

CHAPTER II

LITERATURE REVIEW

2.1 Poly (trimethylene terephthalate)

Poly(trimethylene terephthalate) (PTT, or 3GT) (Figure 2.1) is an aromatic polyester that prepared by the melt polycondensation of 1,3-propanediol (PDO) with terephthalic acid (TPA) or dimethyl terephthalate (DMT). It was one of three polyesters that first synthesized by Whinfield and Dickson in 1941 (Rex *et al.*, 1949). Two of these are poly(ethylene terephthalate) (PET or 2GT) and poly(butylene terephthalate) (PBT or 4GT) and more readily available than PTT due to PDO, the main starting material for PTT production, was very expensive and available only in small-scale production.

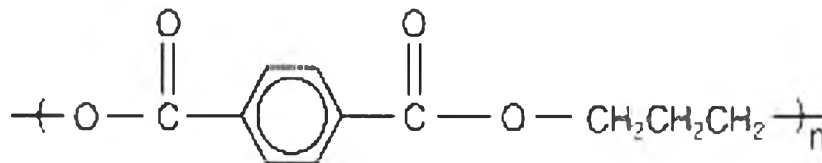


Figure 2.1 Structure of poly(trimethylene terephthalate).

In the late 1980s, PTT's value as a commercial polymer has improved with the development of more economical and efficient methods to produce 1,3-propanediol (PDO) via continuous hydroformylation of ethylene oxide (Figure 2.2) by Shell Chemical Co. In 1998, Shell began selling PTT and completed building a new PDO plant. Then DuPont announced to build a PTT plant by first using PDO acquired from Degussa, and later using PDO from bioengineering route which lead to PTT becomes commercially available. PTT from Shell is trademarked as Corterra polymer and DuPont's trademark is Sorona 3GT. Polymers are now commercially available for use in carpet fiber, textile fiber, monofilament, film, non-woven fabric, and engineering thermoplastic applications (Chuah, 2001).

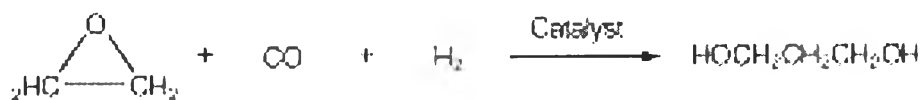


Figure 2.2 Synthesis of PDO.

PTT is a semicrystalline polymer with a glass-transition temperature (T_g) of 45°C and a melting temperature (T_m) of 228°C (measured by a differential scanning calorimeter or DSC). PTT has many of the same advantages as PBT and PET. When compared PTT with PBT, PTT shows better tensile strengths, flexural strengths, and stiffness. They also have excellent flow, surface finish and excellent resistance to a broad range of chemicals at room temperature, including aliphatic hydrocarbons, gasoline, carbon tetrachloride, perchloroethylene, oils, fats, alcohols, glycols, esters, ethers and dilute acids and bases. Because of its chemical structure, PTT may have more uniform shrinkage and better dimensional stability in some applications than competing semicrystalline materials (especially PBT). PTT has limitation in impact resistant which can be improved by using impact modifiers, reinforcing fibers or polymer blending.

2.2 Polyethylene (PE)

A simplest form of polyethylene molecule consists of a long backbone of an even number of covalently linked carbon atoms with a pair of hydrogen atoms attached to each carbon and methyl groups terminate at chain ends. This structure is shown in Figure 2.3

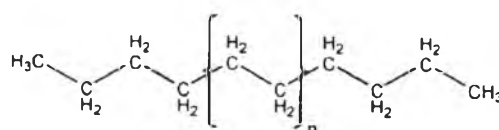


Figure 2.3 Chemical structure of polyethylene.

There are many type of polyethylene which variations arise from branches that modify the nature of the material. The most commercially important of these polymers are low density polyethylene (LDPE), high density polyethylene (HDPE), and more recently, linear low-density polyethylene (LLDPE).

