>504 (±12)</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>1.62 (±0.07)</td>
<td>130 (±3)</td>
<td>294 (±20)</td>
<td>289 (±21)</td>
<td>514 (±25)</td>
</tr>
<tr>
<td></td>
<td>75/25</td>
<td>1.62 (±0.05)</td>
<td>153 (±2)</td>
<td>355 (±15)</td>
<td>394 (±19)</td>
<td>507 (±25)</td>
</tr>
<tr>
<td></td>
<td>100/0</td>
<td>1.44 (±0.05)</td>
<td>157 (±4)</td>
<td>333 (±15)</td>
<td>362 (±27)</td>
<td>492 (±18)</td>
</tr>
</tbody>
</table>
Figure 4.6 SEM pictures of bicomponent nonwoven fiber cross-sections: (a) PET/PE, (b) PA6/PE, (c) PA6/PP, and (d) PP/PE (50/50 wt/wt %)

In order to make accurate predictions, the nature of the mixture should be known. There are two types of mixtures: single phase and two-phase. In the single phase systems, components are miscible or soluble in each other such as miscible copolymers. Properties of this type of mixture can be predicted by using Equation 4.9. On the other hand, in the two phase systems, components are immiscible or partially miscible in each other such as composites. The mixture rule for this type of system is given in Equation 4.10 which is a modified version of
the ROM (MROM) and may be applicable to a mixture with two continuous phases e.g. laminates and block copolymers.

\[ P = P_1 \phi_1 + P_2 \phi_2 + I \phi_1 \phi_2 \]  

(4.9)

where \( I \) is the interaction term which is related to intermolecular interactions and packing. It must be determined empirically from experiment data and can be either positive or negative. If there is no interaction, \( I = 0 \).

\[ P^n = P_1^n \phi_1 + P_2^n \phi_2 \]  

(4.10)

where \( n \) is a constant and determined by the type of the system and kind of the property.

The ROM is also a simple and useful tool to predict some properties of composite materials. For instance, micromechanical behavior of unidirectionally aligned long-fiber composite can be predicted this way [42]. Bicomponent fibers having a core-sheath structure can also be treated as a unidirectional composite where the core polymer replaces reinforcement fiber and sheath polymer is considered as a matrix. Hence, bicomponent fibers were treated as a composite material and the applicability of the ROM to the bicomponent fibers was investigated in this study.

The ROM (Equation 4.9) was applied to predict the maximum stress values of bicomponent nonwoven fibers. In our treatment, the ROM doesn’t account any positive or negative interaction between two components (\( I = 0 \)), so the Equation 4.9 becomes the simple form of the ROM given in Equation 4.8. Hence, it predicts the maximum stress values of bicomponent fiber without having any intermolecular interactions and packing between sheath and core component.
We also applied the MROM (Equation 4.10) to account for any positive and negative interaction between the components and predicted the maximum stress values of bicomponent nonwoven fibers. Typically, upper bound value for the n in Equation 4.10 is considered to be 1. However, our treatment includes n values that are greater than 1. By doing so, we aimed to predict the properties of polymer pairs that can also show intermolecular interactions and packing. In order to determine n values, we performed a regression analysis.

Figure 4.7 shows the maximum stress values (circle) measured for four types of bicomponent nonwoven fibers: PET/PE, PA6/PE, PA6/PP, and PP/PE. The estimated maximum stress values for these fibers are shown with dashed lines (ROM) and continuous line (MROM). Also, dashed lines are borders where bicomponent fiber systems showed the average property of two components depending on the ratio of each component. In theory, if the measured stress value of a bicomponent fiber falls on this line (estimated by ROM), it may indicate that there is no positive or negative interaction between two components. At the same time, when the measured value falls above or under this line, this may be an indication of the positive or negative interaction between the components causing an improvement or deterioration on tensile response, respectively. For instance, PET/PE yielded maximum stress values under this line suggesting that there is a negative interaction between PET and PE components causing deterioration on the tensile response of the fiber. The negative interaction between these two components can be related to the incompatibility between these two polymers (χ=1.11) which leads to a weak interface and debonding issue (see Figure 4.7a). Thus, load transfer between PET and PE components cannot be effective and therefore premature failure may occur. On the other hand, the measured stress values for PP/PE were above this line suggesting that positive interaction between PP and PE gave rise to the tensile response of the bicomponent fiber. As we suggested before, PP and PE are highly compatible (χ=0.014) in nature and may undergo intermolecular interactions and packing. Therefore, a positive interaction may be expected from these two polymers.
Figure 4.7 Measured and estimated tensile strength values for bicomponent nonwoven fibers: (a) PET/PE, (b) PA6/PE, (c) PA6/PP, and (d) PP/PE
4.4.2.3 Comparison of Interfacial Adhesion, Compatibility, and Tensile Strength

During the application of MROM through regression analysis, different power constant (n) values were determined for each bicomponent nonwoven fiber (see Table 4.8). We obtained the highest “n” value for PP/PE (n=2.884) followed by PA6/PE (n=0.849), PA6/PP (n=0.371), and PET/PE (n=0.085). Note that the predicted tensile property of the bicomponent fiber by MROM is a direct function of the “n” number. So, the estimated tensile strength of the bicomponent fiber increases with increasing the “n” value. When we compared these “n” values with Flory-Huggins interaction parameters and interfacial fracture energies (see Table 4.8), we found that the value of “n” increased with increasing the degree of compatibility and interfacial adhesion between the components. This suggests that the tensile strength of the bicomponent fibers depend on the degree of compatibility and interfacial adhesion between the components. For example, PP/PE bicomponent nonwoven fiber had the highest “n” value of 3 and showed the highest degree of compatibility (χ=0.01) and interfacial adhesion (51 J/m²).

<table>
<thead>
<tr>
<th>Polymers (core/sheath)</th>
<th>Interfacial Fracture Energy, ( G_c ) (J/m²)</th>
<th>Flory Huggins Interaction Parameter, ( \chi )</th>
<th>Power Constant - MROM</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/PE</td>
<td>-</td>
<td>1.11</td>
<td>0.085</td>
</tr>
<tr>
<td>PA6/PE</td>
<td>4.03</td>
<td>0.256</td>
<td>0.849</td>
</tr>
<tr>
<td>PA6/PP</td>
<td>2.15</td>
<td>0.523</td>
<td>0.371</td>
</tr>
<tr>
<td>PP/PE</td>
<td>50.6</td>
<td>0.014</td>
<td>2.884</td>
</tr>
</tbody>
</table>

The relation between compatibility and tensile strength of the bicomponent fibers can also allow us to establish a physical meaning to the “n” value in terms of polymer compatibility. It can be said that for incompatible polymer pairings “n” values smaller than 1 can be expected. When a polymer pairing passes through the incompatible region, the “n” then
becomes 1 and if there is any positive interaction (e.g. intermolecular reaction or entanglement) between components, the “n” will further go up. Therefore, the “n” can be a useful tool to screen and evaluate polymer compatibilities and possible interaction which is either already existing or introduced afterwards. However, it is important to point out that “n” cannot be a global constant for all type of systems because processing conditions may affect mechanical properties. But we may observe similar trends for similar polymer systems.

From a practical point of view, the results listed in Table 4.7 and 4.8 provide a reference guide for those who want to estimate the degree of the compatibility of polymers and its effect on the tensile strength of the bicomponent nonwoven fibers. In light of this study, after obtaining the Flory-Huggins interaction parameter for a spinnable polymer pairings, the interfacial behavior of the bicomponent fiber may be practically estimated by comparing with polymer combinations studied here.

It is also possible to establish a mathematical relation between $\chi$, n, and $G_c$ values (see Figure 4.8). After correlating these values, we obtained linear relations between n and $\ln \chi$ (see Figure 4.8a). Also, a power law relation between $G_c$ and $\chi$ was determined (see Figure 4.8b). These mathematical models strengthen our conclusion based on the dependence of interfacial adhesion and tensile response on polymer incompatibility. We also believe that this study can be extended for other polymer combinations processed at different processing condition and these models can then be redefined or confirmed for these systems in a possible future study.
4.5 Conclusions

The influence of polymer type, composition and interface on the structural and mechanical properties of bicomponent fibers were studied for PET/PE, PA6/PE, PA6/PP, and PP/PE (core/sheath) bicomponent nonwoven fibers. The structural properties of bicomponent nonwoven fibers were shown to depend on the type and composition of each component. In PET/PE, PA6/PE, and PA6/PP, the crystallinity and melting temperature of the core component increased with increasing the volume content of the sheath polymer as compared to those of PET and PA6 single fibers. It was attributed to the difference in thermal and stress histories experienced by core polymer during homocomponent versus bicomponent fiber spinning. It was also postulated that the core polymer having higher consolidation temperature and elongational viscosity may experience improved consolidation stress during bicomponent spinning. Unlike the core polymer, the fiber structure of the sheath polymer suppressed in all bicomponent fibers. The degree of the suppression also increased with
increasing the core volume concentration. This was related to the stress relaxation occurring in the sheath polymer during bicomponent spinning in which the core component solidified earlier and bore the great portion of the spinline stress.

In order to characterize and define polymer interfaces, the compatibility of polymer pairs used in bicomponent fibers was estimated with Flory-Huggins interaction parameter. The interfacial adhesion for these polymer pairs was also characterized using ADCB test method. Our findings indicate that PP/PE is the most compatible polymer pair ($\chi=0.014$) with the highest interfacial adhesion value ($G_c=50.6 \text{ J/m}^2$) followed by PA6/PE ($\chi=0.256$, $G_c=4.03 \text{ J/m}^2$), PA6/PP ($\chi=0.523$, $G_c=2.15 \text{ J/m}^2$), and PET/PE ($\chi=1.11$). After measuring the tensile properties of bicomponent fibers at different composition ratios, it appeared that the tensile strength of the bicomponent fiber deviates from the theoretically estimated value in accordance with the degree of the compatibility and interfacial adhesion between its constituents. Thus, PET/PE being the most incompatible polymer pair in this study showed the highest negative deviation from the theoretically predicted maximum stress value. It was then followed by PA6/PP and PA6/PE. As opposed to other polymer combinations, we observed an improvement on the tensile strength value of PP/PE as compared to theoretical value. This was not only attributed to the high degree of compatibility and interfacial adhesion between PP and PE but also related to possible interfacial interaction between these two polymers during bicomponent spinning. Overall, these results emphasize the importance of considering the interface between two components in bicomponent fiber when predicting the mechanical properties of these fibers. For this purpose, the relation between $n$ and $\ln \chi$ can be used to determine the deviation in actual tensile response of a bicomponent fiber system from the theoretically estimated value. One of the other important outputs of this study is that it provides a reference guide and path for those who want to predict the interfacial behavior of a spinnable polymer pairings in bicomponent fiber structure. This can be achieved practically by calculating the Flory-Huggins interaction parameter for the polymer pairings and using the relation between $G_c$ and $\chi$ or comparing with results presented in this study.
3.6 References


CHAPTER 5

Reactive Compatibilization of Polyamide 6/Polyethylene Nonwoven Based Thermoplastic Composites

This chapter is essentially a manuscript by Dasdemir M, Maze B, Anantharamaiah N, and Pourdeyhimi B, and has been prepared for submission to Polymer.
Reactive Compatibilization of Polyamide 6/Polyethylene Nonwoven Based Thermoplastic Composites

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Abstract

In this study, the interface of polyamide 6/polyethylene (PA6/PE) was altered with compatibilizers in an effort to promote adhesion between PA6 reinforcement and PE matrix in nonwoven based thermoplastic composites. The compatibilizers chosen were triblock copolymer of styrene and ethylene/butylene (SEBS) and maleic anhydride (MA) functionalized SEBS with 1 wt% (SEBS-g-MA1) and 2 wt% (SEBS-g-MA2) MA contents. The interfacial adhesion in PA6/PE+Compatibilizer laminates was initially characterized using asymmetric double cantilever beam (ADCB) test. The effects of compatibilizer type, functional group content and concentration on the interfacial fracture toughness were determined. Also, the influence of lamination temperature and time on the interface enhancement was studied. Core/sheath type PA6/PE bicomponent fibers and nonwovens were then produced with the incorporation of varying amount of compatibilizers into PE in fiber spinning stage. Lastly, the compatibilization was performed during composite fabrication stage which was modified in accordance with the obtained interface results from ADCB test. After characterizing the tensile properties of nonwoven composites, it was found that tensile responses of PA6/PE composites were greatly improved in the presence of functional compatibilizers. The best improvement on the overall tensile properties was achieved with SEBS-g-MA2 at the lowest compatibilizer concentration level of 2 wt%. The examination of fractured surfaces showed the clear evidence of the enhanced adhesion of matrix polymer to reinforcement fiber for the composites including SEBS-g-MA1 and SEBS-g-MA2. These results suggest that reactive compatibilization was achieved during composite fabrication stage and improved the adhesion between PA6 reinforcement and PE matrix resulting in a higher load transfer and better mechanical properties.

