



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Blends of PA 6 and LDPE

Polyamide was first synthesized by Carothers and his colleagues in 1935. The presence of amide (-CONH-) group can increase resistance to swelling and dissolution in hydrocarbons, increase interchain attraction and hence stiffness and heat deformation resistance, reduce electrical insulation resistance, particularly at high frequencies and increase water absorption. Aliphatic polyamide such as polyamide 46, 66, 6, and 10 are linear polymers and thus thermoplastics. They contain polar -CONH- groups spaced out at regular intervals so that the polymers crystallize with a high intermolecular attraction. These polymer chains also have aliphatic chain segments which give a measure of flexibility in the amorphous region. Thus the combination of high interchain attraction in the crystalline zones and flexibility in the amorphous zones leads to polymers which are tough above their apparent glass transition temperatures. However, polyamide is expensive, has poor impact strength, poor dimension stability and poor barrier properties to moisture. Blending polyamide with polyolefin is another way to decrease cost due to polyolefin has high impact strength, easy to process and good barrier properties to moisture. However many researchers [Macknight *et al.*(1985), Fairley *et al.*(1987), and Silva *et al.* (1996)] reported that blended PA6/LDPE is immiscible blend due to poor interfacial adhesion. So a third component, copolymer or compatibilizer, is added to the mixture to act as a compatibilizing agent. These mixtures are generally aimed at improving the barrier properties, impact strength (toughness), or dimensional stability of PA6. However, small amounts of PA6 are also added to polyethylene in order to reduce the solvent and gas permeability of the latter.

2.2 Compatibilizer

Compatibilizer is a copolymer which consists of both polar part and non polar part in the chain molecules. It is used to improve the compatibility of the

immiscible blends. There are four types of compatibilizer which are used in blended PA6/LDPE

1. Maleic anhydride copolymer such as ethylene-g-maleic anhydride Valenza *et al.* (1997), Jurkowski *et al.* (1998)
2. Acrylic acid copolymer such as ethylene methacrylic acid copolymer Macknight *et al.* (1985) Fairley *et al.* (1987), Kudva *et al.* (1999)
3. Acrylate copolymer such as ethylene-g-butyl acrylate Willis *et al.* (1993)
4. Ionomer such as partial neutralized ethylene methacrylic acid by metal ion (i.e. Na^+ , Zn^{2+} or Li^+) Willis *et al.* (1988), Armat *et al.* (1993), Yeh *et al.* (1995), Sheng *et al.* (2000), Leewajankul *et al.* (2003) Lahor *et al.* (2004)

The suitable type of compatibilizer is ionomer, partial neutralized ethylene methacrylic acid by metal ion, because metal ion in ionomer can react with carboxylic group in polyamide with ionic interaction which is shown in Figure 2.1.

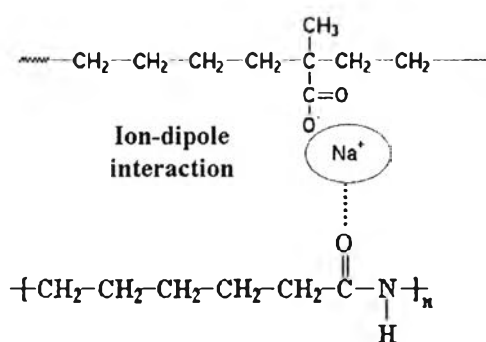


Figure 2.1 Ionic interaction between PA6 and ionomer [Degee *et al.* (1997)].

2.3 Ionic Polymer

Ionic sites are introduced into polymers through chemical modification or copolymerization. Ionic polymers derived from synthetic organic polymers and containing up to 10 to 15 mol % ionic content are called *ionomers* [Tant *et al.* (1997)]. Those with higher ionic content are called *polyelectrolytes*. Polyelectrolytes are soluble in water but insoluble in common organic solvents. Typical applications

for ionomers include ion-exchange resins, membranes for liquid and facilitated gas separations.

The ionic sites are typically pendant carboxylic or sulfonic acid groups that are partially or completely neutralized to form the polymeric salt. Counterions may be sodium, zinc, lithium or a halide. Typical nonionic polymer backbones include polyethylene, polystyrene. Small aggregates consisting of only ionic material are termed multiplets, while larger aggregates that also include nonionic material are called clusters. Multiplets, consisting of only a few ions or ion pairs, act as moderately strong, temporary, ionic crosslinks. The larger clusters also act as mechanical reinforcement.

The introduction of ionic groups can have significant effects on the properties of polymers. For example, ionic sites can increase T_g , modulus, and melt viscosity. The extent of property modification depends upon the dielectric constant of the backbone, the position and type of ionic group, the type of counterion, ionic concentration, and the degree of neutralization. The concentration of ionic groups and the strength of interaction between the anion and cation determine the increase in T_g with a relationship given as

$$T_g = \frac{cq}{a} \quad (1)$$

where c is the concentration of ionic repeat units in the backbone, q is the charge of the counterion, and a is the distance of closest approach between the centers of charge of anion and cation. Generally, T_g is observed to increase 2° to 10°C per mole% ionic repeat units.

2.4 Theory of Polymer Blends

2.4.1 Thermodynamic of Polymer Blends

There are two type of blends; miscible blend and immiscible blend. From the Flory-Huggins theory

$$\Delta G_{mix}/V = RT \left[\frac{\rho_A \phi_A}{M_A} \ln \phi_A + \frac{\rho_B \phi_B}{M_B} \ln \phi_B \right] + \chi \phi_A \phi_B \quad (2)$$

where χ is polymer-polymer interaction energy

When the polymer-polymer interaction energy is less than a critical value, χ_{crit} , dictated by the molecular weight of the components, the blend will be thermodynamically miscible. From the Figure 2.2, the details of the interaction energy determine the specifics of the phase its diagram.

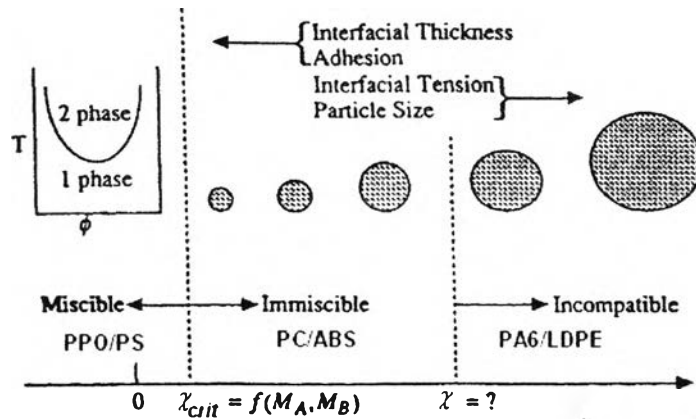


Figure 2.2 Illustration of the role of polymer-polymer interaction energy on blend structure, hence, properties [Paul *et al.* (1999)]

Another type of blend is immiscible blend such as blended PA6/LDPE. When the interaction energy exceeds a small (positive), B_{crit} , a two-phase mixture is formed. If the value of B is not too much greater than B_{crit} , the interfacial tension is small and it is possible to achieve a fine dispersion. Furthermore, the interfacial thickness will be large and the interface will be strong.

2.4.2 Hydrogen Bonding

The immiscible blend can be compatible blend when it has an interaction between two polymeric phases although ΔG_{mix} is positive. The effect of hydrogen bonding in blend polymers was explained by Flory [Flory, P.J. (1953)]. The critical value of the interaction free energy is so small for any pair of polymers

of high molecular weight that it is permissible to state as a principle of broad generality that *two high polymers are mutually compatible with one another only if their free energy of interaction is favorable, i.e. negative*. Since the mixing of a pair of polymers, like the mixing of simple liquids, in the great majority of cases is endothermic, incompatibility of chemically dissimilar polymers is observed to be the rule and compatibility is the exception. The principal exceptions occur among pairs in possession of polar substituents which interact favorably with one another. Moreover Macknight *et al.* (1985) suggested that blended PA6/EMAA is compatible blend because of reaction between the acid and terminal amine, and physico-chemical interactions, such as hydrogen bonding, taking place between the two components.