2.2.1 Linear Low Density Polyethylene (LLDPE)

Linear low density polyethylene (LLDPE) resins consist of molecules with linear polyethylene backbones to which are attached short alkyl groups at random intervals. These materials are reproduced by the copolymerization of ethylene with 1-alkenes. The general structure of linear low density polyethylene resins is shown schematically in Fig 2.4. The branches most commonly encountered are ethyl, butyl, or hexyl groups but can be a variety of other alkyl groups, both linear and branched. A typical average separation of branches along the main chain is 25–100 carbon atoms. Linear low density polyethylene resins may also contain small levels of longchain branching, but there is not the same degree of branching complexity as is found in low density polyethylene. Chemically these resins can be thought of as a compromise between linear polyethylene and low density polyethylene, hence the name. The branches hinder crystallization to some extent, reducing density relative to high density polyethylene. The result is a density range of approximately 0.90–0.94 g/cm³ (Peacock, 2000).

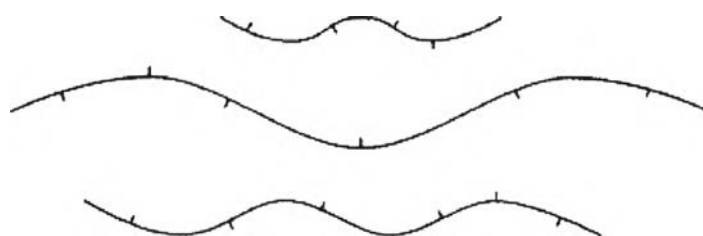


Figure 2.4 Schematic representations of linear low density polyethylene.

2.2.2 High Density Polyethylene (HDPE)

High density polyethylene (HDPE) can be produced by the polymerization of ethylene with supported metal–oxide catalysts or coordination catalysts. The first class of metal–oxide catalyst (Phillips type) consisted of chromium oxide (CrO_3) supported on alumina (Al_2O_3) or silica–alumina base. Polymerization is carried out at 100 atm and 60 to 200°C in hydrocarbon solvents in which the catalysts are insoluble using fixedbed, moving bed, fluidized-bed, or slurry processes. The coordination polymerization of ethylene uses Ziegler-type catalysts. These are complexes of aluminum trialkyls and titanium or other transition-metal halides (e.g., TiCl_4). Coordination polymerization of ethylene requires lower temperatures and pressures than those that supported metal–oxide catalysts, typically 60 to 70°C and 1 to 10 atm (Peacock, 2000).

High density polyethylene (HDPE) is the closest in structure to pure polyethylene. The general form of high density polyethylene is shown in Figure 2.5. A high degree of crystallinity can be achieved because of an extremely low level of defects to hinder organization which result resins have a high density (relative to other types of polyethylene). Some resins of this type are copolymerized with a very small concentration of 1-alkenes in order to reduce the crystallinity level slightly. High density polyethylene resins typically have densities about 0.94–0.97 g/cm^3 . Due to its very low level of branching, high density polyethylene is sometimes referred to as linear polyethylene (Ebewele, 1996).

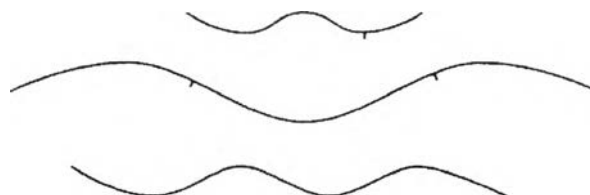


Figure 2.5 Schematic representations of high density polyethylene.

2.3 Polymer Blends

Polymer blending is mixing of more than one polymer which is a one way for development of new polymeric materials. Blending of polymer will combine the excellent properties of more than one existing polymer which is usually cheaper and less time-consuming than the development of new monomers and/or new polymerization routes. Polymer blending usually takes place in processing machines, such as twin-screw extruders, two-roll mill, and Banbury internal mixer. Moreover, the advantage of polymer blending is the wide range material properties obtained by changing the blend composition. For the drawback is the difficult recyclability of these materials in comparison with pure resins. However the market for polymer blend based materials has increased continuously. The major markets are automotive, electrical and electronic, packaging, building and household.

There is both homogeneous and heterogeneous polymer blending. For homogeneous blend, each blend component loses their unique properties and the blend properties are about the average of both blend components. For heterogeneous blends, the properties of each blend component still present. The poor properties of one component can be improved by the strength of the other blend component. There are several of morphologies of heterogeneous blends. The most frequently founded are i) a dispersion of one polymer in the matrix of another polymer, ii) a co-continuous two-phase morphology. The type morphology that will be obtained depends on the characteristic of the blend component.