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5.1 Introduction

A thermoplastic composite material consisting of PA6 and PE components can utilize important characteristics of these two polymers. As a reinforcement component, PA6 offers good mechanical properties, while PE matrix provides excellent impact property and resistance to chemicals and environmental conditions. However, these two polymers are thermodynamically immiscible and therefore they show high interfacial tension leading to poor adhesion or even phase separation at the interface. For this reason, the load transfer between these two components in the composite is not expected to be efficient. As a result of this interface issue, the mechanical performance of the composite will be negatively affected.

Historically, for PA6/PE polymer blends, the interface issue has been addressed by using a compatibilization approach [1-17]. In this approach, compatibility is promoted through either block or functional graft copolymers that can provide interaction and reaction between the components at the interface [18]. These compatibilization agents are known as “compatibilizers”. When the compatibilizer with a given functional group is added during the blending, this process is often called “reactive compatibilization” [19].

Several compatibilizers listed in Table 5.1 have been extensively used for compatibilizing the PA6/PE blends. It has been shown that adding the compatibilizers into the blends lowers the interfacial tension [8] and enhances the adhesion at the interface [1]. The performance of these compatibilizers has also been compared by many researchers [1-5, 8, 9, 12, 13, 15].

Jiang et al. [2] studied the effectiveness of LDPE-g-MA and HDPE-g-MA on the compatibilization of PA6/LDPE blends and compared their effectiveness with that of previously reported E-AA copolymer [1]. They found that maleic anhydride (MA) functionalized PE can react faster with PA6 than E-AA. However, due to the high miscibility between LDPE-g-MA and LDPE, there was less amount of PE-g-MA available at the interfacial region where reaction with PA6 is expected to occur. On the other hand, using HDPE-g-MA, which is comparatively less miscible with LDPE yielded better migration to
PA6-LDPE interface and was shown to be more effective compatibilizer than E-AA and LDPE-g-MA. In addition to above mentioned compatibilizers, GMA bearing compatibilizers such as E-GMA [3, 12, 13, 16], LDPE-g-GMA [12] and SEBS-g-GMA [4, 12] were also employed. Even though epoxy functional group on glycidyl methacrylate (GMA) offers higher reactivity towards to end groups of PA6, these compatibilizers showed comparable performance with E-AA and lower performance than HDPE-g-MA [3]. This was mainly attributed to cross-linking resulting from reactions of the epoxy with both the amine and the carboxyl end groups of PA6 [4]. MA functionalized thermoplastic elastomers such as SEP-g-MA [5] and SEBS-g-MA [4, 5, 8, 13, 15] were also used as compatibilization precursors for PA6/PE blends and shown to be the most effective among compatibilizers listed in Table 5.1. They not only improve minor phase dispersion but also enhance the mechanical properties of the PA6/PE blends.

Table 5.1 Compatibilizers used in the compatibilization of PA6/PE blends

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Polymer</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-AA</td>
<td>Ethylene-b-Acrylic Acid</td>
<td>[1, 8, 9, 13]</td>
</tr>
<tr>
<td>E-AA-Zinc</td>
<td>Ethylene-b-Acrylic Acid with Zinc ionomer</td>
<td>[1, 8]</td>
</tr>
<tr>
<td>E-AA-PBO</td>
<td>Ethylene-b-Acrylic Acid combined with a low molar mass bis-oxazoline compound</td>
<td>[9]</td>
</tr>
<tr>
<td>PE-g-MA</td>
<td>Polyethylene grafted with Maleic Anhydride</td>
<td>[15]</td>
</tr>
<tr>
<td>LDPE-g-MA</td>
<td>Low Density Polyethylene grafted with Maleic Anhydride</td>
<td>[2, 17]</td>
</tr>
<tr>
<td>HDPE-g-MA</td>
<td>High Density Polyethylene grafted with Maleic Anhydride</td>
<td>[2, 5]</td>
</tr>
<tr>
<td>SEBS</td>
<td>Styrene-b-Ethylene-co-Butylene-b-Styrene</td>
<td>[4, 8]</td>
</tr>
<tr>
<td>SEBS-g-MA</td>
<td>Styrene-b-Ethylene-co-Butylene-b-Styrene grafted with Maleic Anhydride</td>
<td>[4, 5, 8, 13, 15]</td>
</tr>
<tr>
<td>SEP-g-MA</td>
<td>Styrene-b-Ethylene-co-Propylene grafted with Maleic Anhydride</td>
<td>[5]</td>
</tr>
<tr>
<td>E-GMA</td>
<td>Ethylene-b-Glycidyl MethAcrylate</td>
<td>[3, 12, 13, 16]</td>
</tr>
<tr>
<td>LDPE-g-GMA</td>
<td>Low Density Polyethylene grafted with Glycidyl MethAcrylate</td>
<td>[12]</td>
</tr>
<tr>
<td>SEBS-g-GMA</td>
<td>Styrene-b-Ethylene-co-Butylene-b-Styrene grafted with Glycidyl MethAcrylate</td>
<td>[4, 12]</td>
</tr>
</tbody>
</table>
In addition to the type of compatibilizer, its molecular architecture [2, 4], the functional group content [1, 2, 4, 12, 15], its content in the blend [1-3, 8, 12, 13], and composition of the blend polymers [1, 4, 5, 12] were other factors that can influence the compatibilization of PA6/PE blend. It was reported that compatibilization effectiveness of HDPE-g-MA increased with decreasing the molar mass of PE backbone and using uniformly distributed MA groups along the chains [2]. On the other hand, for MA-grafted elastomers molecular characteristics did not play important role on the level of compatibilization achieved [4]. The effectiveness of the compatibilizer (E-AA) was shown to increase with an increase of the functional group content [1]. The saturation point of the compatibilizer added in the blend varied with blend composition and compatibilizer type [1-3, 8, 12, 13].

Even though the interface issue has been extensively addressed for polymer blends, there has been very limited effort made for bicomponent fibers [20, 21] and composites [22, 23]. Godshall et al. [20, 21] performed in situ reactive compatibilization for core-sheath type PA6/polypropylene (PP) melt spun bicomponent fiber with the addition of high content of PP-g-MA (up to 67 wt% in the sheath component) as a compatibilizer. They indicated that the molecular weight and the functional group content of the compatibilizer were two critical parameters affecting the degree of interfacial adhesion attained in bicomponent fiber. For composites, the reactive compatibilization approach was typically used to improve the adhesion between natural reinforcement fiber and a thermoplastic matrix [22, 23]. Pracella et al. [22] studied the compatibilization and properties of hemp fiber reinforced thermoplastic composite with polypropylene (PP) matrix. They found that tensile modulus of the composite increased with the addition of the compatibilizer (PP-g-GMA). This was attributed to the enhanced interfacial adhesion at the fiber-matrix interface and improved dispersion of the fiber in the composite. The compatibilization process for this type of short fiber reinforced composite involves blending all components in single step and is very similar to the compatibilization process used for polymer blends. However, for long fiber reinforced composites this compatibilization route cannot be followed since the process of making these composites does not involve combining all components in a blender.
In our previous study we characterized the interfaces in bicomponent fibers and observed debonding at the interfacial region for incompatible polymer pairings such as poly(ethylene terephthalate) (PET)/PE, PA6/PP, and PA6/PE [24]. We also found that the compatibility of these polymers has profound effect on the tensile properties of bicomponent fibers. Similarly, nonwoven based thermoplastic composites made from these materials showed the same interface issue [25]. We anticipated that this problem can also negatively affect the mechanical performance of these composites. Therefore, in this study, we focused our effort on the interface enhancement in PA6/PE nonwoven based composite to improve mechanical performance of this composite. For this purpose, SEBS and SEBS-g-MA with two MA contents (1 wt% and 2 wt%) were used as compatibilizers to promote adhesion between PA6 and PE components. The interfacial adhesion between PA6 and PE+compatibilizer was initially characterized to determine the effect of processing variables (time and temperature) and material variables (compatibilizer type, functionality, and content) on the interfacial adhesion. PA6/PE bicomponent nonwovens were then produced with the addition of different amount of compatibilizers (into the sheath component of the bicomponent fiber) in fiber spinning stage. Lastly, the compatibilization was performed during composite fabrication stage using different processing temperatures. Tensile properties of the compatibilized composites and morphological analysis of the fractured surfaces are reported here and compared with control nonwoven composites.

5.2 Materials

Commercial fiber grades of PA6 and linear low density PE were used for making films, fibers and composites. Some of the basic properties and suppliers of these polymers are listed in Table 5.2. A triblock copolymer of styrene and ethylene/butylene (SEBS) and MA functionalized SEBS with varying functional group content (see Table 5.3) were used as compatibilizers.
Table 5.2 Properties and suppliers of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Trade Name</th>
<th>Supplier</th>
<th>Density $^{1}\rho$ (g/cm$^3$)</th>
<th>Melting Temperature $^{2}T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6</td>
<td>Ultramid BS-2702</td>
<td>BASF</td>
<td>1.13</td>
<td>220</td>
</tr>
<tr>
<td>PE</td>
<td>Aspun 6850A</td>
<td>Dow Chemical Co.</td>
<td>0.955</td>
<td>129</td>
</tr>
</tbody>
</table>

1. The density values of polymers were obtained from corresponding polymer data sheet supplied by the producer.
2. The melting temperatures of all polymers were peak melting temperatures and measured by means of a differential scanning calorimeter at a heating rate of 10°C/min.

Table 5.3 Properties of compatibilizers [26]

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Trade Name</th>
<th>Functional Group Content (wt%)</th>
<th>Styrene Content (wt%)</th>
<th>Solution Viscosity (cps)</th>
<th>Melt Index at 230°C (g/10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEBS</td>
<td>G-1643</td>
<td>-</td>
<td>20</td>
<td>210</td>
<td>12.5-25</td>
</tr>
<tr>
<td>SEBS-g-MA1</td>
<td>FG-1924</td>
<td>1</td>
<td>13</td>
<td>19000</td>
<td>40</td>
</tr>
<tr>
<td>SEBS-g-MA2</td>
<td>FG-1901</td>
<td>2</td>
<td>30</td>
<td>5000</td>
<td>22</td>
</tr>
</tbody>
</table>

5.3 Methods

5.3.1 Preparation of Samples for the Measurement of Interfacial Adhesion

Compatibilizers were compounded on a 40 mm co-rotating twin screw extruder with PE at 4/96, 10/90, and 20/80 wt% (compatibilizer/PE) ratios. Screw speed was 300 rpm, feed rate was 45 kg/hour, and the maximum zone temperature was 210°C.

A heat press was used for the preparation of films. Before making films, PA6 polymer pellets were dried at 80 °C for 24 hours under vacuum while other polymers were used as-received. PE and PE+Compatibilizer were processed at 180 °C while PA6 was processed at 240°C.
The residence time in which polymer pellets melt in a defined geometry without any pressure was set to 5 minutes. The pressure was then applied with 500 psi increment at every 30 seconds until pressure level reached to 5000 psi. Cooling was done by circulating high pressure air (30 psi) in the system. The cooling rate was noted to be between 8-10 °C/min.

The lamination of two polymer films was also done in the heat press. Before the lamination, film surfaces were cleaned and films were dried at 80 °C for 6 hours under vacuum. The residence time for all laminates was kept at 5 min in which polymer films reached a certain temperature and melted. The temperature values used for laminates were varied between 130 °C and 255 °C. Lamination time ranged between 1 min and 60 min. The pressure during lamination was kept low (250 psi) to only provide enough contact between two films. The cooling rate was the same as that of films (8-10 °C/min).

A reinforced blade and a rotary cutting tool were used to cut specimens from laminates. 50 mm × 10 mm coupons were prepared. These coupons were then conditioned at room condition (22 °C and 50 % relative humidity) for 24 hours before the asymmetric double cantilever beam (ADCB) test.

5.3.2 Production of Bicomponent Fibers and Nonwovens

Bicomponent nonwovens were produced using the spunbonding process (see Figure 5.1) at the Nonwovens Institute’s pilot facility (NC State University, Raleigh, NC, USA). The bicomponent fiber cross-section chosen was a core/sheath structure with a polymer ratio of 50/50 wt% (core/sheath). The compatibilizers which were dry blended with PE matrix at 4/96, 10/90, and 20/80 wt% (compatibilizer/PE) ratios were spun into the sheath side. Hence, additive contents of 2, 5, and 10 wt% with respect to whole weight fraction were used. Attenuated fiber samples which are continuous oriented filaments were collected before the deposition on the forming belt during the process for evaluation. Spunbond nonwoven fabrics with 250 g/m² basis weight were also produced using unheated calendering rolls which can provide sufficient web integrity for handling at subsequent composite fabrication stages.
Overall throughput was adjusted to 0.7 g/min for each hole for an 1162-hole spinneret. Fibers were quenched with double side quencher and the quench air temperature was 11 °C. Screw pressures for both extruders were adjusted to 750 psi. Processing temperatures for each polymer are listed in Table 5.4.