2.4.3 Ionic bonding

2.4.3.1 *Effect of Metal Ion Type*

An early report of the effect of cation type on melt rheology was given by Bonotto and Bonner(1968), who noted that the melt indices (inversely related to melt viscosities) of ethylene acrylic acid ionomers were consistently lower when metal divalent was used as opposed to metal monovalent, over a range of neutralization levels and at two stress values. In 2002 Nishioka *et. al* were studied rheological characterization of ionic bonding in ethylene-ionomer melts with low neutralization degree. Figure 2.3 they suggested that sodium ion has three sites in which COO^- and maximum two COOH s can enter. One is ion bonding (COO^- , Na^+) and the other two are coordinate bondings (COOH , Na). Zinc ion has two sites where two COO^- bonds with Zn^{2+} . However, they found that the bond energy of Zn-EMAA was stronger than Na-EMAA because the Zn-EMAA is more stable bond than Na-EMAA.

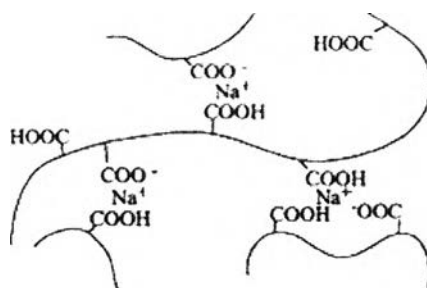


Figure 2.3 Model structure of molten ethylene-methacrylic acid sodium ionomer [Nishioka *et. al* (2002)].

2.4.3.2 Effect of Metal Ion Size

In 1981 Bronze *et.al* studied about the effect of metal ion size. They founded that the flow activation energy of partial neutralized carboxy-telechelic polylbutadienes by different size of metal ions was higher when the small size of metal ion was used. However Degee *et al.* (2002) found that shear viscosity of blended polymethacrylic ionomer/PA6 increased as the metal ion in ionomer size was increased.

2.4.3.3 Effect of Neutralization Level

Otocka *et al.* (1969) reported that the increase in neutralization level caused an increased viscosity of material. However the increase of viscosity was depended on metal ion which monovalent ions caused an increase in viscosity lower than divalent ions.

2.4.3.4 Effect of Content

Leewajanakul *et al.* (2003) reported that the addition small amount of Zn-EMAA can improve the compatibility of PA6/LDPE blends. At high level of Zn-EMAA mechanical, thermal properties were increased and the optimum condition was 5 phr. After increasing Zn-EMAA content no improvement was seen. They suggested that the improvement of compatibility was limited by PA6 functional group. If the interaction between functional groups of PA6 and ionomer is complete, increasing content of compatibilizer will not improve the compatibility between polymer blends.

2.4 Polyelectrolyte Theory

In electrolyte solution, one expects there are strong electrostatic interactions between the ions. Ions of unlike charge will strongly attract each other. It turns out that the strength of the interaction between two ions is very much dependent on the total concentration of ions in the solution. Because the electrostatic interactions, and ion of given charge will have on average more ions of opposite charge in its vicinity than ions of like charge. That is an ion of given charge is surround by an ion atmosphere of excess opposite charges. Because of this, when two ions approach each other, their mutual interaction, whether attractive or repulsive, is screened, i.e. diminished, by the surrounding ion atmosphere. Essentially, the ions in question will only experience an interaction when their ion atmosphere begin to overlap. The range of the ion atmosphere is very dependent on the total concentration of ions since the more ions in the solution, the stronger the screening effect. A theoretical estimate of the range of the ion atmosphere was derived by Debye, P. who derived an expression for the radius of the ion atmosphere as what is now referred to as the Debye length $\ell_D = K^{-1}$

$$K^{-1} = \sqrt{\frac{1000\epsilon kT}{8\pi N_A e^2 I}} \quad (3)$$

where N_A is Avogadro's number, e is the charge on an electron, ϵ is the dielectric constant of medium, k is Boltzmann's constant, T is temperature (deg. Kelvin), and the quantity I is the ionic strength:

$$I = \frac{1}{2} \sum c_i z_i^2 \quad (4)$$

where c_i is the molar concentration of ions of species i , and z_i is the charge on that ion

Examining eqs. (3) and (4), it is clear that ℓ_D decreases as I increase, i.e. as the concentration of all ion increases, and, further that multivalent ions more effectively screen electrostatic interactions than monovalent ions.

2.6 Measurement of Compatibility of Blends

2.6.1 Morphology

One of the most common applications of microscopy in the analysis of polymer blends is to measure the size of the dispersed phase. Kamal *et al.* (1995) had used formic acid to selectively etch PA/HDPE blends. For well-mixed polymer blends, the dispersed phase commonly exhibits log normal behavior. The character of the distribution does not appear to be substantially altered by changes in interfacial energy or chemical compatibilization, although there may be large state changes in the mean size of the particles.

2.6.2 Thermal Analysis of Solid Polymer

2.6.2.1 Dynamic Mechanical Thermal Analysis [DMA]

Dynamic mechanical studies of polymer blends are typically accomplished using forced-vibration methods. The equation, applied stress is

$$\sigma = \sigma_o e^{i(\omega t + \delta)}, \quad (5)$$

and the resulting strain is given by

$$\varepsilon = \varepsilon_o e^{i(\omega t + \delta)} \quad (6)$$

The complex modulus can be expressed by

$$E^* = \frac{\sigma(t)}{\varepsilon(t)} = E_o e^{i\delta} = E_o (\cos \delta + i \sin \delta) = E' + iE'' \quad (7)$$

where E' is the storage modulus and E'' is the loss modulus. The loss factor is given by

$$\frac{E''}{E'} = \tan \delta \quad (8)$$

Glass transition temperature (T_g) can be found from plot of $\tan \delta$ vs temperature which T_g is the maximum value of $\tan \delta$.

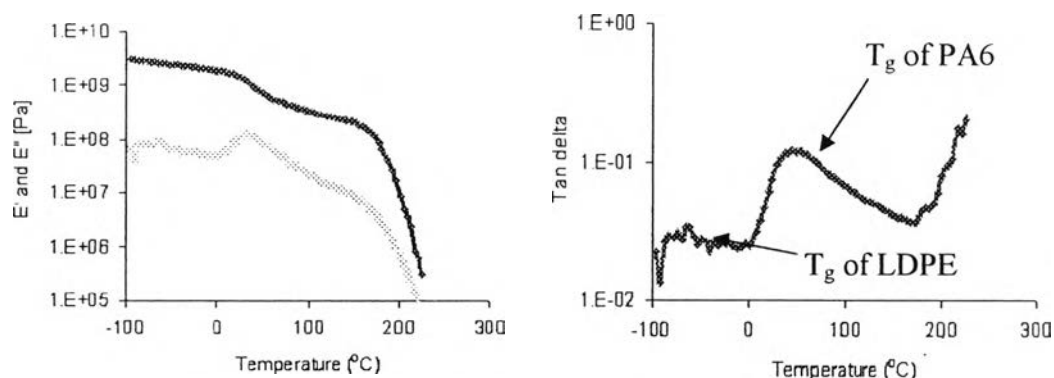


Figure 2.4 Plot of E' , E'' and $\tan \delta$ vs temperature of blended PA6/LDPE Sinthavathavorn *et al.* (2008).

Leewajanakul *et al.* (2003) used DMA to probe the compatibility between PA6/LDPE by using Zn-EMAA as a compatibilizer. They found that the compatible blend had storage modulus drop off at higher temperature than incompatible blend.