However main problem of polymer blending are miscibility and compatibility. Two important characteristic when selecting polymer for blending have to be considered are thermodynamically miscible and also mechanical compatibility (Koning *et al.*, 1998).

2.4 Thermodynamic Miscibility

To study miscibility of polymer blending from two or more different types of polymer is based on knowledge of polymer solubility. Investigation of mixing

ability between two polymers is determined by the Gibbs free energy which can be calculated from equation following:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$

Where ΔG_{mix} refer to the changing in Gibbs free energy of mixing, ΔH_{mix} is the changing in enthalpy of mixing, T is absolute temperature, and ΔS_{mix} is the changing in entropy of mixing

However, if two high molecular weight polymers are blended entropy (ΔS_{mix}) must be insignificant, and the free energy of mixing can only be negative if the heat of mixing (ΔH_{mix}) is negative. In other words, the mixing must be exothermic reaction, which must have some interactions between the blend components. These interactions may range from strongly ionic to weak and nonbonding interactions, such as hydrogen bonding, ion-dipole, dipole-dipole and donor-acceptor interactions. Usually, only Van der Waals interactions occur interactions occur, which explains why polymer blends are not miscible (Koning *et al.*, 1998).

2.5 Types of Blend

Basically, there are three different types of blends can be distinguished.

2.5.1 Completely Miscible Blends

This kind of blend has specific interaction and also has $\Delta H_{\text{mix}} < 0$. A well known example of this miscible blend is PS/PPO blend that combines the heat resistance, the inflammability and the toughness of PPO with the good processability and the low cost of PS. This type of blend has only one glass transition temperature (T_g), which is between the T_g of both blend components in a close relation to the blend components.

2.5.2 Partially Miscible Blends

Part of one blend component is dissolved in the other. This type of blend, which shows a fine phase morphology and satisfactory properties, is referred to as compatible. Both blend phases are homogeneous, and have their own T_g . Both T_g s are shifted from the values for the pure blend components. An example is the PC/ABS blends, which combine the heat resistance and toughness of PC with the

low temperature impact, processability, stress cracking resistance and low cost of ABS. In these blends, PC and the SAN phase of ABS partially dissolve in one another.

5.3 Fully immiscible

They have coarse phase morphology, the interface is sharp, and the adhesion between both blends phases is poor. T_g of the pure blend components can be seen. Fully immiscible blends are poor properties in all directions, so that these blends are useless without being compatibilized. Well known examples of this fully immiscible blend are PA/ABS, PA/EPDM and PA/PPO (Koning *et al.*, 1998).

2.6 **Compatibilization**

From thermodynamics, the blends of immiscible polymers from simple mixing show a separation tendency, and lead to a coarse structure and low interfacial adhesion which result in poor mechanical properties of the final material. To get miscible blends, it is necessary to ensure proper phase dispersion by decreasing interfacial tension to suppress phase separation and improve adhesion which results in good mechanical properties of the final material. This can be achieved by modification of the interface by the formation of bonds (physical or chemical) between the polymers which is known as compatibilization. There are two methods are used for compatibilization of immiscible polymers:

1. By addition of: (i) a small quantity of a third component that is miscible with both phases (cosolvent, e.g., Phenoxy); (ii) a small quantity of copolymer whose one part is miscible with one phase and another with another phase (e.g., 0.5 to 2 wt% of tapered block copolymer); (iii) a large amount of a core-shell, multi-purpose compatibilizer-cum-impact modifier.

2. By reactive compatibilization, which uses such strategies as: (i) trans-reactions; (ii) reactive formation of graft, block or lightly crosslinked copolymer; (iii) formation of ionically bonded structures; and (iv) mechano-chemical blending that may lead to chains' breakage and recombination, thus generation of copolymers (even at liquid nitrogen temperature), etc (Utracki, 2002).

2.7 Addition of Reactive Polymers

The addition of a reactive polymer, miscible with one blend component and reactive towards functional groups attached to the second blend component results in the “in-situ” formation of block or grafted copolymers. Usually reactive polymers can be generated by free radical copolymerization or by melt grafting of reactive groups on to chemically inert polymer chains. Furthermore, reactive polymers only generate block or grafted copolymers at the site where they are needed and use a shorter processing time than the adding of premade block or graft copolymer due to relatively higher diffusion rate of shorter chains moving to the interfaces (Koning *et al.*, 1998).