**Figure 5.1** Schematic drawing of the bicomponent spunbonding process at NCSU [27]
Table 5.4 Processing conditions for the production of nonwoven fibers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Processing Temperature (°C)</th>
<th>Extruder</th>
<th>Spin Head¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zone 1</td>
<td>Zone 2</td>
<td>Zone 3</td>
</tr>
<tr>
<td>PA6</td>
<td>232</td>
<td>246</td>
<td>255</td>
</tr>
<tr>
<td>PE</td>
<td>204</td>
<td>218</td>
<td>224</td>
</tr>
</tbody>
</table>

¹ Spin head is common to both extruders in bicomponent spinning.

5.3.3 Formation of Nonwoven Composites

Nonwoven fabrics were cut to 20 cm × 20 cm dimensions. Four separate layers of nonwoven fabrics were stacked on top of one another. Each layer of these nonwoven fabrics had the dominant orientation in the machine direction. In order to get balanced structures, cross-layering (0° and 90°) was employed to configure the stacks of nonwoven fabrics. A hot press was used to produce nonwoven composite.

The principle of making thermoplastic composites from bicomponent nonwoven fabrics in a single step was extensively explained in our previous study [25]. However, composite fabrication technique used in this study differs from the previously developed technique (1st generation). The 1st generation composite making process was limited in terms of the temperature values used for preheating and consolidation stages [25]. In the current composite making process (2nd generation), this limitation was overcome using a closed molding configuration. Thus, the composite’s integrity was upheld by preventing the escape of the molten matrix polymer from the structure, allowing us to operate at higher temperatures. During composite fabrication, residence pressure (P_r) and time (t_r) were kept at 1000 psi and 5 min, while the consolidation time (t_c) and pressure (P_c) were kept at 8000 psi and 30 min, respectively. The temperature values for residence (T_r) and consolidation (T_c) were same and ranged from 180 to 200 °C. Composite samples were cooled in between two metal plates at room temperature.
5.3.4 Asymmetric Double Cantilever Beam Test

An asymmetric double cantilever beam (ADCB) tester (see Figure 5.2) was designed and built at the Nonwovens Institute (NC State University, Raleigh, USA). This test was performed to determine the interfacial adhesion between PA6 and PE+Compatibilizer. In this test, an ADCB test coupon (laminate) was mounted on a sample stage. A small crack was initially opened between two polymer sheets in the laminate with a razor blade. A moving blade was then inserted into the opening and pushed forward at a constant speed of 3µm/sec. After the crack was stabilized, the length of the opening crack which is an inverse function of the strength of interface between two films was obtained and recorded from several locations along the specimen during the test. This was done by taking the picture of the crack with an interval of 5 min. A total of 34 pictures of the crack were taken for each specimen. The first 10 and last 4 images were omitted and the remaining 20 images were analyzed. From each image, 5 measurements along the crack were done using an image analysis program. Three specimens for each sample were tested in the ADCB tester and a total of around 300 measurements were analyzed for each sample set.

![Figure 5.2 The design of the ADCB tester](image)
5.3.5 Tensile Testing of Films

Samples for the film tensile test were prepared exactly as same condition as the films used in the laminates. Film tensile tests were performed to determine Young’s modulus of films according to ASTM standard D882 under standard test conditions (21±1°C and 65±2 % relative humidity). The polymer films were preconditioned for one day. At least 5 specimens were prepared for each sample set using a dog-bone shaped template. MTS Q-Test machine with 1100 N load cell was used for tensile test. The gauge length for the test was adjusted to 50 mm. Tensile tests were carried out under constant rate of extension with a strain rate of 5 mm/min.

5.3.6 Tensile Testing of Single Fibers

Fiber tensile tests were performed according to ASTM standard D3822-07 under standard test conditions (21±1°C and 65±2 % relative humidity). The fibers were preconditioned for two days. Linear density of the single fibers was measured using vibroscope method (ASTM D 1577-07) in Vibromat ME Textechno test equipment and fiber deniers were noted. Each individual fiber was then pasted on paper cardboards. Great care was taken not to deform the fibers. At least 10 specimens were prepared for each sample set. MTS Q-Test machine with 50 g load cell was used for tensile test. The gauge length for the test was adjusted to 25.4 mm (1 inch). Tensile tests were carried out under constant rate of extension with an extension rate of 15 mm/min.

5.3.7 Tensile Testing of Nonwoven Composites

Composite tensile testing was performed to determine the tensile strength of the composites formed with 4 plies of nonwoven fabrics. Slippage in the grips was prevented by using diamond grip faces, while the sample fracture at the grip were prevented by using dog bone shaped specimens as specified in the ASTM Standard D 638-08. MTS Q-Test machine with 90 kN load cell was used for the test. The crosshead speed was adjusted to 51 mm/min.
Mechanical parameters: initial modulus, secant modulus at 5% and 10% strain values, tensile strength, strain at break and tensile energy to break were measured.

5.3.8 Scanning Electron Microscopy

Scanning electron microscope (SEM) images were taken for fractured tensile test specimens. Samples were initially cleaned using dry nitrogen and then coated with AuPd for 2 min at 600 volts and 5 mA current. SEM analysis was then performed on the samples at a 5kV accelerating voltage and 40 mA beam current in a Hitachi S-3200 SEM.

5.4 Results and Discussions

5.4.1 Improving Interfacial Adhesion in PA6/PE

5.4.1.1 Determination of Interfacial Fracture Energy

The interfacial adhesions in PA6/PE and PA6/PE+Compatibilizer were measured using ADCB test method. This test method has been widely used to measure the strength of polymer-polymer interfaces by many researchers [28-35]. In this test, a blade is inserted between two rectangular polymer beams (see Figure 5.3) and moved into the crack at a constant speed. The interfacial fracture energy ($G_c$) between these two polymer beams is measured by equating the energy needed to generate two new surfaces with the elastic energy stored in these beams [36].

In order to obtain reliable results in the ADCB test two important precautions has to be taken [28]. First, the correct polymer beam thickness ratio must be used to obtain true crack length. This is important because during the test the crack can propagate into the more compliant material (PE in our case) instead of along the interface. When this happens, an artificial crack length which is typically smaller than the true crack length is obtained. Thus, the interfacial fracture energy may be overestimated. To prevent from this happening, we have to ensure that the obtained crack length is a result of the crack propagation along the interface. This
can be achieved by using the correct thickness ratio. The correct thickness ratio is typically determined by varying the thickness ratio of one beam relative to the total thickness until the minimum fracture toughness value is obtained [28, 30, 37-39]. For this purpose, we prepared PA6/PE+Compatibilizer laminates using the same compatibilizer (SEBS-g-MA2) and experimental conditions but varying the thickness ratio for the PE side of the laminates \((h_{PE}/h_{total}=0.3 - 0.77)\). After testing these samples, we obtained different crack lengths for different thickness ratios. For these samples, the interfacial fracture toughness values were calculated and results were plotted in Figure 5.4. In the figure, it can be seen that ADCB test yielded very large \(G_c\) values in the thickness ratios smaller than 0.6. This was a result of the deviation of the crack into PE side which led to an increase in the dissipated energy and caused the overestimation of the \(G_c\) value. The reason is that PE is more ductile than PA6 and therefore has lower crazing stress. During the crack growth, this can lead to the formation of small crazes in the PE side which increases the obtained fracture energy. We obtained the minimum \(G_c\) value at thickness ratio of 0.63 suggesting that the crack growth mainly occurs at the interface. Therefore, we used this ratio in our following experiments in this study.

![Figure 5.3 Sample geometry of the ADCB test](image)

A second important precaution has to be taken for the calculation of the \(G_c\). It has been shown that the simple beam theory (Equation 5.1) can yield reliable results for long crack lengths \((a/h_i \geq 10)\) or weak interfaces [40]. However, for small crack lengths, a correction factor (second part of the Equation 5.2) is required to calculate the \(G_c\) in the proper limit [40].
PA6/PE (control sample) had considerably large cracks ($a/h_{PA6}>10$) in which simple beam theory yielded more reliable results. On the other hand, we obtained small crack lengths ($a/h_{PA6}<10$) for most of the PA6/PE+Compatibilizer system and therefore the correction factor was applied in our calculations.

\[
G_c = \frac{3\Delta^2 E_i h_i^3 E_2 h_2^3}{8a^4} \tag{5.1}
\]

\[
G_c = \frac{3\Delta^2 E_i h_i^3 E_2 h_2^3}{8a^4} \times \frac{E_i h_i^3 C_i^2 + E_2 h_2^3 C_i^2}{(E_i h_i^3 C_2^3 + E_2 h_2^3 C_1^3)^2} \tag{5.2}
\]

\[
C_i = 1 + \frac{0.64h_i}{a} \tag{5.3}
\]

where $G_c$ is the critical energy release rate or the interfacial fracture energy; $\Delta$ is the thickness of the wedge; $E_i$ is the stiffness (Young’s Modulus) of the beam $i$; $h_i$ is the thicknesses of the beam $i$; $a$ is the crack length; $C_i$ is the correction factor.

### 5.4.1.2 Effect of Compatibilizer Type, Functional Group Content, and Concentration

The characterization of the adhesion between PA6 and PE+Compatibilizer gives us the opportunity to test the effectiveness of the compatibilizers. For this purpose, we tested three different compatibilizers. The compatibilizer loading in the PE was 4, 10, and 20 wt%. Figure 5.5 shows the results obtained for PA6/PE and PA6/PE+Compatibilizer laminates with different compatibilizer content. For PA6/PE laminate, the average $G_c$ was found to be 4 J/m$^2$, while the same for SEBS, SEBS-g-MA1, and SEBS-g-MA2 containing PA6/PE laminates with 20 wt% compatibilizer content were 12 J/m$^2$, 40 J/m$^2$, and 122 J/m$^2$, respectively. These results suggest that SEBS based compatibilizers improved the PA6/PE
interface. However, MA functionalized SEBS additives were much more effective than SEBS as a compatibilizer. This is in accordance with previous blending studies in which SEBS-g-MA compatibilizers outperformed the SEBS in terms of compatibilizing activity towards the blends of PA6 and PE [4, 8]. This is due to the fact that MA functionalized compatibilizers can react with the amine end groups or the backbone amide groups of the PA6 and form covalent bond at the interfacial region. Thus, it leads to a reduction in the interfacial tension and enhances the adhesion between PA6 and PE. The reaction between MA functional group of the compatibilizer and amine end groups or with the in-chain amide groups of PA6 has also been reported in the literature [2] and considered by many authors [2, 4, 5, 8, 13, 17] as the route for reactive compatibilization of PA6/PE blends. Minkova et al. [8] used the breaking thread method to characterize the interfacial tension in PA6/PE system with the addition of SEBS-g-MA as a compatibilizer. Their findings also suggest that adding the SEBS-g-MA in PA6/PE blend significantly reduces the interfacial tension.

**Figure 5.4** Determination of optimum thickness ratio for PA6/PE laminates
When we compare the effect of MA content on compatibilization (see Figure 5.5), 2 wt% MA containing compatibilizer (SEBS-g-MA2) performed better than 1 wt% MA containing compatibilizer (SEBS-g-MA1). This suggests that increasing the functional group content leads to the formation of more PA6-g-Compatibilizer copolymers near to interface and therefore increases the interfacial adhesion. The effect of MA functionalized group content of compatibilizers including LDPE-g-MA [2] and SEBS-g-MA [4] on the compatibilization efficiency was previously studied for PA6/PE blends. It was reported that varying the MA group of the compatibilizer did not influence the compatibilization efficiency in PA6/PE blends. This contradicts with our findings in this study. It can be attributed the difference in processing components during reactive compatibilization. For PA6/PE blends, all components were mixed in a blender which gave more chance to compatibilizer to react with...
terminal amine or backbone amide groups of PA6. In our case (lamination), there was a defined interface between PA6 and PE+Compatibilizer polymer sheets and the reaction was more dependent on the available functional group in the proximity of the interface between two polymeric sheets. Therefore, it can be expected that more functional group leads to the formation of more copolymers of PA6 and compatibilizer at the interface until it reaches a saturation point.

The compatibilizer concentration in the PE phase of the laminate was also varied to determine the effect of compatibilizer content on the compatibilization efficiency (see Figure 5.5). It was found that increasing the compatibilizer content result in more improvement to the interfacial adhesion. It is also important to point out that the saturation of the interface enhancement was not observed at studied range of compatibilizer loading for all compatibilizers.

5.4.1.3 Effect of Lamination Time and Temperature

The influence of lamination time on the adhesion strength of PA6/PE laminates (see Figure 5.6) was determined for the best performing additive (SEBS-g-MA2) with highest loading (20 wt%). Lamination temperature for all samples was chosen to be 255 °C. There were two reasons for choosing this relatively high temperature. First, we wanted to match it with spinning temperature of the bicomponent fiber for the evaluation of possible reactive compatibilization during spinning. Second, we aimed to monitor the difference in the $G_c$ at even short time scale (1 min).