2.6.3 Rheology

Rheology can be defined as the science of the flow and deformation of materials. For many simple fluids, the study of rheology involves the measurement of viscosity. For such fluids, the viscosity depends primarily on the temperature and hydrostatic pressure. However, the rheology of polymers is much more complex because polymeric fluids show nonideal behavior. In addition to having complex shear viscosity behavior, polymeric fluid show elastic properties, normal stress phenomena and prominent tensile viscosities. All these rheological properties depend on the shear rate, the molecular weight, and structure of the polymer, the concentration of various additives, as well as upon the temperature.

There are two types of flow: shear flow and elongation flow which is shown in Figure 2.5

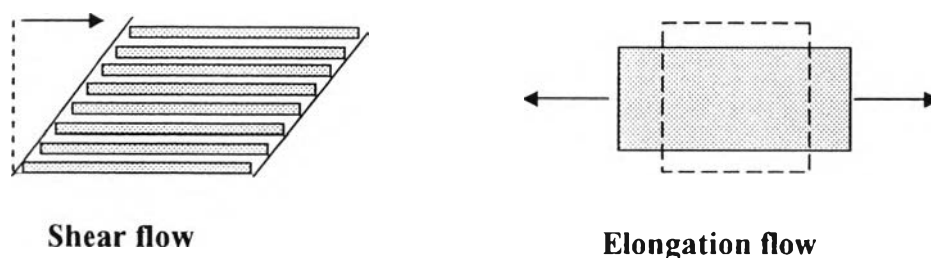


Figure 2.5 Two types of flow in Rheology.

Measuring shear viscosity can be defined as follow equation

$$\text{Shear stress } \tau = \frac{\text{Shear force}}{\text{Area of shear face}} \quad (9)$$

$$\text{Shear strain } \gamma = \frac{\text{Amount of shear displacement}}{\text{Distance between shearing surfaces}} \quad (10)$$

$$\text{Shear viscosity } \eta = \frac{\text{Shear stress}}{\text{Rate of shear strain}} = \frac{\tau}{\dot{\gamma}} \quad (11)$$

For elongation viscosity can be defined as follow equation

$$\text{Tensile stress } \sigma = \frac{\text{Force}}{\text{Area}} = \frac{F}{A} \quad (12)$$

$$\text{Elongation } \varepsilon = \frac{\text{Final length} - \text{Initial length}}{\text{Initial length}} = \frac{L - L_0}{L_0} \quad (13)$$

$$\text{Elongational viscosity } \eta_e = \frac{\text{Tensile stress}}{\text{Elongational rate}} = \frac{\sigma}{\dot{\varepsilon}} \quad (14)$$

2.6.3.1 Capillary Rheometer

Shear/Elongational Viscosity

A very popular type of instrument for studying the rheological behavior of molten polymers is the capillary rheometer. As shown in Figure 2.6, a liquid polymer is forced by a piston or by pressure from a reservoir through a capillary. The quantity of polymer coming from the capillary per unit of time at a given pressure drop is the basic measurement used to calculate the viscosity. The

capillary rheometer has a number of advantages. First, the instrument is relatively easy to fill. This is an important consideration since most polymer melts are too viscous to pour readily even at high temperatures. The test temperature and shear rate are varied readily. The shear rate and flow geometry are similar to the extrusion and injection molding. In addition to the viscosity, some indication of polymer elasticity is found from the die swell of extrudate. However, the shear is not constant but varies across the capillary. Another disadvantage is the necessity of making a number of corrections in order to get accurate viscosity values. The important equations pertaining to the capillary viscometer for Newtonian fluids are:

$$\eta = \frac{\pi R^4 P}{8 L Q} \quad (15)$$

$$Q = V/t, \tau_w = \frac{RP}{2L} \quad (16)$$

$$\gamma_w = \frac{4Q}{\pi R^3} = \frac{RP}{2L\eta} = \frac{4\bar{v}}{R}; \bar{\gamma} = \frac{8Q}{3\pi R^3} \quad (17)$$

$$\bar{v} = \frac{R^2 P}{8L\eta}; \eta = \frac{\tau_w}{\gamma_w} \quad (18)$$

In these equations, η is the viscosity, R is the radius of the capillary which has a length L , Q is the volumetric flow rate through the capillary under a pressure drop P along the capillary, V is total volume of fluid extruded in a time interval t , and $\bar{\gamma}$ is shear rate dy/dt . The rate of shear at the wall of the capillary is γ_w while $\bar{\gamma}$ is the average rate of shear across the capillary. The shear stress at the wall is τ_w , and \bar{v} average velocity across the capillary cross sectional area. The shear rate is a maximum at the wall, but the velocity is zero at the wall. The characteristics of capillary flow are shown in the Figure 2.5. The solid line are for Newtonian fluids. The dashed lines are typical of polymeric non-Newtonian liquids.

Two corrections are commonly applied to capillary data in order to obtain the correct viscosity of polymeric fluids. The Rabinowitsch equation corrects the rate of shear at the wall for non-Newtonian liquids

It changes equation (17) to

$$\gamma_w = \frac{4Q}{\pi R^3} \left(\frac{3n+1}{4n} \right); n = \frac{d \log \tau}{d \log \dot{\gamma}} \quad (19)$$

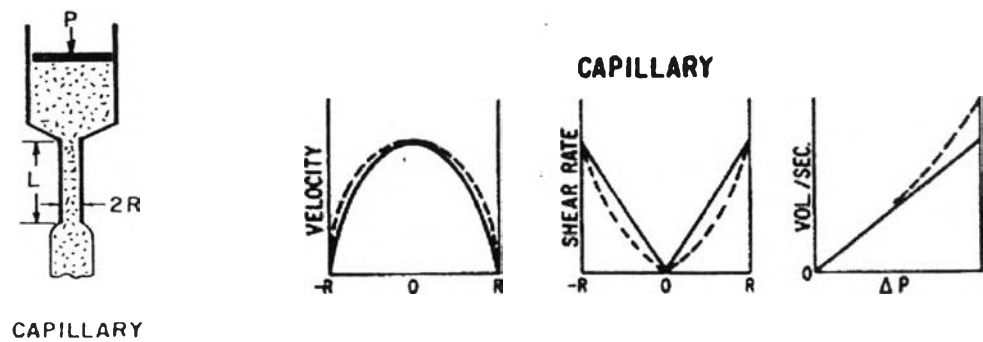


Figure 2.6 Schematic diagram of capillary rheometer and characteristics of capillary rheometer. Solid line refer to Newtonian fluids and dotted line are typical of non-Newtonian polymer melts [Nielsen L. (1977)].

The factor n is power law index. For a Newtonian fluid, $n=1$; for a dilatant fluid $n > 1$; and for a pseudoplastic fluid, $n < 1$.

The Bagley correction takes care of non-ideality arising from viscous and elastic effects at the entrance to the capillary. The effective length of a capillary is greater than its true length. The shear stress at the wall of equation (16) becomes

$$\tau_w = \frac{RP}{2(L+eR)} = \frac{P}{2(L/R+e)} = \frac{P-P_o}{2L/R} \quad (20)$$

The Bagley correction factor e should be independent of capillary length, but in general it does vary somewhat with L/R because of elasticity of polymer melts. The Bagley correction is determined by measuring the pressure drop ΔP at constant rate of shear for several capillary lengths and extrapolating to

zero pressure drop as shown in Figure 2.7. In equation (20), P_0 is the pressure drop corresponding to a capillary of zero length for a given rate of shear rate.

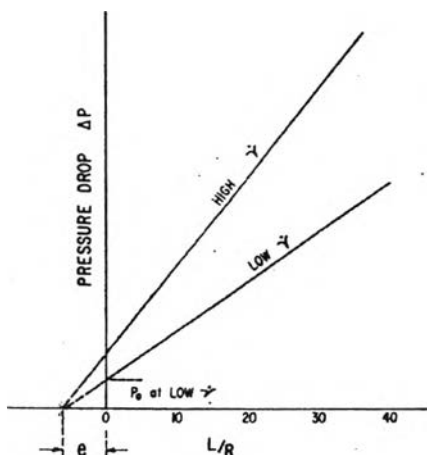


Figure 2.7 The Bagley correction for capillary rheometer [Bagley E.B. (1961)].