Maleated polymers are among the widest known family of functionalized polymers used as compatibilizer and adhesion promoters. The reactive monomer is generally maleic anhydride. They can be prepared directly by polymerization or by modification during compounding (this process is called reactive extrusion). Anhydride groups can react with amine groups, epoxy groups and eventually alcohol groups. Maleated resins are also used for increasing adhesion of plastics to metal, improving cohesion between a polymer and fillers (e.g. ash, wood, mica...), improving adhesion between polymer and glass fiber in thermoplastics and composites, and impact modification.

Fusabond is one of commercially maleated polymer. It is a product line of polyolefins, grafted with Maleic Anhydride. Fusabond draws its functionality as an adhesion promoter or compatibilizer. It consists of 2 parts (see Figure 2.6); one is compatible or miscible with the nonreactive component of the mixture, and the other one (MAH group) will interact with the reactive part of the mixture.

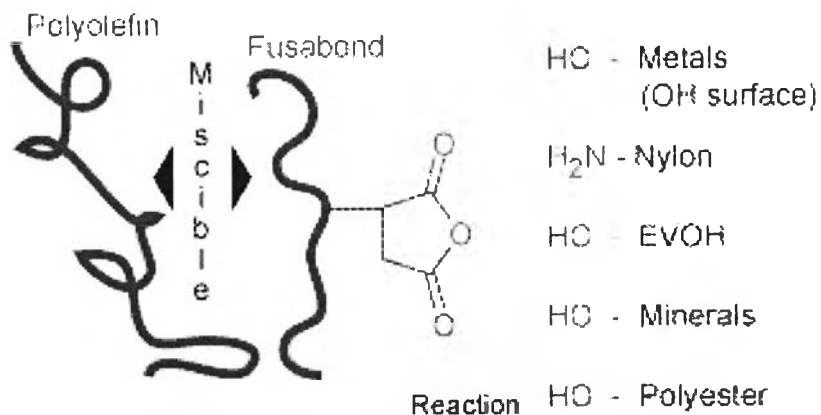


Figure 2.6 Role of Fusabond as a compatibilizer.

2.8 Compatibilization using Ionomers

Ionomers are polymeric material which consist of hydrocarbon backbone and pendant acid functionality (small concentration) such as carboxylic or sulfuric acid, neutralized (completely or partially) by either monovalent (e.g. Na⁺, K⁺) or divalent (e.g. Zn²⁺) metal cations. Sulphonic acid or carboxylic acid groups are introduced into the polymer chains by copolymerization or chemical modification of existing polymers. Whatever the cation, the ionic groups tend to associate into multiplets, which at sufficiently high concentrations can associate into clusters. Multiplets and clusters act as physical crosslinks between polymer chains. At elevated temperatures, these ionic crosslinks become reversible (see Figure 7) (Koning *et al.*, 1998).