After analyzing the results shown in Figure 5.6, we found that even at 1 min there was a considerable improvement on the $G_c$ compared to control sample. Even though, we can infer that reactive compatibilization can also occur at short time scale at high temperature, we have to consider the additional time passed for the preheating stage of polymer sheets. But, we can definitely say that the interfacial adhesion between PA6 and PE +SEBS-g-MA2 is highly time dependent and increasing the time promotes more adhesion for them. Our findings also
imply that at short lamination times, especially at 1 min, the reaction was mostly dependent on the already available compatibilizer near the interface region. On the other hand, at 30 min, it seems that some of the other available SEBS-g-MA2 molecules in the PE phase also diffused to the interface region and reacted with PA6 to form more copolymers. In accordance with our explanation, the time dependency of the compatibilizer diffusion to the vicinity of the interface during reactive compatibilization was demonstrated for PA6/PP laminates with the addition of PP-g-MA as a compatibilizer [28].

![Figure 5.6](image.png)

**Figure 5.6** Effect of lamination time on the interfacial adhesion of PA6/PE laminates with the addition of 20 wt% SEBS-g-MA2 in PE (processed at 255 °C)

When we compare the 30 min and 60 min lamination times, it can be said that saturation of the interface with reacted copolymers was mostly achieved at 30 min. The reaction kinetics in the reactive compatibilization was studied by O'Shaughnessy and Vavylonis [41]. In this study, it was shown that at a certain time scale the interface saturates with reacted copolymer
product and reactions are strongly suppressed. This also supports our conclusion and emphasizes the importance of the time factor in achieving certain level of interfacial strength.

The effect of lamination temperature on the interfacial adhesion of PA6/PE+SEBS-g-MA2 (20 wt%) was also determined (see Figure 5.7). The lamination time for this set of samples was maintained at 30 min. Our findings suggest that after 170 °C the interfacial adhesion climbs steeply up and continues to increase with temperature. It is well known that increasing the temperature provides more mobility to polymer chains and therefore enhances the diffusion of the compatibilizer to the interface region. Thus, more compatibilizer chains underwent reaction with PA6. Similar results were also reported for PA6/PP+PP-g-MA laminates in the literature [28, 37].

![Figure 5.7](image_url)

**Figure 5.7** Effect of lamination temperature on the interfacial adhesion of PA6/PE laminates with the addition of 20 wt% SEBS-g-MA2 in PE (processed for 30 min)
One of the important findings is the achievement of reactive compatibilization at temperature values between 170 °C and 210 °C which were lower than the peak melting temperature of the PA6 (220 °C). We believe that using a relative long time (30 min) helped the reaction to spread in time at lower temperatures and resulted in considerable improvement on adhesion between PA6 and PE+SEBS-g-MA. This suggests that reactive compatibilization of nonwoven composite during composite fabrication can be possible if a temperature window between 170 °C and 200 °C is used.

5.4.2 In-Situ Reactive Compatibilization of Bicomponent Nonwoven Fibers

Core-sheath type bicomponent nonwoven fibers were produced using PA6 as the core and PE as the sheath with polymer composition of 50/50 wt%. Compatibilizers were dry blended with PE prior to the spinning at same concentration levels, 96/4, 90/10, and 80/20 wt% (PE/Compatibilizer), used in the lamination studies. Since the composition of the PE component in the fiber was 50 wt%, the composition of the compatibilizer containing bicomponent fibers became 50/48+2, 50/45+5, and 50/40+10 wt% (PA6/PE+Compatibilizer). Therefore, from this point forward the compatibilizer content appears to be 2, 5, and 10 wt % although they correspond to same compatibilizer loading (4, 10, and 20 wt%) used in the lamination study.

During bicomponent fiber production, in-situ reactive compatibilization may start to occur when two molten polymer streams (PA6 and PE+Compatibilizer) come into contact. It may also continue until the bicomponent fiber solidifies. The schematic representation of possible in-situ reactive compatibilization in bicomponent fibers is shown in Figure 5.8. As illustrated, MA functional group of SEBS may undergo reaction with amine end group or the backbone amide groups of PA6 and form amide. Thus, block copolymer of PA6-g-Compatibilizer may form at the core-sheath interface. At the same time, ethylene/butylene block of the SEBS may interact or even entangle with PE chains in the sheath component. Thus, several bridging between sheath and core component may be provided by the formed copolymers at the interface.
5.4.2.1 Tensile Properties of Nonwoven Fibers

In our previous study [24], we showed that tensile properties of core-sheath type bicomponent fibers are dependent on the incompatibility of polymer pairings and their interfacial adhesion. Therefore, in this study, we compared the tensile properties of bicomponent fibers to monitor any interfacial improvements that can be promoted during in-situ reactive compatibilization of fibers. The representative stress-strain graphs of PA6/PE (control) and PA6/PE+Compatibilizer (50/45+5 wt%) bicomponent fibers were shown in Figure 5.9. As seen in the figure, we did not observe any significant change in the tensile responses of bicomponent fibers with the addition of all type of compatibilizers. Similarly, other additive loadings (2 and 10 wt%) did not promote any improvement on the tensile properties of bicomponent fibers.

Figure 5.8 Schematic representation of the possible in-situ reactive compatibilization between terminal group of PA6 and functional group of compatibilizer in bicomponent fiber
In other study, which was conducted for PET/PE+Compatibilizer bicomponent fibers [42], we calculated the residence time in which core and sheath molten polymers spent together in the spinneret section since most of the reaction and interaction occur in this time frame. It was found to be around 11 seconds. As discussed in the Section 5.4.1.3, the reactive compatibilization of PA6 and PE with MA functionalized SEBS compatibilizers is highly time dependent. At spinneret temperature (255 °C), we reported a reduction in the interfacial adhesion with decreasing time. Even though we obtained a decent interfacial adhesion at 1 min of lamination time (excluding the preheating time), we believe that 11 seconds may be too short to promote sufficient bridging between PA6 and PE components by means of the reaction between compatibilizer and PA6. This may be the reason why we did not obtain any significant improvement on the tensile properties of compatibilized bicomponent fibers. This
suggests that in-situ reactive compatibilization was not sufficiently achieved during bicomponent spinning of fibers.

5.4.3 Reactive Compatibilization of Nonwoven Composites

In our previous study [25], we developed a composite fabrication technique that can convert bicomponent nonwovens to thermoplastic composites in a single step. In this technique, we utilized thermoforming process and used a processing temperature of 130 °C for the composites with PE matrix. Also, the total composite formation time for these composites was set to be between 1 and 5 min. These processing conditions were optimized for an open molding system.

In the Section 5.4.1.3, we showed that the reactive compatibilization of PA6 and PE+Compatibilizer is time and temperature dependent. For PA6/PE+Compatibilizer laminates, it was determined that at 30 min lamination time, temperature values of 170 °C and higher were required to achieve improvement in the interfacial adhesion. However, we were restricted in terms of temperature and time in the above mentioned composite formation process. This is due to the fact that in open molding system, molten matrix polymer can overflow under high pressure and temperature. Therefore, we modified our first generation composite fabrication protocol. In the current composite fabrication process (second generation), we used closed molding system to process bicomponent nonwovens at higher temperature and longer time. Thus, we applied a confined space during the formation of composites. This prevented the overflow of the molten matrix polymer at comparatively high temperature values and kept the forming composite intact. In the light of obtained results from the interface studies (see Section 5.4.1.3), we selected temperature values of 180, 190, and 200 °C and a consolidation time of 30 min. We employed these processing conditions in the composite fabrication stage and successfully produced composites from bicomponent nonwovens. At all temperature values, PA/PE (control sample) and PA6/PE+Compatibilizer composites were produced. Note that compatibilizers were already incorporated during the production of bicomponent fibers and nonwovens. The compatibilizer content (2, 5, 10 wt%)
and types (SEBS, SEBS-g-MA1, and SEBS-g-MA2) were the same used in the interface studies. Our approach for the reactive compatibilization of the composites followed the same route that was suggested for bicomponent fibers (see Figure 5.8) but differed in terms of time and temperature values employed.

5.4.3.1 Tensile Properties of Nonwoven Composites

After producing nonwoven composites, tensile properties of these composites were measured. When we compared the tensile properties of the PA6/PE composites (control sample) at different processing temperature (see Table 5.5), we noticed that the tensile modulus was improved with increasing the temperature while the tensile strength and energy to break values were decreased gradually. This is probably due to the annealing effect promoted at different temperature. As a result of the processing temperature increase, the composite structure became stiffer and therefore tensile failure shifted from ductile to brittle.

Table 5.5 Tensile properties of PA6/PE (control sample) nonwoven composites (standard errors are given in parentheses)

<table>
<thead>
<tr>
<th>Processing Temperature (°C)</th>
<th>Maximum Stress (MPa)</th>
<th>Strain at Break (%)</th>
<th>Energy to Break (J)</th>
<th>Initial Modulus (MPa)</th>
<th>Secant Modulus at 5% (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>75.3 (±0.4)</td>
<td>61 (±0.5)</td>
<td>41.7 (±0.3)</td>
<td>1530 (±20)</td>
<td>362 (±2)</td>
</tr>
<tr>
<td>190</td>
<td>62 (±0.7)</td>
<td>38.4 (±0.6)</td>
<td>21 (±0.4)</td>
<td>1820 (±20)</td>
<td>416 (±8)</td>
</tr>
<tr>
<td>200</td>
<td>29.7 (±1.4)</td>
<td>13 (±0.9)</td>
<td>4.2 (±0.5)</td>
<td>1850 (±40)</td>
<td>418 (±8)</td>
</tr>
</tbody>
</table>

Figures 5.10-12 show the tensile test results for PA6/PE composites including SEBS based additives. These results indicate that tensile properties (maximum stress, energy to break, and secant modulus at 5%) of PA6/PE nonwoven composites were improved with the addition of SEBS-g-MA1 and SEBS-g-MA2. This can be interpreted by the enhanced interfacial adhesion in the compatibilized composites. It was also found that adding 2 wt%
compatibilizer yields in better modulus values than 5 and 10 wt% concentration levels. This can be attributed to the rubbery nature of the additive which may disrupt the crystallization of PE and lower the tensile modulus of PE component. Therefore, we observed a decrease in modulus when we increased the compatibilization content. Similarly, at 10 wt% SEBS-g-MA2 concentration, the energy to break value decreased when compared to other concentration levels. The possible reason can be the decrease in miscibility between PE and this compatibilizer which may also negatively affect the contribution of PE phase on tensile response.

Figure 5.10 Effect of compatibilizer type and content on composite tensile strength (processed at 180 °C for 30 min)
Figure 5.11 Effect of compatibilizer type and content on composite tensile energy to break (processed at 180 °C for 30 min)

Figure 5.12 Effect of compatibilizer type and content on composite modulus at 5% strain (processed at 180 °C for 30 min)
Stress-strain graphs of PA6/PE nonwoven composites including varying amount of SEBS-g-MA2 are given in Figure 5.13. We observed a shift on the tensile response to higher strength values at same strain values with control sample. This is a clear indication of an improvement on the tensile behavior of PA6/PE composites with the addition of SEBS-g-MA2 compared to control samples. Therefore, energy to break values of the composites including compatibilizer were much higher than those of the control sample (see Figure 5.14). When the effect of composite processing temperature was investigated, we found that the relative difference on the tensile energy values were consistent at all temperature values used.

**Figure 5.13** Representative stress-strain graphs of PA6/PE (control) and PA6/PE+SEBS-g-MA2 nonwoven composites with varying compatibilizer content (processed at 180 °C for 30 min)
Figure 5.14 Effect of processing temperature on composite tensile energy to break for PA6/PE+SEBS-g-MA2 (processed for 30 min)

5.4.3.2 Analysis of Fractured Surfaces

The fracture surfaces of tensile test specimens were analyzed using SEM. The influence of additive type on the characteristic of the fractured surfaces and fibers is shown in Figure 5.15. As seen in the SEM micrographs (see Figure 5.15a and b), fractured fibers in the control and SEBS containing composites had very less matrix polymers adhered to fiber surface. On the other hand, SEBS-g-MA1 and SEBS-g-MA2 containing composites (see Figure 5.15c and d) clearly showed the adhesion of matrix polymers to the PA6 fibers. Among those two compatibilizers, SEBS-g-MA2 seems to be adhering better. These results are also in agreement with ADCB and tensile test results suggesting that SEBS-g-MA1 and SEBS-g-MA2 functioned as effective compatibilizers. We can also say that in the presence of these two compatibilizers the reactive compatibilization of PA6/PE composites was achieved.
The effect of compatibilizer (SEBS-g-MA2) concentration on the fracture behavior of composites was shown in Figure 5.16. It is clearly seen that the surfaces of PA6 (reinforcement) fibers are mostly free of matrix in control sample. This indicates that the fracture occurred in the form of fiber pull-out. Such kind of failure is typically observed for weak interfaces. On the other hand, when the fractured surfaces of other composites including SEBS-g-MA2 as a compatibilizer were investigated, we observed that matrix
polymer adhered to PA6 better and therefore the fracture mode shifted to cohesive failure. We also discovered that addition of 10 wt% additive promotes more adhesion (see Figure 5.16b, c, and d). However, as explained before it causes a reduction in the tensile properties (especially modulus) of composite samples in comparison with 2 and 5 wt% loading. In overall, the interfacial adhesion between PA6 and PE was improved gradually with an increase in the SEBS-g-MA2 content.