Effect of Temperature to Viscosity

The viscosity of most polymers changes greatly with temperature. For Newtonian liquids and for polymer fluids at temperatures far above the glass transition temperature or the melting point, the viscosity follows a simple exponential equation, the Andrade-Eyring equation:

$$\eta = ke^{E/RT} \quad (21)$$

where η is shear viscosity, k is a constant, and R and T are the universal gas constant (8.314 J/mol.K) and the absolute temperature (K), respectively. The flow activation energy E describes the energy needed for the molecules to exceed the liquid-specific energy barrier. This energy is related to movement against the internal flow resistance caused by the friction between neighboring molecules.

Effect of Shear Rate to Viscosity

The characteristic of polymer melt is their non-Newtonian behavior whereby the apparent viscosity decreases as the shear rate increases. This decrease in viscosity extends over many decades of change in shear rate and the viscosity at high shear rate may be several orders of magnitude smaller than the

viscosity at low shear rate because at high shear rate chain is alignment in the flow direction.

Effect of Molecular Weight

The molecular weight dependence of the viscosity is shown in Figure 2.6. The solid lines show the dependence of the viscosity on molecular weight at zero rate of shear. There is some doubt about this dependence at high shear stresses as indicated by the dashed lines in Figure 2.8A and 2.8B indicate two of the possibilities with the arrows indicating the direction of the shifts as τ increases.

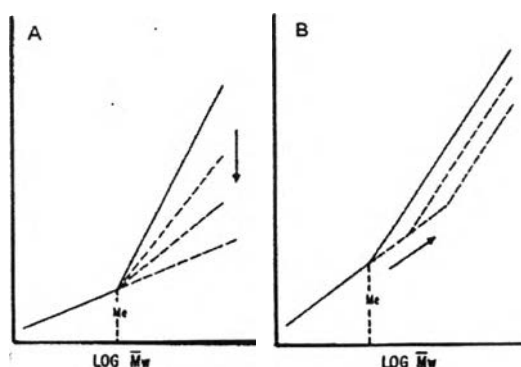


Figure 2.8 Two possible ways of the melt viscosity with different molecular weight where M_e is entanglement molecular weight [Nielsen L. (1977)]

In Figure 2.8A the slope of the line decreases as increased shear force which the shearing force destroys the entanglement faster than they can reform so that the number of entanglements decrease as shear force increase. The type of behavior shown in Figure 2.8B would be expected if M_e increase as shear force increases.

Effect of Branched Polymer

Polymer can have a great variety of branched structures. The branches can be short or long. The branches can be randomly spaced along the backbone chain, or several branches can originate from a single point to give a star-shaped molecule.

Short branches generally do not affect the viscosity of a molten polymer very much. On the other hand, long branches can have a very large effect. Branches which are long but still shorter than those required for entanglements decrease the viscosity when compared to a linear polymer of the same molecular weight because branched molecules are less compact than linear polymer. However, if the branches are so long that they can participate in entanglements, the branched polymer may have a viscosity at low shear rates greater than that of linear polymer of the same molecular weight.

Die Swell

The elasticity of a liquid produces die swell in the process of extruding a strand through a capillary is shown in Figure 2.9

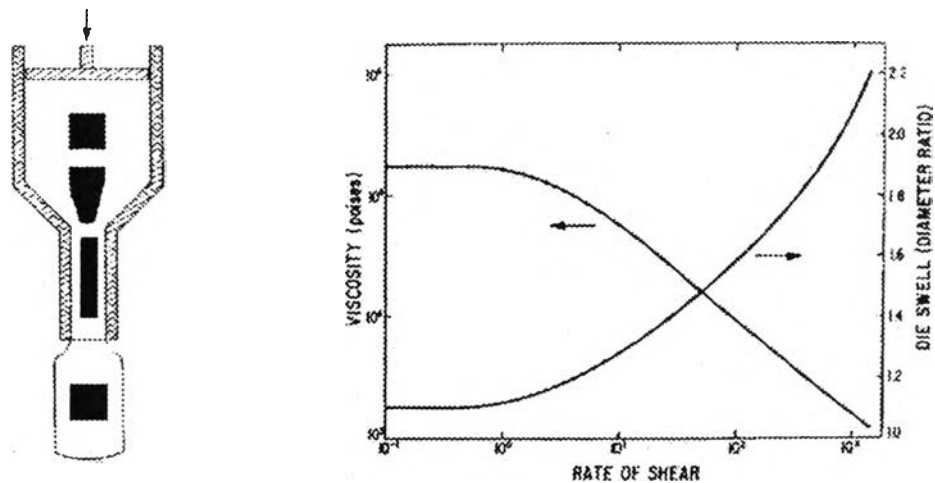


Figure 2.9 Die swell in capillary and general behavior die swell and viscosity as a function of shear rate [Nielsen L. (1977)].

The elastic fluid is stretched by the shear field in the capillary and by the extensional flow in the entrance region to the capillary. On leaving the capillary, the restraining forces are removed from the polymer so that the elastic material snaps back like a stretched rubber band with a consequent increase in diameter. The general behavior die swell and viscosity as a function of shear rate is shown in Figure 2.7. Newtonian liquids and polymers at very low shear rate expected to have die swell of 1.0, but actually they have a die swell of 1.1 as measured by the radius of the extruded. The

die swell of polymer melt increases as increased shear rate and the die swell goes through maximum about the shear rate at which melt fracture occurs because at higher shear rates, the polymer spends a shorter time in the capillary and hence the greater is the die swell.

2.6.4 Crystallization of Polymer Blends

The crystallization of immiscible blend of homo/heteropolymer should have the same crystallization of pure component. If the polymer blends is a compatible blends, the crystallization of blended material is changed because the interaction between two polymeric phases causes the difficult movement in molecular chain resulting in decrease of crystallization. Lahor *et al.* (2004). investigated the PA6/LDPE blends with sodium ionomer as a compatibilizer. They found that PA6/LDPE blends have the same crystallization as a pure polymer. After adding ionomer into the polymer blends, the crystallization of LDPE and PA6 decreased because the interaction between ionomer/PA6 and ionomer/LDPE made PA6 and LDPE difficult to move to achieve a good alignment and more packing.

2.6.5 Mechanical Properties

For the immiscible blend, polymer blend has poor mechanical properties due to high interfacial tension between two polymeric phases. The PA6/LDPE blends are a typical example of immiscible blend due to the presence of polar group in the PA6 and the non-polar ones of LDPE. Leewajanakul *et al.* (2003) reported that the addition of compatibilizer can improve the mechanical properties of PA6/LDPE blends because compatibilizer decreased the interfacial tension between two polymeric phase which allowed better force-transfer from the polymer matrix to the polymer dispersed phase.

2.7 **Polypropylene Fibers**

In 1970s Polypropylene was introduced to the textile area and has become rapidly growing family of synthetic fibers. However, the fiber is not dye-able with

the existing classes of dyes because of the lack of polar sites in the molecular structure.

2.8 Colorant

2.8.1 Pigments

Pigments are insoluble color particles that are held on the surface of a fabric by a binding agent. Pigments need to be bonded to fiber surface. The binder works like a glue and binds the pigment to the fiber. Binder is used to produce soft and flexible fabrics.

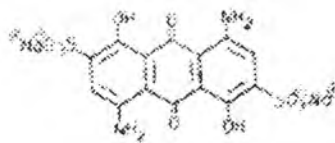
Pigment is rather popular because pigment colors are easier to match than dye colors. Dyes are more difficult due to chemical reactions of dyeing causing have shifted.