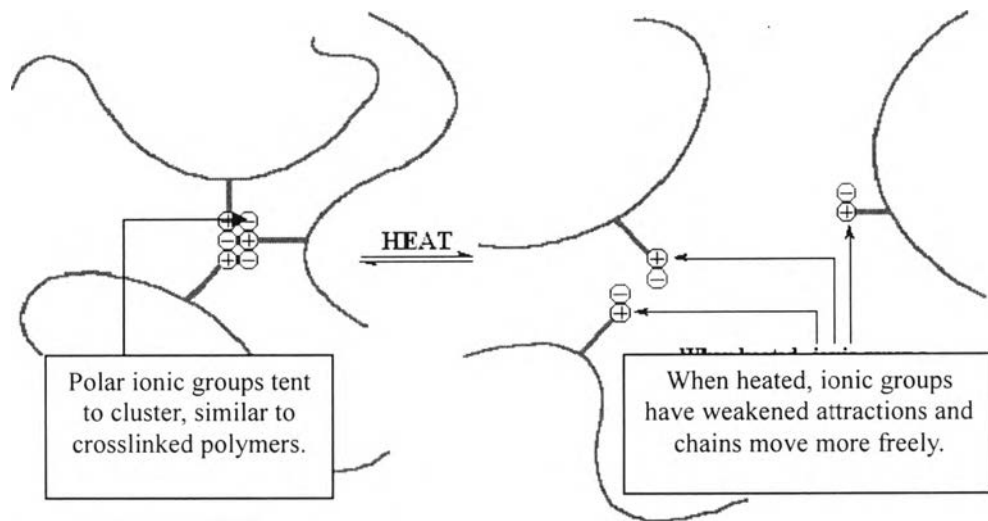


Figure 2.7 Illustration of ionomer.

Random copolymers of ethylene and methacrylic acid where some of the acid groups (15-80%) are neutralized to form metal salts are a commercially important class of ionomers. The morphology of ionomers based on poly(ethylene-co-methacrylic acid) (EMAA) (Figure 2.8) consists of three regions: amorphous phases, crystalline phases, and ionic clusters. The ionic clusters act as thermoreversible crosslinks and improve the toughness, melt viscosity, clarity, and adhesion properties of the copolymer. The Surlyn is a commercially available ethylene-methacrylic acid based ionomer which sometime is used as an impact modifier.

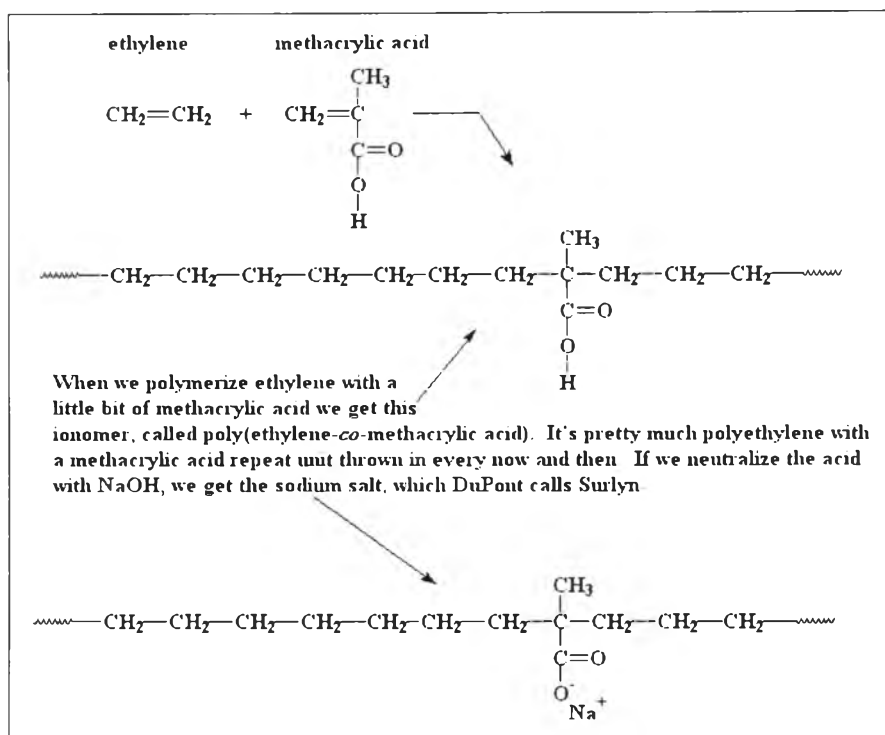


Figure 2.8 Illustration of EMAA ionomer.

Now, if two different ionomers, based on two different and immiscible polymers, are intensively mixed in the melt, the ionic domains may reorganize. The newly formed clusters may contain ionic species of both immiscible polymers. As a result, branched copolymers in which the link between both polymer chains is an ionic bond, are generated at the interface, and a stable compatibilized multiphase blend is generated. However, if one of the blend components contains highly polar groups, such as PA in a PE/PA blend, then the addition of a PE based ionomer should be sufficient for obtaining a compatible blend since the interactions between the ionic groups of PE and the polar functional groups of the polyamide are strong enough to generate a kind of a grafted copolymer at the interface. In blends of PTT/PE, PTT has polarity while PE has non-polarity, the addition of EMAA ionomer would be optimum.