Figure 5.16 SEM micrographs of the fractured surface of tensile samples with varying compatibilizer (SEBS-g-MA2) content: (a) control, (b) 2 wt%, (c) 5 wt% , and (d) 10 wt% (processed at 190 °C for 30 min)
5.5 Conclusions

In the present work, we aimed to improve the interface in PA6/PE nonwoven based thermoplastic composites. For this purpose, we used SEBS and SEBS-g-MA with 1 wt% (SEBS-g-MA1) and 2 wt% (SEBS-g-MA2) MA contents as compatibilizers to promote adhesion between PA6 and PE components. A reliable and widely used test technique (ADCB) was initially employed to measure the interfacial adhesion in PA6/PE laminates in the presence of compatibilizers. The compatibilizers were incorporated into the PE phase to improve the poor interfacial adhesion between PA6 and PE (4.1 J/m²). We showed that interfacial adhesion in these polymer pair could be greatly improved with the addition of all three compatibilizers. Among these compatibilizers, SEBS-g-MA2 (121 J/m²) was the best performing compatibilizers. We also determined the effect functional group content and concentration of the compatibilizer on the interfacial adhesion in PA6/PE laminates and found that these factors increased the level of compatibilization achieved. Similarly, raising the lamination temperature and/or time greatly improved the interfacial fracture energy of the compatibilized PA6/PE laminates.

The same compatibilizers were also used in the production of core-sheath type of PA6/PE bicomponent fibers and nonwovens. After analyzing the tensile properties of bicomponent fibers, we did not observe any improvement on tensile responses of fibers. This suggests that sufficient level of in-situ compatibilization during fiber production was not provided and therefore enhanced adhesion between sheath and core components was not achieved. The inadequacy of compatibilization was attributed to the short contact time in which molten sheath and core polymers spent together during fiber spinning.

Analysis of the effect of processing temperature on the interfacial adhesion also revealed that there is a temperature window available for the reactive compatibilization of PA6/PE during composite fabrication stage. Therefore, we modified composite fabrication protocol and used closed molding to process bicomponent nonwovens which were already loaded with compatibilizers, at higher temperature and longer time. After successfully producing
nonwoven composites, the tensile properties of these composites were measured. Our results indicate that tensile strength, tensile modulus at 5% strain and tensile energy to break values were improved for the composites containing compatibilizers. The best performing compatibilizer was found to be SEBS-g-MA2. The optimum compatibilizer concentration in terms of tensile properties was the lowest compatibilizer loading of 2 wt%. The characterization of fractured surfaces showed the evidence of adhesion of matrix polymer to reinforcement fiber. As a result, cohesive failure was observed for the composites including compatibilizers. These results suggest that reactive compatibilization was achieved during composite fabrication stage and improved the adhesion between two polymers resulting in a higher load transfer and better mechanical properties.
5.6 References


CHAPTER 6

Reactive Compatibilization of Poly(ethylene Terepthalate)/Polyethylene Nonwoven Based Thermoplastic Composites

This chapter is essentially a manuscript by Dasdemir M, Maze B, Anantharamaiah N, and Pourdeyhimi B, and has been prepared for submission to Composites Science and Technology.
Reactive Compatabilization of Poly(ethylene Terephthalate)/Polyethylene Nonwoven Based Thermoplastic Composites

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Abstract

This study focuses on the reactive compatibilization of core-sheath type poly(ethylene terephthalate)/polyethylene (PET/PE) bicomponent fibers and composites made from them. Ethylene-ethylene acrylate-glycidyl methacrylate with 5 wt% (E-EA-GMA5) and 9 wt% (E-EA-GMA9) GMA contents and a maleic anhydride functionalized (2 wt%) triblock copolymer of styrene and ethylene/butylene (SEBS-g-MA2) were chosen as compatibilizers to promote adhesion between PET and PE. The compatibilizers were incorporated into the sheath component (PE) of the bicomponent fibers at varying concentrations. To determine the effectiveness of the compatibilization in fiber spinning stage, tensile properties of the fibers were analyzed. Also, the chemical imaging of the fiber cross-sections were obtained to evaluate the migration behavior of the compatibilizer. Our findings indicate that the compatibilization effectiveness was low in the bicomponent fibers due to the short contact time allowed for the reaction during fiber spinning. Reactive compatibilization was also performed in composite fabrication stage using the same compatibilizers, but for comparatively longer times and varying temperatures. When the tensile properties of the composites were evaluated, it was found that the tensile responses of PET/PE composites were significantly improved for E-EA-GMA9 and SEBS-g-MA2 bearing composites. The best overall tensile properties were obtained for the composites including 2 wt% of SEBS-g-MA2 and 10 wt% E-EA-GMA9. The characterization of the fracture surfaces allowed us to provide the evidence of enhanced adhesion between matrix polymer and reinforcement fiber for the composites including compatibilizers. Therefore, we can conclude that the reactive compatibilization was achieved during composite fabrication stage and improved the adhesion in PET/PE resulting in a better load transfer and enhanced mechanical properties.

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6.1 Introduction

Poly(ethylene terephthalate) (PET) and polyethylene (PE) are the most commonly used polymers and are exploited in many applications such as fibers, films, and textiles. One of the other important application areas for these polymers is bicomponent nonwovens in which PET/PE polymer configuration provides economical advantage and combines important characteristics of each polymer. Similarly, thermoplastic composites made from these materials can utilize from these advantages and can be a good and inexpensive alternative for conventional thermoplastic composites [1]. In such composite, PET fiber offers good mechanical properties, while PE matrix provides excellent impact properties and resistance to chemicals and environmental conditions. However these two polymers are thermodynamically immiscible, so the composite material consisting of these two polymers is expected to have high interfacial tension and weak adhesion. This problem also arises for PET/PE bicomponent fiber structures [2] and nonwoven based thermoplastic composites made from these materials [1] and usually leads to phase separation at the interface. Therefore, the tensile properties of these materials can exhibit poor performance as a result of the inefficient load transfer between two components. It can be noted that this poor adhesion is actually looked after in configurations like segmented pie, where it facilitates the separation of the individual wedges.

The compatibilization approach has been widely used for PET/PE polymer blends to lower the interfacial tension and enhance the adhesion at the interface [3-12]. In the reactive compatibilization of the PET/PE, a compatibilizer with functional group is added to the blend to provide interaction and reaction between the components. Thus, the functional group on the compatibilizer can react with hydroxyl and/or carboxylic terminal groups of the PET and form a block copolymer at the interface [5, 6]. For instance, when a maleic anhydride functionalized compatibilizer is used, terminal hydroxyl group of PET and anhydride group reacts and yields esterification [6]. At the same time, if this compatibilizer has an ethylene block, this ethylene block can entangle with the PE polymer chains and anchor the PE component [5].
Several compatibilizers have been used for compatibilizing the PET/PE blends (see Table 6.1). The performance of some of these compatibilizers has been studied by many researchers [4, 5, 7-10]. It was reported that SEBS-g-MA performs better than HDPE-g-MA and SEBS in the PET/HDPE blend, and improves the toughness of the blend with a considerable increase in elongation at break [4]. The effectiveness of diethyl maleate (DEM) functionalized SEBS and LDPE as a compatibilizer in the PET/LDPE blend was also investigated [5]. It was speculated that the SEBS-g-DEM could lower the interfacial tension more than the LDPE-g-DEM and promote co-continuous phase in the blend.

**Table 6.1** Compatibilizers used in the compatibilization of PET/PE blends

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Polymer</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-AA</td>
<td>Ethylene-(b)-Acrylic Acid</td>
<td>[10]</td>
</tr>
<tr>
<td>PE-g-MA</td>
<td>Polyethylene grafted with Maleic Anhydride</td>
<td>[3]</td>
</tr>
<tr>
<td>HDPE-g-MA</td>
<td>High Density Polyethylene grafted with Maleic Anhydride</td>
<td>[4, 8, 10]</td>
</tr>
<tr>
<td>EPR-g-MA</td>
<td>Ethylene-(b)-Propylene grafted with Maleic Anhydride</td>
<td>[10]</td>
</tr>
<tr>
<td>E-MeA-g-MA</td>
<td>Ethylene-(b)-Methyl Acrylate grafted with Maleic Anhydride</td>
<td>[7, 9]</td>
</tr>
<tr>
<td>SEBS</td>
<td>Styrene-(b)-Ethylene-(co)-Butylene-(b)-Styrene</td>
<td>[4, 9]</td>
</tr>
<tr>
<td>SEBS-g-MA</td>
<td>Styrene-(b)-Ethylene-(co)-Butylene-(b)-Styrene grafted with Maleic Anhydride</td>
<td>[4, 7, 8, 10, 11]</td>
</tr>
<tr>
<td>E-GMA</td>
<td>Ethylene-(b)-Glycidyl MethAcrylate</td>
<td>[7-10]</td>
</tr>
<tr>
<td>E-EA-GMA</td>
<td>Ethylene-(b)-Ethylene Acrylate-(b)-Glycidyl MethAcrylate</td>
<td>[7, 9]</td>
</tr>
<tr>
<td>ULDPE-g-DEM</td>
<td>Ultra Low Density Polyethylene grafted with Diethyl Maleate</td>
<td>[5]</td>
</tr>
<tr>
<td>SEBS-g-DEM</td>
<td>Styrene-(b)-Ethylene-(co)-Butylene-(b)-Styrene grafted with Diethyl Maleate</td>
<td>[5]</td>
</tr>
</tbody>
</table>

Kalfoglou et al. [7] also conducted morphological analysis and tensile testing on PET/HDPE blends and showed that SEBS-g-MA performs better than E-EA-g-MA. However, the compatibilizers having glycidyl methacrylate (GMA) as a functional group such as E-EA-
GMA and E-GMA were found to be more effective than the compatibilizers functionalized with MA [5, 7, 10]. It is due to the fact that the reactivity of the GMA functionality is higher than that of MA [7]. Coltelli et al. [5] also reviewed that the GMA functionalized polyolefins perform better than MA functionalized polyolefins in terms of tensile and impact properties. On the other hand some studies found that E-GMA and SEBS-g-MA showed comparable compatibilization effectiveness in the PET/HDPE blend [8].

In addition to the type of the compatibilizer, the amount of the compatibilizer [5, 8-10, 12], blend composition [5, 9, 10], the functional group content [7, 9], the molecular weights of the PET [3] and PE [11] are other factors that can influence the compatibilization.

All compatibilization studies mentioned above were conducted on PET/PE blends. According to our knowledge, there is no such study available in the literature for the PET/PE bicomponent fibers or composites made from these polymers. The reactive compatibilization of the polymers during the bicomponent fiber production or composite formation stages is different from that of blending in terms of the time and temperature allowed for the reaction and the geometry obtained or defined for the end product. In a consecutive study, we investigated the applicability of the reactive compatibilization approach for polyamide 6 (PA6)/PE nonwoven based composites [13]. After determining the proper processing conditions for the compatibilization, we achieved a considerable improvement on the interfacial adhesion between fiber and matrix polymers and therefore, enhanced the tensile responses of the composite.

Our main objective in this study is to enhance the adhesion at the interface of PET/PE in order to improve the mechanical performance of nonwoven based thermoplastic composites. For this purpose, commercially available SEBS-g-MA with 2 wt% MA content and E-EA-GMA with 5 and 9 wt% GMA contents were chosen as compatibilizers to promote adhesion between PET and PE components. PET/PE bicomponent fibers and nonwovens were produced with the addition of different amount of compatibilizers (into the sheath component of the bicomponent fiber) in fiber spinning stage. Tensile properties of bicomponent fibers
and chemical imaging of fiber cross-sections were analyzed to determine the effectiveness of the compatibilization in fiber spinning stage. Lastly, the compatibilization was performed during composite fabrication stage using different processing temperatures. Tensile properties of the compatibilized composites and morphological analysis of the fractured surfaces were recorded and compared with control nonwoven composites.