2.8.2 Dyes

Dye is an organic compound composed of a chromophore, the color portion of dye molecule, and an auxochrome, which slightly alters the color. The auxochrome makes the dye soluble and has a functional group to react with the fiber. Dye must be dissolved in water or some other carrier so as to penetrate the fiber. Dyes have great color strength; a small amount of dye can color fabric of large quantities. Most dye bonded chemically with the fiber and found in the interior of the fiber more than surface area.

2.8.3 Classification of Dyes

Acid dye is an anionic dye which is shown in Figure 2.10. It is used in fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dyebaths. Dye attaches on fiber by using interaction between anionic groups from dye and cationic group from fiber through the ionic and dispersion force.

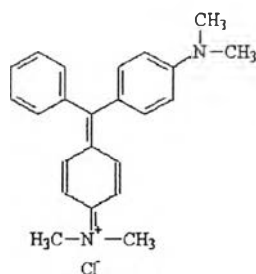


anthraquinone dye

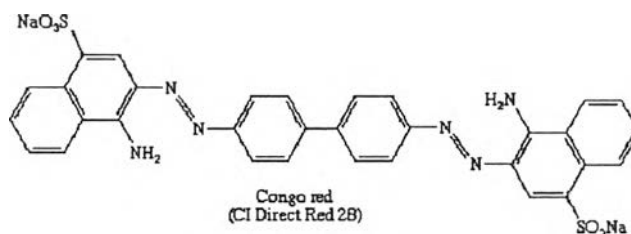
Figure 2.10 Acid dye molecules.

[http://aida.ineris.fr/bref/bref_text/bref/bref/bref/BREF_tex_gb45.html].

Basic dye is a cationic dye which is shown in Figure 2.11. It is used in acrylic fibers, and some use for wool and silk. Typically acetic acid is added to the dye bath to improve the dye absorption on the fiber. Dye attaches on fiber by using interaction between cationic groups from dye and anionic group from fiber through the ionic force

**Figure 2.11** Basic dye molecules [<http://www.chm.bris.ac.uk>].

Direct dye is an anionic dye which is normally applied from aqueous dye bath containing an electrolyte which is shown in Figure 2.12. Direct dye is used on cotton, paper, leather, wool, silk and nylon. This dye can interact with fiber by hydrogen bonding.

**Figure 2.12** Direct dye molecules [<http://www.britannica.com>].

2.8 Organoclay

Clay minerals, or phyllosilicate, consist of sheets of silica tetrahedral and alumina octahedral which are held together by only weak interatomic forces between the layers. Owing to their chemical composition and crystal structure, they are divided into four main groups which are illite, smectite, vermiculite and kaolinite. Among these, the one that is found to be useful in the field of polymer composites is a group of expandable clay known as smectite clay.

Smectite clay is a phyllosilicates or layer silicates having a layer lattice structure in which two-dimensional oxoanions are separated by hydrated cations. Montmorillonite, which is the main constituent of bentonites, is a main species of smectite clay. The structure of MMT is made of several stacked layers, with a layer thickness around 0.96 nm and a lateral dimension of 100-200 nm. Its crystal lattice consists of a central octahedral sheet of alumina fused between two external silica tetrahedral sheets (in such a way that the oxygens from the octahedral sheet also belong to the silica tetrahedral), as shown in Figure 2.13. These layers organize themselves in a parallel fashion to form stacks with a regular gap between them, called interlayer.

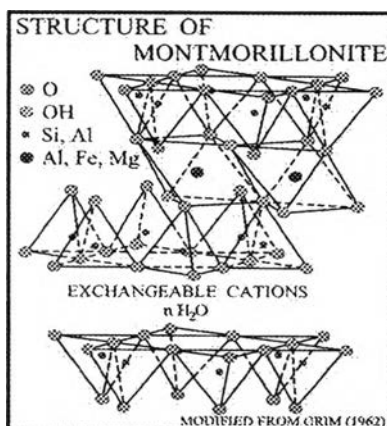


Figure 2.13 Structure of montmorillonite [<http://pubs.usgs.gov/of/2001/of01-041/htmldocs/images/monstru.jpg>].

In this work, bentonite is a clay mineral used for the preparation of polymer-clay nanocomposites fiber. The organoclay was made of bentonite modified with cationic surfactant (Methyl di-[(partially hydrogenated) tallow carboxymethyl]-2-hydroxyethyl ammonium methylsulfate) which is shown in Figure 2.14.

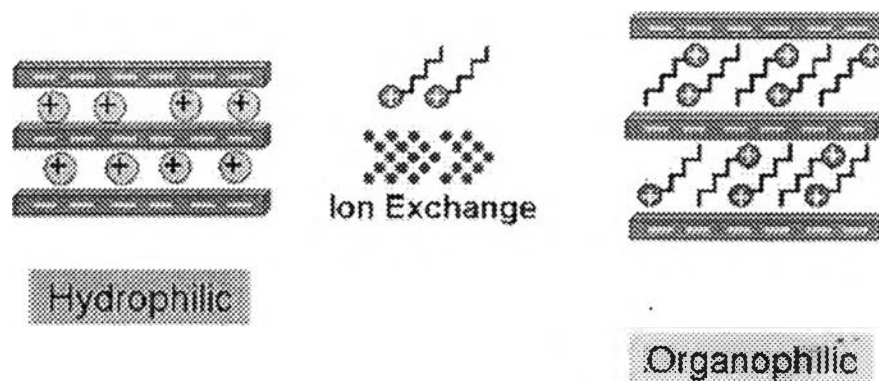


Figure 2.14 Ion exchange between surfactant and clay.

2.10 Literature Reviews

2.10.1 Binary Blends of Nylon with Multifunctional Polymers

Macknight *et al.* (1985) studied the binary blends of polyamide 6 as the major component and ethylene-methacrylic acid copolymer (EMAA) as the minor component. Increasing the methacrylic acid content in EMAA led to a decrease in the particle size of the dispersed phase and yielded an improvement in the mechanical properties of these blends. This behavior was attributed to a series of chemical, such as a reaction between the acid and terminal amine, and physico-chemical interactions, such as hydrogen bonding, taking place between the two components. The presence of the polyethylene component in the polyamide matrix did not affect its thermal properties.

The same system was more thoroughly examined by Fairley *et al.* (1987) with the hope that the role of E-MAA as a compatibilizer in polyethylene/E-MAA/polyamide 6 ternary blends might be better understood. Differential scanning calorimetry (DSC) measurements showed that one component of the binary blends does not modify the crystallinity of the other, and indicated no interaction between

the crystalline components of the mixtures and weak interactions in the amorphous phase.

Willis *et al.* (1993) investigated the binary blend of polyamide/ionomer, where the ionomer was a copolymer of polyethylene, methacrylic acid, zinc-neutralized methacrylic acid, and isobutylacrylate. The PA/ionomer blends demonstrated a very fine multiphase structure evident after microtoming/etching of the sample and strong additive behavior in the viscosity/composition curve. Formation of an amide bond was identified by FTIR. DSC data showed that the maximum crystallization temperature of the PA/ionomer blends decreased with ionomer concentration. There was also an increase in the half time of the crystallization, which indicated that the ionomer was interfering with the crystallization of the polyamide in these blends.

Silva *et al.* (1996) investigated the effect of poly (ethylene-co-vinyl alcohol-co-vinyl mercaptoacetate) (EVASH) on the compatibilization of polyamide 6 (PA6)/low-density polyethylene (LDPE). EVASH was prepared from hydrolyzed EVA through an esterification reaction with mercaptoacetic acid. Mechanical properties, differential scanning calorimetry, and scanning electron microscopy results were discussed. The mechanical properties were improved with the addition of EVASH. The compatibilizing agent also affected the crystallinity degree of both components of the blend, as indicated by the results obtained from the DSC studies. The addition of EVASH resulted in a reduced dispersed-phase particle size.