2.9 Blends based on PTT with Compatibilizer

Aravind *et al.* (2004) studied the morphology of immiscible and highly incompatible blends of Sorona®, poly(trimethylene terephthalate) (PTT) and ethylene propylene diene rubber (EPDM) blends by using EPM-g-MA as compatibilizer. The blends were prepared in an internal mixer. Sorona was melted first at a temperature of 235°C and then EPDM was added after 2 min. These incompatible blends are characterized by a two-phase morphology, narrow interphase, and poor physical and chemical interactions across the phase boundaries. Therefore, a reactive route was employed to compatibilize these blends by the addition of maleic anhydride grafted ethylene propylene rubber (EPM-g-MA). The morphology of the blends indicated that the EPDM phase was preferentially dispersed as domains in the continuous Sorona matrix up to 30% of its concentration. A co-continuous morphology was observed above 30 wt% of EPDM content followed by a phase inversion beyond 60 wt% of EPDM. The influence of EPM-g-MA on the phase morphology of blends was found that the addition of EPM-g-MA reduces the domain size of the dispersed phase followed by a leveling off at higher concentrations of the compatibilizer. This is an indication of interfacial saturation.

Compatibilizing effects on the phase morphology and thermal properties of polymer blends based on PTT and m-LLDPE by using a terpolymer based on glycidyl methacrylate (GMA) as compatibilizer were studied by Jafari *et al.* (2005). DMA results showed two distinct peaks in all blends. DSC thermograms of the blends also showed two separate melt crystallization peaks and two distinct melting peaks meaning that two polymers crystallize separately to form their own crystallites. Melt crystallization degree of both phases in all blends was lower than the neat components, except for PTT-rich phase, which slightly increases. The adding of the terpolymer to the system is found that it can reduce the droplet size of the dispersed phase, increase phase adhesion and also increase the crystallinity of PTT in the system with PTT as the matrix. The influence of the compatibilizer is ascribed to the chemical interaction of PTT functional end groups with GMA functionalities. The efficiency of the terpolymer as a compatibilizer at 5 wt% content decreases because of the interface saturation and formation of micelles in the bulk phases.

Xue *et al.* (2007) studied miscibility and compatibilization of poly(trimethylene terephthalate)/acrylonitrile–butadiene–styrene blends by using epoxy or styrene–butadiene–maleic anhydride copolymer (SBM) as a reactive compatibilizer. The melt blending of the dried PTT and ABS with different compositions was carried out by using a 35-mm twin-screw co-rotating extruder, the miscibility of PTT/ABS with and without compatibilizer blends were investigated by using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), capillary rheometer and scanning electron microscopy (SEM). They found that the rheological behavior of the epoxy compatibilized PTT/ABS blends showed an epoxy content-dependence. In contrast, when the SBM content was increased from 1 wt% to 5 wt%, the shear viscosities of the PTT/ABS blends increased and exhibited much clearer shear thinning behavior at higher shear rates. The SEM micrographs of the epoxy or SBM compatibilized PTT/ABS blends showed a finer morphology and better adhesion between the phases.

In the same year, Xue *et al.* (2007) also studied crystallization behavior of poly(trimethylene terephthalate)/polypropylene blends by using polypropylene-graft-maleic anhydride (PP-g-MAH) as compatibilizer. In this publication demonstrated that PTT and PP crystallization rates were accelerated by the presence of each other. Furthermore the addition of PP-g-MAH in PTT/PP blend was a larger effect on crystallization temperature (T_c) of PTT and PP. The crystallization of PTT and PP shifted significantly to lower temperature. Beside the shift of PTT's T_c was larger than that of the PP, suggesting that addition of PP-g-MAH had a larger effect on PTT's crystallization than on PP due to chemical reaction between maleic anhydride ring and PTT.

In 2009, PTT/PP blends by using maleic anhydride grafted polypropylene as compatibilizer was studied non-isothermal crystallization kinetic and compatibility by Wang *et al.* (2009). The research indicated that the addition PP-g-MAH in blends accelerated the crystallization of PTT. Whereas the crystallization rate of PP component is retarded by introduction of PP-g-MAH. Moreover the SEM results suggested that the introduction of PP-g-MAH greatly improved the compatibility between PTT and PP, and decreased the size of dispersed particles.