6.2 Materials

Commercial fiber grades of PET and linear low density PE used in spunbond nonwoven manufacturing were used for making fibers, nonwovens, and composites. Some of the basic properties and suppliers of these polymers are listed in Table 6.2. We also used two different grades of E-EA-GMA with varying GMA contents and an MA functionalized SEBS elastomer as compatibilizers. The properties of these compatibilizers are given in the Table 6.3.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Trade Name</th>
<th>Supplier</th>
<th>Density $^1$, $\rho$ (g/cm$^3$)</th>
<th>Melting Temperature $^2$, $T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>F-61HC</td>
<td>Eastman Chemical Co.</td>
<td>1.41</td>
<td>250</td>
</tr>
<tr>
<td>PE</td>
<td>Aspun 6850A</td>
<td>Dow Chemical Co.</td>
<td>0.955</td>
<td>129</td>
</tr>
</tbody>
</table>

$^1$ The density value of PE was obtained from corresponding polymer data sheet supplied by the producer. PET density value was taken from the reference [14].

$^2$ The melting temperatures of all polymers were peak melting temperatures and measured by means of a differential scanning calorimeter at a heating rate of 10°C/min.
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Trade Name</th>
<th>Supplier</th>
<th>Functional Group Content, (wt%)</th>
<th>Weight Average Molecular Weight, $M_w$ (g/mol)</th>
<th>Polydispersity Index, PDI</th>
<th>Melt Index (g/10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-EA-GMA5</td>
<td>Elvaloy® PTW</td>
<td>Dupont®</td>
<td>5</td>
<td>157000</td>
<td>7.5</td>
<td>12 (at 190 °C)</td>
</tr>
<tr>
<td>E-EA-GMA9</td>
<td>Elvaloy® 4170</td>
<td>Dupont®</td>
<td>9</td>
<td>98000</td>
<td>5.1</td>
<td>8 (at 190 °C)</td>
</tr>
<tr>
<td>SEBS-g-MA2</td>
<td>FG-1901</td>
<td>Kraton Polymers</td>
<td>2</td>
<td>52500</td>
<td>-</td>
<td>22 (at 230 °C)</td>
</tr>
</tbody>
</table>

1 The functional group content values of E-EA-GMA5 [15], E-EA-GMA9 [16], and SEBS-g-MA2 [17] were taken from references.
2 The molecular weight of E-EA-GMA5 and E-EA-GMA9 were measured in the Dupont’s laboratory and provided to us, while that of SEBS-g-MA2 was previously reported in the literature [17].
3 The melt index values were obtained from corresponding polymer data sheets supplied by the producers.
6.3 Methods

6.3.1 Production of Bicomponent Fibers and Nonwovens

Bicomponent nonwovens were produced using the spunbonding process (see Figure 6.1) at the Nonwovens Institute’s pilot facility (NC State University, Raleigh, NC, USA). The bicomponent fiber cross-section chosen was a core/sheath structure with a polymer ratio of 50/50 wt%. The compatibilizers which were dry blended with PE matrix at 4/96, 10/90, and 20/80 wt% (compatibilizer/PE) ratios were spun into the sheath side. Therefore, the additive contents of 2, 5, and 10 wt% with respect to whole weight fraction were used. Attenuated fiber samples which are continuous oriented filaments were collected before the deposition on the forming belt during the process for investigation. Spunbond nonwoven fabrics with 250 g/m² basis weight were also produced and compacted using unheated calendering rolls which can provide sufficient web integrity for handling at subsequent composite fabrication stages, but at the same time would not affect the structure or properties of the web.

Overall throughput was adjusted to 0.7 g/min for each hole for an 1162 holes spinneret. Fibers were quenched with quenchers on either side and the quench air temperature was 11 °C. Screw pressures for both extruders were adjusted to 750 psi. Processing temperatures for each polymer are listed in Table 6.4. Drawn fibers with an expected fiber denier value of 2 were collected during the process for investigation.

6.3.2 Formation of Nonwoven Composites

Nonwoven fabrics were cut to 20 cm × 20 cm dimensions. Four separate layers of nonwoven fabrics were stacked on top of one another. Each layer of these nonwoven fabrics had the dominant orientation in the machine direction. In order to get balanced structures, cross-layering (0° and 90°) was employed to configure the stacks of nonwoven fabrics. A hot press was used to form nonwoven composite.
**Figure 6.1** Schematic drawing of the bicomponent spunbonding process at NCSU [18]

**Table 6.4** Processing conditions for the production of nonwoven fibers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Processing Temperature (°C)</th>
<th>Extruder</th>
<th>Spin Head $^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zone 1</td>
<td>Zone 2</td>
<td>Zone 3</td>
</tr>
<tr>
<td>PET</td>
<td>232</td>
<td>274</td>
<td>282</td>
</tr>
<tr>
<td>PE</td>
<td>204</td>
<td>218</td>
<td>221</td>
</tr>
</tbody>
</table>

$^1$ Spin head is common to both extruders in bicomponent spinning.
The principle of making thermoplastic composites from bicomponent nonwoven fabrics in a single step was extensively explained in our previous study [1]. However, composite fabrication technique used in this study differs from the previously developed technique (1st generation). The 1st generation composite making process was limited in terms of the temperature values used for preheating and consolidation stages [1]. In the current composite making process (2nd generation), this limitation was overcome using a closed molding configuration. Thus, the composite’s integrity was upheld by preventing the escape of the molten matrix polymer from the structure.

During composite fabrication residence pressure ($P_r$) and time ($t_r$) were kept at 1000 psi and 5 min, while the consolidation time ($t_c$) and pressure ($P_c$) were kept at 8000 psi and 30 min, respectively. The temperature values for residence ($T_r$) and consolidation ($T_c$) were same and ranged from 220 to 240 °C. Composite samples were quenched in between two metal plates at room temperature.

6.3.3 Tensile Testing of Single Fibers

Fiber tensile tests were performed according to ASTM standard D3822-07 under standard test conditions (21±1°C and 65±2 % relative humidity). The fibers were preconditioned for two days. Linear density of the single fibers was measured using vibroscope method (ASTM D 1577-07) in Vibromat ME Textechno test equipment and fiber deniers were noted. Each individual fiber was then pasted on paper cardboards. Great care was taken not to deform the fibers. At least 10 specimens were prepared for each sample set. MTS Q-Test machine with 50 g load cell was used for tensile test. The gauge length for the test was adjusted to 25.4 mm (1 inch). Tensile tests were carried out under constant rate of extension with an extension rate of 15 mm/min.
6.3.4 Tensile Testing of Nonwoven Composites

Composite tensile testing was performed to determine the tensile strength of the composites formed with 4 plies of nonwoven fabrics. Slippage in the grips was prevented by using diamond grip faces, while the sample fracture at the grip were prevented by using dog bone shaped specimens as specified in the ASTM Standard D 638-08. MTS Q-Test machine with 90 kN load cell was used for the test. The crosshead speed was adjusted to 51 mm/min. Mechanical parameters: initial modulus, secant modulus at 5% strain, tensile strength, strain at break and tensile energy to break were measured.

6.3.5 Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is one of the most sensitive surface analysis techniques [19]. It provides both high spatial (surface selectivity of 1Å-3Å) and mass resolution data from a specimen surface. In this study, the Physical Electronics Instruments (PHI) TRIFT I ToF-SIMS was initially used to obtain mass spectrums of PET, PE, and E-EA-GMA9 polymers. Chemical images of PET/PE (control) and PET/PE+E-EA-GMA9 (50/45+5 wt%) undrawn fiber cross-sections were then obtained via ToF-SIMS to trace elements present in the compatibilizer. During sample preparation, we did not use any embedding media in order to minimize the background effect for obtaining better contrast and avoid contamination by diffusion of embedding media into the sheath component. Instead of embedding and then microtoming, a clean razor blade and a fiber cross-section kit was used for each sample.

6.3.6 Scanning Electron Microscopy

Scanning electron microscope (SEM) images were taken for fractured tensile test specimens. Samples were initially cleaned using dry nitrogen and then coated with AuPd for 2 min at 600 volts and 5 mA current. SEM analysis was then performed on the samples at a 5kV accelerating voltage and 40 mA beam current in a Hitachi S-3200 SEM.
6.4 Results and Discussions

6.4.1 In-Situ Reactive Compatibilization of Bicomponent Fibers

The reactive compatibilization of polymers during bicomponent fiber spinning stage is different from that of polymer blending. This is due to the processing parameters and time allowed for the reaction between the polymers. It is therefore important to explain the bicomponent fiber spinning briefly and determine the possible reaction time. In the spinning of core-sheath type bicomponent fibers (see Figure 6.1), polymer pellets for the core and sheath components are separately fed to two individual extruders in which they melt progressively. The molten core and sheath polymers are then separately filtered and conveyed to spinpack by means of the metering pump. After they enter the spin pack, they pass several distribution plates and reach the spinneret. In the spinneret, the molten core and sheath polymer streams go into a section called “spinneret counterbore” (see Figure 6.2). This is the location where the two polymer streams first meet and take the final cross-section form. Interaction between two components and any arrangement of polymer melt starts to occur in the spinneret counterbore and continues until they are solidified.

In order to determine the residence time \((t)\) of the two components in the spinneret counterbore, the total volume \((V)\) of this section and the flow rate per orifice \((\dot{Q})\) should be calculated. The volume calculations are given by Equations 6.1-6.5:

\[
V = V_1 + V_2 + V_3 \tag{6.1}
\]

\[
V_1 = \frac{1}{4} L_1 \pi D_1^2 \tag{6.2}
\]

\[
V_2 = \frac{1}{4} L_2 \pi D_2^2 \tag{6.3}
\]
\[ L_3 = \left( \frac{D_1 - D_2}{2} \right) \tan Q \] (6.4)

\[ V_3 = \frac{1}{12} L_3 \pi \left( D_1^2 + D_1 D_2 + D_2^2 \right) \] (6.5)

where \( D_1 \) is the counterbore diameter; \( D_2 \) is the orifice diameter; \( L_1 \) is the counter length; \( L_2 \) is the capillary length; \( L_3 \) is the length of the merging orifice; \( L_4 \) is the length of the upper counter section; \( Q \) is the angle for the merging orifice.

Figure 6.2 Spinneret counterbore
Volume flow rate per each orifice can be calculated using following Equations 6.6-6.8:

\[ \dot{Q} = \frac{m_r}{\rho_r n} \]  

\[ \rho_r = f_c \rho_c + (1 - f_c) \rho_S \]  

\[ f_c = \frac{w_c / \rho_c}{w_c / \rho_c + w_s / \rho_s} \]  

where \( m_r \) is the overall mass flow rate; \( \rho_r \) is the overall melt density of two polymers; \( n \) is the number of orifices in the spinneret; \( f_c \) is the volume fraction of the core; \( \rho_c \) is the melt density of the core polymer; \( \rho_S \) is the melt density of the sheath polymer; \( w_c \) is the weight ratio of core component; \( w_s \) is the weight ratio of the sheath component. After calculating the volume and flow rate, the residence time can be determined (Equation 6.9).

\[ t = \frac{V}{Q} \]  

The residence time for the molten PET/PE bicomponent polymer stream in the spinneret counterbore was found to be 10.9 seconds for our production line. Even though some additional time passed between the exit of the spinneret and the point where filaments solidified, it was negligibly small compared to the residence time in the counterbore. Therefore, we can say that the time allowed for a possible reactive compatibilization during bicomponent fiber spinning was approximately 11 seconds. This can be considered a very
short time compared to the reaction time allowed for polymer blending which is typically in the order of minutes [3, 5, 10].

In order to compensate the short residence time, we chose highly reactive compatibilizers of E-EA-GMA with 5 wt% (E-EA-GMA5) and 9 wt% (E-EA-GMA9) GMA contents. The reactivity of the GMA epoxide groups was shown to be higher than that of other functional groups such as MA and AA [6, 7, 20]. This is due to the fact that epoxide functional group on the polar GMA block can either react with hydroxyl or carboxylic terminal groups of PET (see Figure 6.3). But the reaction between carboxyl and epoxy is more favorable than hydroxyl and epoxy [6].

![Figure 6.3 Reaction between E-EA-GMA and PET](image-url)
In our previous study, we showed that SEBS-g-MA2 promoted considerable adhesion and enhanced the tensile properties of PA6/PE nonwoven based thermoplastic composites [13]. Even though the reactive compatibilization of PA6/PE in the presence of this compatibilizer was not achieved in bicomponent fiber spinning stage, it was achieved in the composite fabrication stage and yielded a significant compatibilization effect. Considering the second stage of compatibilization (during composite formation) and high effectiveness of the SEBS-g-MA, this compatibilizer was therefore chosen in this study. In the reactive compatibilization of PET/PE, MA group in SEBS-g-MA can react with hydroxyl end group of PET and form ester.

The schematic representation of possible in-situ reactive compatibilization in bicomponent fibers is shown in Figure 6.4. In this approach, the functional group of the compatibilizer reacts with the terminal groups of the core polymer (PET) and form block copolymer at the interface. At the same time, ethylene blocks of the compatibilizer interact or even entangle with the sheath polymer (PE) and anchor this phase. For this purpose, we added compatibilizer into the sheath polymer. The contents of the compatibilizer were 2, 5, and 10 wt% with respect to the total polymer contents (PET + PE).