The addition of up to 5 wt% of a random copolymer of methyl methacrylate-methacrylic acid (P(MMA-co-MAA)) and the related ionomers (P(MMA-co-metal MA)), remarkably increased the melt viscosity of polyamide (PA), as shown by Degee *et al.* (1997). The PA melt viscosity increased with the cation as follows: $\text{Ni}^{2+} < \text{Ba}^{2+} < \text{Mg}^{2+} < \text{Li}^{+} < \text{Na}^{+} < \text{K}^{+} < \text{Cs}^{+}$. The major effect was believed to occur when polymer compatibility was improved to the point where a finely dispersed two-phase system with low interfacial tension was reached, as a result of strong ion-dipole interaction.

Koulouri *et al.* (1997) studied the grafting efficiency on different polyamides (6, 11, 12, 6.10, and 6.12) of ethylene-glycidyl methacrylate copolymers (PE-g-GMA) and ethylene-ethyl acrylate copolymers at a composition of 85/15,

when melt-mixed under optimum conditions. Polyamides 6 and 11 were selected to be studied in the complete composition range using techniques like dynamic mechanical analysis (DMA), tensile testing, DSC, scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) for the characterization of the blends. The results showed that the most efficient grafting occurred in the case of polyamide 11/PE-g-GMA blends. The formation of a copolymer was confirmed using solvent extraction technique. The existence of both polymers in the isolated copolymers was proved by FTIR and thermal analysis. Overall, the concept of the compatibilization of the polyamide-polyethylene system was confirmed in the case of polyamide 11/HDPE compatibilized by PE-g-GMA copolymer.

The fusion bonding of maleated polyethylene blends to polyamide 6 was investigated by Valenza *et al.* (1997). Blends of linear low-density polyethylene (LLDPE) and linear low-density polyethylene-grafted maleic anhydride (LLDPE-g-MA) were used to promote the adhesion to polyamide 6 (PA6) in a three-layer coextruded film without using an additional adhesive or tie layer. The effect of bonding time and molecular weight (MW) of different maleated polyethylenes on the peel strength of the joints was analyzed. Direct evidence of a copolymer formed in-situ at the interfaces was also considered. The peel strength of fusion-bonded layers of LLDPE/LLDPE-g-MA blends with PA6 strongly depended on bonding time and the molecular weight of the maleated polymer. Tensile properties of three-layered films, made up of PA6 as the central layer and LLDPE/LLDPE-g-MA blends as the two external layers, were improved with increases in the maleic anhydride (MA) content in the blend. The in-situ formation of a copolymer between the MA in the blend and the terminal amine groups of the PA6 was confirmed by the Molau test, FTIR spectroscopy, and DSC.

Jurkowski *et al.* (1998) studied the influence of chemical and mechanical compatibilization on the structure and properties of polyethylene/polyamide blends. LDPE/PA6 binary blends and LDPE/PA6/compatibilizer ternary blends were prepared in a Brabender extruder, equipped with a prototype static mixer. The compatibility of the components was estimated by rheological properties (viscosity and melt flow index), and observations of the structure were made with the help of SEM and tensile strength testing. The

structure and properties of the blends were dependent on the recipe content of the polymer blends and the conditions of their manufacturing. Uniformity of the blends of the thermodynamically immiscible polymers was improved by using a prototype static mixer giving mechanical compatibilization and a compatibilizer giving chemical compatibilization. LDPE grafted with a maleic anhydride (LDPE-g-MAH) was used as a compatibilizer.

The thermal stability of blends of nylon 6 with polyolefins that contain acrylic acid was studied by Lamas *et al.* (1998). They focused on the effect of interfacial interactions of blends of nylon 6 with polypropylene (iPP), polypropylene grafted with 6 wt% acrylic acid (iPP-AA), and a random copolymer of ethylene and acrylic acid with 8 wt% acrylic acid (PE-AA). Thermogravimetric analysis (TGA) was performed on all samples and both qualitative and quantitative analysis was done in order to evaluate the thermal stability of the materials under investigation. The results indicated that when strong molecular interactions were present between the polymers to be mixed (and therefore strong interfacial activity), the thermal stability in the blends could be increased with expected in view of a simple additive rule of mixing and synergistic effects could be produced.

The melt-mixing of polyester-type polyurethane (PU) with the Zn^{2+} ionomer of poly(ethylene-co-methacrylic acid-co-isobutylate) terpolymer blends were shown to be compatible throughout their composition range by Papadopoulou *et al.* (1998). DMA and DSC results supported the view that the amorphous components of the blend more miscible. Miscibility was less at PU-rich compositions and miscibility was mostly attributed to dipole-dipole and hydrogen bonding interactions.

Kudva *et al.* (1999) studied the morphology and mechanical properties of compatibilized polyamide 6/polyethylene blends. Blends of polyamide 6 and polyethylene were investigated over a range of compositions. Polyethylenes were grafted with MA and, thus, had the potential to react with the amine end groups of polyamide 6 during melt processing. This study focused on the effects of the concentration, viscosity, and functionality of the maleated polyethylenes (PE-g-MA) on the rheological, morphological, and mechanical properties of polyamide 6/PE-g-MA blends. The impact properties of these blends were strongly influenced by the

amount and type of maleated polyethylenes used. A low viscosity maleated polyethylene was shown to be ineffective in toughening polyamide 6; this was because of the propensity of polyethylene to become continuous, even when polyamide 6 was the majority component. Two higher viscosity maleated polyethylenes were able to produce blends with high impact strength and excellent low temperature toughness over a range of compositions. The result demonstrated that polyethylene materials containing a very low degree of anhydride functionality could generate blends with excellent impact properties. A brief portion of this study focused on ternary blends of polyamide 6, maleated polyethylene, and nonmaleated polyethylene; in general, the impact properties of these blends improved as the molecular weight of polyamide 6 increased, and as the ratio of maleated polyethylene to nonmaleated polyethylene increased.

The morphology, thermal behavior, and mechanical properties of PA6/UHMWPE blends, with HDPE-g-MA as a compatibilizing agent were studied by Yao *et al.* (2000) A functionalized high-density polyethylene (HDPE) with MA was prepared using a reactive extruding method. This copolymer was used as a compatibilizer of blends of polyamide 6 (PA6) and ultrahigh molecular weight polyethylene (UHMWPE). The morphologies of the blends were examined by SEM. This study found that the dimension of UHMWPE and HDPE domains in the PA6 matrix decreased dramatically compared with that of the uncompatibilized system. The size of the UHMWPE domains was reduced from 35 μm (PA6/UHMWPE, 80/20) to less than 4 μm (PA6/UHMWPE/HDPE-g-MAH, 80/20/20). The tensile strength and Izod impact strength of PA6/UHMWPE/HDPE-g-MAH (80/20/20) were 1.5 and 1.6 times higher than those of PA6/UHMWPE (80/20), respectively. 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.

Crystallization behavior and the resulting PA6 crystalline structure were studied by Psarski *et al.* (2000). The blends of PA6 and polyolefins functionalized with acrylic acid (polyethylene-PE-AA, polypropylene-PP-AA) were investigated.

Thermal analysis showed that in the case of blends with functionalized polyolefin as a matrix: (a) PA6 crystallization was spread and dramatically shifted toward lower temperatures, approaching that of the polyolefin component 125-132°C; and (b) the PA6 γ crystal was the major phase present; confirmed and quantitatively evaluated by the use of deconvolution computations performed on the WAXS spectra of the blend.

When PA6 was dispersed in a functionalized polyolefin matrix, the weight content of the PA6 γ crystal increases up to three times with respect to analogous, non-compatibilized blends, and up to ≈ 16 times with respect to the PA6 homopolymer. These phenomena were explained by the reduction of size of PA6 dispersed particles, caused by the interactions between the functional groups of polyolefin and the polar groups in the polyamide chain. The nucleation mechanism was changed due to the lack of the heterogeneous nuclei in most small PA6 droplets, which resulted in the enhanced γ crystal formation.