2.10 Blend based on PE with Compatibilizer

PA6/UHMWP blend is one of the example using HDPE-g-MAH as a compatibilizer (Yao *et al.*, 2000). HDPE-g-MAH showed abilities to be a good compatibilizer for PA6/UHMWPE blending system. The morphology of blends was significantly improved. The average size of the UHMWP particles was reduced from 30-35 to 2-4 micron. Moreover mechanical properties such as tensile strength, Young's modulus, elongation at break, flexural strength, flexural modulus and Izod impact strength were also dramatically increase. This behavior could be attributed to chemical reactions between the anhydride groups of HDPE-g-MAH and the terminal amino groups of PA6 in PA6/UHMWPE/HDPE-g-MAH blends. Thermal analysis was performed to confirm that the above chemical reactions took place during the blending process.

Joshi *et al.* (1991) studied PBT/HDPE alloys by using ionomer as compatibilizer. Alloys of PBT and HDPE with varying amounts (2-8%) of ionomer were prepared by melt blending. The ultimate mechanical properties were improved significantly on the addition of the ionomer due to an increase in interfacial adhesion between PBT and HDPE. DSC results showed that the presence of ionomer facilitated the crystallization of PBT in the alloy. DMA studies show that more of PBT (amorphous) was going into the HDPE-rich phase in the presence of ionomer. The morphology of the alloy showed improved dispersion of HDPE domains in PBT matrix with increasing ionomer content and changing in the type of superstructure on adding the ionomer. Rheological measurements showed that shear viscosity increased for the blend with the addition of the compatibilizer. An explanation for this behavior is presented on the basis of the theory of emulsions (Joshi *et al.*, 1992). It had been shown that an alloy of PBT and HDPE with improved mechanical properties and homogeneous morphology can be made with use of ionomer as a compatibilizer. Such alloys are cost effective and can find use in several engineering applications.

Effect of the compatibilization of linear low-density polyethylene-g-acrylic acid on the morphology and mechanical properties of poly(butylenes terephthalate)/linear low-density polyethylene blends was studied by Yang *et al.*

(2002). LLDPE grafted with acrylic acid (LLDPE-g-AA) by radiation was adopted in place of plain LLDPE. The impact strengths and elongations at break of the PBT/LLDPE-g-AA blends increased when compared with the PBT/LLDPE blends at the same compositions which indicate that the toughness and extensibility of PBT/LLDPE-g-AA were improved. However, there was not much difference in their tensile (or flexural) strengths and moduli. These might be caused by the limited compatibility effect and low strength and modulus of LLDPE. SEM photographs showed that the domains of PBT/LLDPE-g-AA were much smaller and their dispersions were more homogeneous than the domains and dispersions of the PBT/LLDPE blends

Lahor *et al.* (2004) studied blends of low-density polyethylene with nylon compatibilized with a sodium-neutralized carboxylate ionomer. They found that an ethylene-methacrylic acid copolymer partially neutralized with sodium (Na-EMAA) was successfully used to compatibilize Nylon 6 (PA6) and low-density polyethylene (LDPE) blends. The compatibility of PA6/LDPE blends was improved by addition of small amounts (0.5 phr) of Na-EMAA because of reduction in disperse phase sizes. TGA results showed an improvement in thermal stability when Na-EMAA was added to either LDPE or PA6. DSC results of PA6/Na-EMAA binary blends showed that with increasing Na-EMAA content, the crystallization temperature of PA6 phase decreased indicating that Na-EMAA retarded crystallization of PA6.

Sinthavathavorn *et al.* (2008) studied blends of PA6 with LDPE compatibilized with sodium-, zinc-, and lithium-neutralized ethylene-methacrylic acid ionomers were investigated at 11, 33, and 55 wt% neutralization of the ionomers. Blends of PA6 with LDPE without a compatibilizer had poor properties characteristic of incompatible polymer blends. After the addition of a compatibilizer, tensile properties improved, the modulus drop associated with melting point increased to higher temperature, and the dispersed phase size decreased. The improvement of the mechanical properties and thermomechanical properties was less with the acid copolymer than with the ionomers. Overall, ionomers neutralized with sodium, zinc, or lithium showed little difference in their compatibilization efficiency.