6.4.1.1 Fiber Tensile Properties

In our previous study we showed that compatibility and interfacial adhesion of polymers used in bicomponent fibers has profound effect on the tensile properties of fibers [2]. Therefore, in this study we analyzed the tensile properties of PET/PE bicomponent fibers with or without the addition of compatibilizers to determine if any changes were introduced by possible compatibilization effect. Figure 6.5 shows the representative stress-strain graphs of PET/PE (control) and PET/PE+Compatibilizer (50/45+5 wt%) bicomponent fibers. Our results indicate that bicomponent fibers including SEBS-g-MA2 exhibited almost the same tensile response. This suggests that the reactive compatibilization of bicomponent fibers was not achieved in the presence of this compatibilizer. Similar result was also obtained for PA6/PE+SEBS-g-MA2 bicomponent fibers [13]. Tensile responses of the bicomponent
fibers including GMA bearing compatibilizers were slightly improved when compared to the tensile response of control sample. Even though, we did not observe any improvement on the maximum stress, strain at break, and fiber toughness values, there was a change in the tensile response at strain values between 2.5 and 70%. The tensile response of the fibers including E-EA-GMA5 and E-EA-GMA9 was enhanced in this region compared to that of the control sample. This improvement was more pronounced in the presence of higher GMA content (9 wt%) bearing compatibilizer (E-EA-GMA9). These results may indicate that some adhesion might be promoted as a result of the reactive compatibilization and therefore it might affect the low strain tensile response. Our hypothesis is that the degree of adhesion achieved was not sufficient to hold the bicomponent structure intact in the entire range of tensile behavior. Therefore, we believe that the effectiveness of the compatibilization was not high enough to promote decent adhesion between PET and PE.

![Figure 6.4](image.png) **Figure 6.4** Schematic representation of the possible in-situ reactive compatibilization between terminal group of PET and functional group of compatibilizer in bicomponent fiber
6.4.1.2 Determination of the Location of Compatibilizer in Fiber

ToF-SIMS was used to trace the location and intensity of compatibilizer (E-EA-GMA9) along the fiber cross-section to determine the effectiveness of compatibilization during fiber spinning stage. First, the mass spectrums of all individual components (PET, PE, and E-EA-GMA9) in the form of polymer pellets were analyzed. Our aim was to determine distinct chemical species present in each component. It was found that E-EA-GMA9 yielded very high intensity at 30, 44, and 61 mass to charge ratios (see Figure 6.6). These peaks are distinct to the composition and can be called as fingerprints of this compatibilizer in PET/PE+E-EA-GMA9 structure since none of the other components shows these peaks. Even though, E-EA-GMA9 chemistry does not include nitrogen, these peaks originate from nitrogen bearing segments. Therefore, we repeated the test twice using two different polymer
pellets, but found no change in the results. These nitrogen bearing segments could be any fragment of a stabilizer or additive incorporated during the polymerization of this compatibilizer. A fingerprint for PET was found at 76 mass to charge ratio which is the benzene ring in PET molecule (see Figure 6.6).

After obtaining distinct fingerprints of the compatibilizer and PET, we investigated the chemical images of fiber cross-sections for undrawn PET/PE (control) and PET/PE+E-EA-GMA9 (50/45+5 wt%) bicomponent fibers. The overlaid chemical images of these cross-sections are shown in Figure 6.7. While the first image (Figure 6.7a) represents the control sample, the second and third images (Figure 6.7b and c) represent the two different samples of E-EA-GMA9 bearing bicomponent fibers. Red regions in the images show the location of a fragment of the PET molecule (benzene ring, C₆H₄), whereas green regions indicate the location of a molecular segment (H₃N[CH₂]₂NH₂⁺) present in the additive found in the E-EA-GMA9. We assume this additive would follow a diffusion pattern similar to the E-EA-GMA9 itself. As seen in Figure 6.7b and c, E-EA-GMA9 was found to be well distributed in the sheath component instead of clustering at the neighborhood of the interface. This can be attributed to the short residence time experienced during bicomponent fiber spinning which was not sufficient for the compatibilizer to migrate to the interface as a result of polar interaction between epoxide functional group of the compatibilizer and the hydroxyl and carboxyl terminal groups of the PET. This indicates that only available compatibilizer in the proximity of the PET/PE interface might have chance to react with the PET. Therefore, the compatibilization efficiency can be expected to be low in bicomponent fiber spinning.
Figure 6.6 Mass spectrum analysis (8-87 u) of E-EA-GMA9, PE, and PET polymers
Figure 6.7 Overlaid chemical images of the undrawn bicomponent fiber cross-sections (a) PET/PE (control), (b) and (c) PET/PE+E-EA-GMA9 (50/45+5 wt%)
6.4.2 Reactive Compatibilization of Nonwoven Composites

The reactive compatibilization of PET/PE nonwoven based thermoplastic composites was performed in the composite fabrication stage. We modified initially established composite formation process [1] based on the results that we obtained for the reactive compatibilization of PA6/PE nonwoven composites [13]. However, we increased the consolidation temperature up to 240 °C. This is due to the fact that PET/PE+Compatibilizer requires higher temperature than PA6/PE+Compatibilizer to achieve reactive compatibilization during composite making stage. PET/PE nonwoven composites were then processed at 220, 230, and 240 °C for 30 min to achieve reactive compatibilization. In addition to control composite samples, we made composites from bicomponent nonwovens including E-EA-GMA5, E-EA-GMA9, and SEBS-g-MA2 at 2, 5, and 10 wt% compatibilizer contents. Note that these compatibilizers were already loaded in bicomponent nonwovens. The reactive compatibilization approach in the composites was the same as described for bicomponent fibers (see Section 6.4.1) but differed in terms of the time and temperature allowed for the reaction.

6.4.2.1 Composite Tensile Properties

After producing nonwoven composites, tensile properties of these composites were measured. Table 6.5 presents the tensile test results obtained for control samples at different consolidation temperatures. These results indicate that with increasing the consolidation temperature, the initial modulus values of these composites were enhanced while other tensile properties (maximum stress, strain at break, and energy to break) reduced. This can be attributed to the enhanced annealing effect experienced at higher temperature which can cause an improvement in the modulus of the composites. However, the composites became more brittle at higher annealing temperature. Therefore, the tensile response shifted from ductile to brittle. Similar effect was also observed for PA6/PE composites in our previous study [13].
Table 6.5 Tensile properties of PET/PE (control sample) nonwoven composites (standard errors are given in parentheses)

<table>
<thead>
<tr>
<th>Processing Temperature (°C)</th>
<th>Maximum Stress (MPa)</th>
<th>Strain at Break (%)</th>
<th>Energy to Break (J)</th>
<th>Initial Modulus (MPa)</th>
<th>Secant Modulus at 5% (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td>41.9 (±1.1)</td>
<td>10.4 (±1.0)</td>
<td>4.1 (±0.5)</td>
<td>2920 (±60)</td>
<td>702 (±7)</td>
</tr>
<tr>
<td>230</td>
<td>34.3 (±0.6)</td>
<td>4.6 (±0.6)</td>
<td>1.5 (±0.2)</td>
<td>3000 (±10)</td>
<td>-</td>
</tr>
<tr>
<td>240</td>
<td>25.8 (±0.8)</td>
<td>1.3 (±0.1)</td>
<td>0.2 (±0.02)</td>
<td>3190 (±70)</td>
<td>-</td>
</tr>
</tbody>
</table>

Figures 6.8-6.10 show the tensile test results for PET/PE control and modified composites including E-EA-GMA5, E-EA-GMA9, and SEBS-g-MA2 compatibilizers with varying content (2-10 wt%). These results indicate that tensile strength, modulus at 5% strain, and energy to break properties for PET/PE nonwoven composites were significantly improved with the addition of E-EA-GMA9 and SEBS-g-MA2. It was also found that adding 2 wt% of SEBS-g-MA2 yields in better strength and modulus values than 5 and 10 wt% additions. This can be attributed to the rubbery nature of the additive which may disrupt the crystallization of PE and lower the tensile properties of PE component at higher loading ratios. Therefore, we observed a slight improvement in 10 wt% SEBS-g-MA2 loading. On the other hand, increasing the content of E-EA-GMA9 resulted in a gradual improvement on tensile strength and energy to break of the resultant composite. This indicates that more compatibilizers contributed to the reactive compatibilization and improved the load transfer without sacrificing in overall properties of the composites. When we compare the effectiveness of E-EA-GMA5 and E-EA-GMA9, we can say that higher GMA content yielded better overall tensile properties. However, the reason for observing decrease in some tensile properties in the presence of E-EA-GMA5 is not clear.
Figure 6.8 Effect of compatibilizer type and content on composite tensile strength (processed at 220 °C for 30 min)

Figure 6.9 Effect of compatibilizer type and content on composite tensile energy to break (processed at 220 °C for 30 min)
Stress-strain graphs of PET/PE nonwoven composites including different amount of SEBS-g-MA2 are given in Figure 6.11. We observed a shift in the tensile response to higher strength values at the same strain values with control sample. This is a clear indication of an improvement on the tensile behavior of PET/PE composites with the addition of SEBS-g-MA2 compared to control samples. Therefore, energy to break values of the composites including compatibilizer were much higher than control sample (see Figure 6.9). When the effect of composite processing temperature was investigated, we found that the relative difference on the tensile strength values were persistent at all temperature values used (see Figure 6.12). This suggests that compatibilization effectiveness increased with increasing the processing temperature.
6.4.2.2 Analysis of Fractured Surfaces

After performing tensile test on the nonwoven composite samples, the surfaces of the fractured tensile test specimens were analyzed via SEM to determine the failure type and fiber-matrix adhesion. The effect of compatibilizer (SEBS-g-MA2) concentration on the fracture behavior of composites was shown in Figure 6.13. It is clearly seen that the surfaces of PET (reinforcement) fibers are mostly free of matrix in control sample. This indicates that the fracture occurred in the form of fiber pull-out. Such kind of failure is typically observed for weak interfaces. On the other hand, when the fractured surfaces of other composites including SEBS-g-MA2 as a compatibilizer were investigated, we observed that matrix polymer adhered to PET better and therefore the fracture mode shifted to cohesive failure. We also found that addition of 10 wt% additive promotes more adhesion (see Figure 6.13b, c,
and d). However, as explained before, due to the rubbery nature of SEBS-gMA2, replacing more PE with compatibilizer causes a reduction in the tensile properties (especially modulus) of composite samples in comparison to 2 and 5 wt% compatibilizer loadings.

![Figure 6.12](image)

**Figure 6.12** Effect of processing temperature on composite tensile strength for PET/PE+SEBS-g-MA2 (processed for 30 min)

The influence of compatibilizer type on the characteristic of the fractured surfaces and fibers is shown in Figure 6.14. As seen in the SEM micrographs (see Figure 6.14b, c, and d), SEBS-g-MA2 containing composites showed better adhesion than other two different E-EA-GMA containing composites at the lowest additive loading (2 wt%). However, when the additive concentration was increased to 10 wt%, the E-EA-GMA5 and E-EA-GMA9 containing composites showed considerable adhesion to PET fiber surface (see Figure 6.15). Therefore the fracture turned out to be cohesive failure. These results are also in agreement with tensile test results. They suggest that the reactive compatibilization was achieved during
composite fabrication stage and significantly enhanced the adhesion between PET fiber and PE matrix.

**Figure 6.13** SEM micrographs of the fractured surface of tensile samples with varying compatibilizer (SEBS-g-MA2) content: (a) control, (b) 2 wt%, (c) 5 wt%, and (d) 10 wt% (processed at 230 °C for 30 min)
Figure 6.14 SEM micrographs of the fractured surface of tensile samples with different compatibilizer type: (a) control, (b) SEBS-g-MA2, (c) E-EA-GMA5, and (d) E-EA-GMA9 (processed at 220 °C for 30 min with compatibilizer content of 2 wt%)
Figure 6.15 SEM micrographs of the fractured surface of tensile samples with varying compatibilizer content: (a) 2 wt% E-EA-GMA5, (b) 10 wt% E-EA-GMA5, (c) 2 wt% E-EA-GMA9, and (d) 10 wt% E-EA-GMA9 (processed at 220 °C for 30 min)
6.5 Conclusions

In this study, we focused our effort on the interface enhancement in PET/PE nonwoven based thermoplastic composite to improve the mechanical performance of this composite. For this purpose, we used E-EA-GMA5, E-EA-GMA9, and SEBS-g-MA2 as compatibilizers. These compatibilizers were added into the sheath component (PE) of the bicomponent fibers at 2, 5, and 10 wt% concentration levels. The bicomponent fibers and nonwovens including compatibilizers were then produced. In order to evaluate the efficiency of the reactive compatibilization possibly occurred during the bicomponent fiber production, the tensile properties of the fibers were characterized. We found that the bicomponent fibers including GMA bearing additives showed some improvement in the tensile responses at low strain regions. However, such improvement was not observed in the overall tensile properties. To clarify the reason for this behavior we traced the compatibilizer in the fiber by obtaining the chemical imaging of the fiber cross-sections. Our findings clearly show that the compatibilizer was well distributed in the sheath component instead of clustering in the interface region. This was attributed to the short residence time experienced in the bicomponent fiber spinning which was not sufficient for the migration of the compatibilizer to the interface. Thus, only compatibilizers present in the proximity of the interface might undergo reaction with PET and therefore, compatibilization efficiency became too low to enhance the overall tensile properties of the bicomponent fiber. A possible solution for improving compatibilization efficiency in the bicomponent fiber spinning stage would be tailoring the molecular architecture of the compatibilizer. We believe that lowering the molecular weight of the compatibilizer may help the diffusion of more compatibilizers through the interface region.