Sailaja *et al.* (2001) studied the use of maleic anhydride-grafted polyethylene as a compatibilizer for HDPE-tapioca starch blends. Tapioca starch in both glycerol-plasticized and unplasticized states was blended with high-density polyethylene (HDPE) using HDPE-g-MA as the compatibilizer. The impact and tensile properties of the blends were measured according to ASTM methods. The results revealed that blends containing plasticized starch had better mechanical properties than those containing unplasticized starch. High values of elongation at break at par with those of virgin HDPE could be obtained for blends, even with high loading of plasticized starch. The morphologies of the blends were studied by SEM of impact-fractured specimens and revealed a ductile fracture, unlike blends with unplasticized starch at such high loading, which showed brittle fracture, even with the addition of a compatibilizer. In general, blends of HDPE and plasticized starch with added compatibilizer showed better mechanical properties than similar blends containing unplasticized starch.

Lagaron *et al.* (2001) studied ethylene-vinyl alcohol blends with polyamide and a polyamide-containing ionomer. Ethylene-vinyl alcohol had excellent barrier properties to gases and hydrocarbons, as well as outstanding

chemical resistance. Their barrier properties increased with increasing vinyl alcohol content. Blending ethylene-vinyl alcohol and polyamide had some miscibility which was dependant on the blend composition. Compatibility increased in the ionomer-rich blends and was thought to be enhanced by the presence of crystalline nylon in the formulation of the ionomer. An increase in flexibility and toughness was measured in the mechanical properties of these EVOH/ionomer blends. The flexibility rose with increasing strain rate in extruded films. The overall crystallinity of the blends was lower than that of neat EVOH, owing to the amorphous condition of the PA and the lower crystallinity exhibited by the ionomer.

Behaviors of blends made with PA6 and ethylene acrylic acid (EAA) copolymer containing different amounts of acrylic acid were investigated by Valenza *et al.* (2002). This study showed that acrylic acid caused a compatibilizing effect between the polyamide and the polyethylene components with modifications of blend morphology and mechanical behavior. These effects were enhanced with an increase in acrylic acid content and were attributed to hydrogen bond interactions among the acrylic acid groups and the functional groups of polyamide. However, other studies were shown that a reaction between terminal amine groups and acid groups led to interface stabilization as well.

Jiang *et al.* (2003) studied reactive compatibilizers for LDPE/PA6 blends. Several home-made and commercially available polyethylene (PE) samples grafted with maleic anhydride (MA), (PE-g-MA), were used for the reactive blending of LDPE with PA6. The effectiveness of these compatibilizers was compared with that of a number of EAA copolymers, which had been employed in a previous study for the reactive compatibilization of the same blends. Furthermore, this study was designed to get a deeper insight into the coupling reactions producing the PA-g-CP copolymers that were thought to act as the true compatibilizers in these systems. To this end, binary compatibilizer/LDPE and compatibilizer/PA and ternary LDPE/PA/compatibilizer blends were prepared with a Brabender mixer and were characterized by DSC, SEM, and solvent fractionation. The results showed that the PE-g-MA copolymers reacted more rapidly with PA than EAA copolymers and that their effectiveness depended critically on the microstructure and the molar mass of their PE backbones. In particular, compatibilizers produced by the functionalization

of LDPE were shown to be miscible with LDPE and to be scarcely available at the interface where the reaction with PA is expected to occur. Conversely, the prepared compatibilizers from HDPE were immiscible with LDPE and showed better performance. Whereas the effectiveness of the EAA copolymers studied earlier had been shown to increase with an increase in the concentration of the carboxyl groups, the concentration of the anhydride groups of the PE-g-MA CPs studied in this work was found to play a minor role, at least in the investigated range (0.3–3.0 wt% MA).

Minkova *et al.* (2003) studied the crystal structure and isothermal crystallization behavior of the LDPE or PA6 with two types of functionalized polyethylene compatibilizers, namely poly(ethylene-co-acrylic acid) and poly(ethylene-co-glycidylmethacrylate) copolymer blends by DSC and Wide angle X-ray scattering (WAXS). Fine dispersed compatibilizer particles in PA6/compatibilizer blends crystallized at large supercoolings exhibiting a low degree of crystallinity and perfectness. PA6 or LDPE in the presence of the compatibilizer crystallizes into spherulites with dimensions smaller than those of the corresponding neat polymers. X-ray measurements demonstrated that there were no interactions in the crystal phase or co-crystallization between the components in the PA6/compatibilizer blends. The functionalized polyethylenes interacted with the polar groups of the polyamide chain, giving rise to the formation of a copolymer with the EAA having a higher compatibilization efficiency. On the other hand, this study found only physical interactions between LDPE and the compatibilizers.

Huang *et al.* (2003) studied HDPE/PA6 blends with respect to parison formation in extrusion blow molding. The dependence of the diameter swell and sag of a parison extruded from blends of high-density polyethylene (HDPE)/polyamide-6(PA6)/compatibilizer on the blend compositions and flow rate was determined by analyzing video images of the parison. Among the blends tested, those with a PA6 concentration of 35% or below exhibited an appreciable swell. A greater degree of sag began to appear for the blend with a PA6 content of 45%. A neural network approach was applied to the experimental data, leading to a model for predicting the diameter swell profile from new levels of input variables, including the blend composition and flow rate.

Lian *et al.* (2004) studied the compatibility of PA6 and electron beam irradiated high density polyethylene (e-HDPE). Oxygen-containing groups (mainly the carbonyl group) were introduced into the molecular chains of HDPE through electron beam irradiation; thus the polarity of HDPE was increased, and the surface tension of HDPE increased from 32.4 dyne/cm to 36.05 dyne/cm, especially the hydrogen bond part of the surface tension, which was increased from 1.21 dyne/cm to 1.74 dyne/cm. With electron beam irradiation, the ability of the irradiated HDPE to form hydrogen bonds with the polar groups of the PA6 was improved resulting in the improvement of the mechanical properties.

Sato *et al.* (2005) investigated the molecular structure, crystallinity, and morphology of uncompatibilized blends of high molecular weight polyethylene (HMWPE) and polyamide 12 (PA12) by using Fourier-transform (FT) Raman spectroscopy, wide-angle x-ray diffraction (WAXD), and scanning electron microscopy (SEM). Uncompatibilized and compatibilized blends of HMWPE/PA12 with a PA12 content ranging from 10 to 90 wt% at increments of 10 wt% were prepared. Compatibilized blends were prepared by adding a small amount of MA (0.5 wt%) yielding a marked improvement of dispersion of HMWPE and PA12. The crystallinity of HMWPE from Raman spectra, the relative intensities of band at 1418 and 1129 cm^{-1} to the intensity of band at 1000 cm^{-1} (I_{1418}/I_{1000} and I_{1129}/I_{1000}) were estimated for all the uncompatibilized and compatibilized blends. Uncompatibilized and compatibilized blends of HMWPE/PA12 (50/50) showed quite different x-ray diffraction patterns; the compatibilized blend showed a significantly larger orientational effect in the x-ray pattern of HMWPE. The increase of interaction of MAH-HMWPE with the PA12 matrix led to additional crystallinity.

2.10.2 Ternary Blends of Nylon/Ionomers/Polyethylene

Willis *et al.* (1988) reported on the application of polyethylene-methacrylic acid-isobutyl acrylate terpolymer as a compatibilizer for polyolefin/polyamide blends. The maximum reduction in phase size was observed when only 0.5% by weight of the ionomer was added to the blend. A more significant reduction of the dispersed size was observed when the minor phase was

nylon, due to interactions that existed between the ionomer and the polyamide. FTIR spectra showed no evidence of such graft reactions, as a result of amidation reactions taking place during melt mixing, as was observed for binary blends of the ionomer and nylon.