We also performed the reactive compatibilization in the composite fabrication stage using longer residence time and different temperatures. After producing nonwoven composites, tensile properties of these composites were measured. Our results indicate that tensile properties were improved for the composites containing E-EA-GMA9 and SEBS-g-MA2.
The best performing compatibilizer was found to be SEBS-g-MA2. The optimum concentration for this compatibilizer in terms of tensile properties was the lowest loading level of 2wt%. The characterization of fractured surfaces showed the evidence of adhesion of matrix polymer to reinforcement fiber. As a result, cohesive failure was observed for the composites including compatibilizers. These results suggest that reactive compatibilization was achieved during composite fabrication stage and improved the adhesion between PET fiber and PE matrix resulting in a higher load transfer and better mechanical properties.
6.6 References


CHAPTER 7

Conclusions and Recommendations
7.1 Overall Conclusions

In this study, a novel thermoplastic composite fabrication technique was developed to produce engineering thermoplastic composites from bicomponent nonwovens without using any additional resin or binder. Inherent composite structure of the bicomponent fibers enabled to obtain fiber reinforced thermoplastic composites in which PET, PA6, and PP were the reinforcement while PP and PE were the matrix.

We studied the effects of temperature and fiber volume fraction on the structure of nonwoven composites by using microstructural analysis. In open molding composite fabrication technique (1st generation), processing temperatures of 130 °C for PE matrix and 165 °C for PP matrix were found to be the most favorable conditions for producing nonwoven composites with the fewer amount of defects under high pressure. Combination of two factors: (i) random distribution of the fibers and (ii) cross-layering limited to achieve high reinforcement volume fraction (e.g. f=0.72 for PA6/PE) in the resultant composite. However nonwoven composites (PET/PE, PA6/PE, PA6/PP, and PP/PE) with f ≤ 0.51 were successfully produced.

In order to provide a better insight for the process-structure relationship, thermal properties, crystallinity, and crystal structure of bicomponent nonwovens and nonwoven composites were analyzed and compared. Our findings showed that the melting temperature and degree of crystallinity of sheath polymers increased when they became matrix. This was attributed to the annealing and constrained fiber effects brought by composite processing. A significant increase in the crystallite sizes for matrix phase achieved after composite fabrication also supports our conclusion. We also observed melting temperature rises for reinforcement fibers. This was also explained to be a result of thermal treatment under pressure which could lead to a better distribution of the crystallite sizes and improved perfections of crystallites.

Mechanical performance of nonwoven composites were also reported and compared with a GMT composite which has a polypropylene matrix and 40% glass fiber content. In general,
Nonwoven composites showed lower specific modulus but higher specific stress than GMT composite. On the other hand they provided superior strain at break (68-152%) and impact strength (48-147 kJ/m2) values compared to GMT composite (4% and 10 kJ/m2, respectively).

Nonwoven composites with different thicknesses achieved with cross-layering 2, 4, and 8 plies of nonwovens having 250 g/m2 were also compared in terms of their mechanical (tensile) performance. Our findings showed that tensile properties are not affected by the number of plies in the composite. Moreover, morphological analysis of the intersection of two layers revealed an intact composite structure without any separation or matrix-free region at the interface.

Overall, we showed that thermoplastic nonwoven composites with random fiber distribution can be produced by using only bicomponent nonwovens as a precursor. The resultant composites have isotropic structure with uniform distribution of matrix and high fiber volume fraction at the same level of fiber orientation. From an industrial point of view this technique permits the transformation of an inexpensive preform into an engineered thermoplastic composite in one step with excellent wetting characteristics of matrix polymer.

The influence of polymer type, composition and interface on the structural and mechanical properties of bicomponent fibers were also studied for PET/PE, PA6/PE, PA6/PP, and PP/PE (core/sheath) bicomponent nonwoven fibers. The structural properties of bicomponent nonwoven fibers were shown to depend on the type and composition of each component. In PET/PE, PA6/PE, and PA6/PP, the crystallinity and melting temperature of the core component increased with increasing the volume content of the sheath polymer as compared to those of PET and PA6 single fibers. It was attributed to the difference in thermal and stress histories experienced by core polymer during homocomponent versus bicomponent fiber spinning. It was also postulated that the core polymer having higher consolidation temperature and elongational viscosity may experience improved consolidation stress during bicomponent spinning. Unlike the core polymer, the fiber structure of the sheath polymer
suppressed in all bicomponent fibers. The degree of the suppression also increased with increasing the core volume concentration. This was related to the stress relaxation occurring in the sheath polymer during bicomponent spinning in which the core component solidified earlier and bore the great portion of the spinline stress.

In order to characterize and define polymer interfaces, the compatibility of polymer pairs used in bicomponent fibers was estimated with Flory-Huggins interaction parameter. The interfacial adhesion for these polymer pairs was also characterized using ADCB test method. Our findings indicate that PP/PE is the most compatible polymer pair ($\chi=0.01$) with the highest interfacial adhesion value ($G_c=51 \text{ J/m}^2$) followed by PA6/PE ($\chi=0.26$, $G_c=4 \text{ J/m}^2$), PA6/PP ($\chi=0.52$, $G_c=2.1 \text{ J/m}^2$), and PET/PE ($\chi=1.11$). After measuring the tensile properties of bicomponent fibers at different composition ratios, it appeared that the tensile strength of the bicomponent fiber deviates from the theoretically estimated value in accordance with the degree of the compatibility and interfacial adhesion between its constituents. Thus, PET/PE being the most incompatible polymer pair in this study showed the highest negative deviation from the theoretically predicted maximum stress value. It was then followed by PA6/PP and PA6/PE. As opposed to other polymer combinations, we observed an improvement on the tensile strength value of PP/PE as compared to theoretical value. This was not only attributed to the high degree of compatibility and interfacial adhesion between PP and PE but also related to possible interfacial interaction between these two polymers during bicomponent spinning. Overall, these results emphasize the importance of considering the interface between two components in bicomponent fiber when predicting the mechanical properties of these fibers. One of the other important outputs of this study is that it provides a reference guide and path for those who want to predict the interfacial behavior of a spinnable polymer pairings in bicomponent fiber structure. This can be achieved practically by calculating the Flory-Huggins interaction parameter for the polymer pairings and comparing with results presented in this study.

The interface issue also arises for PET/PE, PA6/PP, and PA6/PE nonwoven based thermoplastic in which debonding at the interfacial region were observed. Since the
compatibility of these polymers has profound effect on the tensile properties of bicomponent fibers, we anticipated that this problem can also negatively affect the mechanical performance of composites made from these materials. Therefore, we focused our effort to address the interface issue in the nonwoven composites using compatibilization approach that is typically used for polymer blends. Due to the time frame of this study, we applied this approach for PE matrix composites (PET/PE and PA6/PE).

In PA6/PE nonwoven based thermoplastic composites we aimed to improve the interface. For this purpose, we used SEBS and SEBS-g-MA with 1 wt% (SEBS-g-MA1) and 2 wt% (SEBS-g-MA2) MA contents as compatibilizers to promote adhesion between PA6 and PE components. A reliable and widely used test technique (ADCB) was initially employed to measure the interfacial adhesion in PA6/PE laminates in the presence of compatibilizers. The compatibilizers were incorporated into the PE phase to improve the poor interfacial adhesion between PA6 and PE (4 J/m²). We showed that interfacial adhesion in these polymer pair could be greatly improved with the addition of all three compatibilizers. Among these compatibilizers, SEBS-g-MA2 (121 J/m²) was the best performing compatibilizers. We also determined the effect functional group content and concentration of the compatibilizer on the interfacial adhesion in PA6/PE laminates and found that these factors increased the level of compatibilization achieved. Similarly, raising the lamination temperature and/or time greatly improved the interfacial fracture energy of the compatibilized PA6/PE laminates.

The same compatibilizers were also used in the production of core-sheath type of PA6/PE bicomponent fibers and nonwovens. After analyzing the tensile properties of bicomponent fibers, we did not observe any improvement on tensile responses of fibers. This suggests that sufficient level of in-situ compatibilization during fiber production was not provided and therefore enhanced adhesion between sheath and core components was not achieved. The inadequacy of compatibilization was attributed to the short contact time in which molten sheath and core polymers spent together during fiber spinning.
Analysis of the effect of processing temperature on the interfacial adhesion also revealed that there is a temperature window available for the reactive compatibilization of PA6/PE during composite fabrication stage. Therefore, we modified composite fabrication protocol and used closed molding to process bicomponent nonwovens (2nd generation nonwoven composite making process) which were already loaded with compatibilizers, at higher temperature and longer time. After successfully producing nonwoven composites, the tensile properties of these composites were measured. Our results indicate that tensile strength, tensile modulus at 5% strain and tensile energy to break values were improved for the composites containing compatibilizers. The best performing compatibilizer was found to be SEBS-g-MA2. The optimum compatibilizer concentration in terms of tensile properties was the lowest compatibilizer loading of 2 wt%. The characterization of fractured surfaces showed the evidence of adhesion of matrix polymer to reinforcement fiber. As a result, cohesive failure was observed for the composites including compatibilizers. These results suggest that reactive compatibilization was achieved during composite fabrication stage and improved the adhesion between two polymers resulting in a higher load transfer and better mechanical properties.

We also focused our effort on the interface enhancement in PET/PE nonwoven based thermoplastic composite to improve the mechanical performance of this composite. For this purpose, we used E-EA-GMA5, E-EA-GMA9, and SEBS-g-MA2 as compatibilizers. These compatibilizers were also added into the sheath component (PE) of the bicomponent fibers at 2, 5, and 10 wt% concentration levels. The bicomponent fibers and nonwovens including compatibilizers were then produced. In order to evaluate the efficiency of the reactive compatibilization possibly occurred during the bicomponent fiber production, the tensile properties of the fibers were characterized. We found that the bicomponent fibers including GMA bearing additives showed some improvement in the tensile responses at low strain regions. However, such improvement was not observed in the overall tensile properties. To clarify the reason for this behavior we traced the compatibilizer in the fiber by obtaining the chemical imaging of the fiber cross-sections. Our findings clearly show that the
compatibilizer was well distributed in the sheath component instead of clustering in the interface region. This was attributed to the short residence time experienced in the bicomponent fiber spinning which was not sufficient for the migration of the compatibilizer to the interface. Thus, only compatibilizers present in the proximity of the interface might undergo reaction with PET and therefore, compatibilization efficiency became too low to enhance the overall tensile properties of the bicomponent fiber. A possible solution for improving compatibilization efficiency in the bicomponent fiber spinning stage would be tailoring the molecular architecture of the compatibilizer. We believe that lowering the molecular weight of the compatibilizer may help the diffusion of more compatibilizer through the interface region.

We performed the reactive compatibilization in the composite fabrication stage using longer residence time and different temperatures. After producing nonwoven composites, tensile properties of these composites were measured. Our results indicate that tensile properties were improved for the composites containing E-EA-GMA9 and SEBS-g-MA2. The best performing compatibilizer was found to be SEBS-g-MA2. The optimum concentration for thiscompatibilizer in terms of tensile properties was the lowest loading level of 2wt%. The characterization of fractured surfaces showed the evidence of adhesion of matrix polymer to reinforcement fiber. As a result, cohesive failure was observed for the composites including compatibilizers. These results suggest that reactive compatibilization was achieved during composite fabrication stage and improved the adhesion between PET fiber and PE matrix resulting in a higher load transfer and better mechanical properties.

### 7.2 Recommendations for Future Studies

Recommendations for the future studies would be:

(i) Addressing the compatibilization issue in bicomponent fiber spinning stage with molecularly tailored compatibilizers that can provide higher efficiency at shorter time;

(ii) Investigating the compatibilization effectiveness of reactive compatibilizers in tricomponent fiber configuration;
(iii) Compatibilizing PP matrix nonwoven composites such as PET/PP and PA6/PP with reactive compatibilizers to obtain better mechanical properties;
(iv) Developing an interface characterization technique to analyze bicomponent fiber interfaces.