Armat *et al.* (1993) investigated the effect of compatibilizing PE and PA6 on the morphology and mechanical properties of their blends. A functionalized styrene-(ethylene-co-butylene)-styrene block copolymer (MA/SEBS) was added to the blends as the compatibilizer. The compatibilizer was found to play a dual interfacial function. It reduced the interfacial tension of the system, resulting in a reduction of the particle size of the dispersed PE phase, and also enhanced the interfacial adhesion through the formation of micro-bridges. The fine polyethylene phase thus coupled to the matrix in compatibilized blends could carry load and deform co-continuously along with the matrix, causing extensive yielding of the blend to its failure and high ultimate elongation. Unexpectedly, at MA/SEBS contents higher than 10%, the ductility of the blends dropped sharply. This was attributed to flow-induced discontinuities within a large core in the tensile specimens. The lines of instabilities acted as large notches within the specimen, causing brittle failure of the otherwise ductile blend.

Yeh *et al.* (1995) reported a systematic investigation of the effects of type of compatibilizer upon the barrier properties and morphology of PE/PA blends. Three alkyl carboxyl-substituted polyolefins were selected to modify PA in a twin screw extruder by the "reactive extrusion" process. The barrier property of the modified PA (MPA) was better than pure PA, amount of barrier improvement of the blend of PE and MPA depended significantly on the barrier property of the MPA prepared. The extent of mixing PE and MPA before blow-molding had a significant effect on its corresponding to barrier properties. Further analysis of the fracture surfaces indicated that a more demarcated laminar structure of MPA dispersed in the PE matrix was essential for better barrier properties of PE/MPA blends. It was not clear how the type of CP added effect to the barrier properties of MPAs. However, they suggested that a long PA sequence with a shorter grafted CP chain and a high normalized grafting efficiency of MPA were essential for preparing a clear laminar structure of MPA, and good barrier properties of PE/MPA blends.

Sheng *et al.* (2000) prepared binary blends—PA/LDPE or PA/zinc-neutralized EMAA (Zn-EMAA) and ternary blends (PA/LDPE/Zn-EMAA or LDPE-g-AA). DMA and thermally stimulated current (TSC) indicated the incompatibility of PA6/LDPE binary blends, but the binary blends of PA6/Zn-EMAA and the ternary blends of PA6/LDPE/LDPE-g-AA are semi-compatible. Clearly, a reaction took place between the acid groups of the partially-neutralized ionomer or AA and the terminal amino groups of PA6 during melt mixing. The interface layer thickness (σ_b) of the two phases in the semi-compatible blends was calculated by small-angle X-ray scattering (SAXS).

The morphology and thermal properties of blends of LDPE and PA6 with two poly(ethylene-graft-ethylene oxide)s (PE-PEO) as compatibilizers were investigated by Hallden *et al.* (2001). Blends with LDPE/PA6 ratios between 70:30 and 30:70 and copolymer contents between 0 and 6% were prepared by melt mixing in a Brabender Plastograph and the morphology was studied by SEM. The addition of PE-PEO2000 to the PE/PA6 blends significantly decreased the dispersed phase size and increased the adhesion between the phases. The addition of PE-PEO750 did not have any measurable effect on the PE/PA6 blend. At a PE/PA6 ratio of 40:60, a co-continuous blend was formed. The addition of 4% PE-PEO2000 to this blend significantly improved the adhesion between the phases.

Recently, Leewajankul *et al.* (2003) investigated the use of Zn-EMAA ionomer as a compatibilizer for PA6/LDPE blends. The effect of the composition on the morphologies and properties of uncompatibilized and compatibilized blends was studied over a wide range of weight fractions. Uncompatibilized blends had substantially reduced mechanical properties after mixing—almost certainly due to poor interfacial adhesion between the two polymers. The addition of Zn-EMAA as a compatibilizer improved the mechanical properties significantly. The clearest evidence of this improvement came from DMA; for selected blends with high polyethylene contents, the drop in the modulus, corresponding to the transition of a solid to a melt, occurred at higher temperatures with the added compatibilizer. This improvement in the properties was accompanied by a reduction in the dispersed-phase size, especially when PA6 was in the dispersed phase.

Lahor *et al.* (2004) investigated Na-EMAA as a compatibilizer for PA6 and LDPE. Without a compatibilizer, the blend properties were not very good; but, as was found with Zn-EMAA, the addition of Na-EMAA dramatically improved the properties of the blend.

Chen *et al.* (2004) studied polyamide 66 (PA66) and HDPE blends with different compatibilizer concentrations. Upon the addition of a compatibilizer, the mechanical properties of PA66/HDPE blends improved greatly. The wear of PA66/HDPE blends was also strongly affected by the phase structure. The best blend for lower friction coefficient and higher wear resistance was the blend with a miscible structure. SEM on the worn surface and the steel counterface indicated that, for the immiscible and partially miscible blends, dispersed HDPE particles were pulled out from the worn surfaces during sliding because of the poor adhesion between HDPE and PA66, while this was not observed in the miscible blend system.

Nishio *et al.* (2005) studied the rheological properties of ethylene ionomer neutralized with various metal cations. They discovered that sodium ion was not only paired with a single COO⁻ but was also connected with two COOH acid groups by coordinate bonds; therefore, the sodium ion and a proton could be exchanged between COO⁻Na and COOH. This is called acid-cation exchanged reaction. This reaction allowed a polymer segment to easily diffuse from one ion aggregate to another, and lowered the friction for the segmental motion. In the case of zinc ionomers, a zinc ion was coordinated with two COO⁻ groups due to ionic bonds, and no COOH groups exist at around zinc ions. Therefore, in zinc ionomer, the acid-cation exchange did not take place, and the zinc ionomer had much higher viscosity than that of the sodium ionomer at an equivalent neutralization.

2.10.3 Binary Blend of Polypropylene with Other Polymers to Improve Dye-ability

In 1996, Seves *et al.* studied the improvement of dye-ability of polypropylene by introducing PA6. Melted blends of polypropylene and PA6 compatibilized with a poly (propylene)/maleic anhydride copolymer were prepared. The polypropylene fibers obtained by this method were found to be easily dye-able

in an aqueous dye bath. The affinity of dispersed dyes for the dispersed PA6 increased the dye-ability of the new fibrous materials.

Akrman *et al.* (1997) investigated the dye-ability of polypropylene fibers modified by two nitrogen polymeric additives containing dye sites of different basicity and accessibility using an acid dye. Thermodynamic and kinetic parameters of dyeing under infinite bath conditions were determined for four aqueous dye solutions. It was postulated that ionized molecules of acid dyes diffused within the fiber after activation of a dye site by a suitable agent. The dyeing mechanism of these fibers with anionic dyes came from an ion exchanger.

Yu *et al.* (2000) prepared a dye-able polypropylene fiber by mixing polystyrene to the polymer prior to extrusion. Polystyrene was synthesized at a suitable molecular weight and narrow distribution. The dye-ability, mechanical properties, shrinkage, degree of crystallinity, and orientation of pure polypropylene or blend fibers were investigated. In addition, the structure of the blend containing 4% and 6% polystyrene was also studied to explain the interesting dyeing behavior of the blend fibers. The degree of crystallinity and orientation were not only important to dye blend fibers, but a network of microchannels among additive particles was also important. Dyeing behavior among the blend fibers with various amounts of polystyrene, different from those of mechanical properties and shrinkage, increased irregularly.

Liao *et al.* studied the dyed polypropylene fibers in supercritical carbon dioxide. Dye uptake values showed that polypropylene fiber dyeing was much better in carbon dioxide than in water. They found that carbon dioxide made the molecular chain more mobile and led to an increase in the dyeing of the polypropylene fibers.

Ujhelyiova *et al.* (2005) studied the effect of polyester on polypropylene/polyester (PP/PES) fiber blends. Polyester was able to fix dispersed dyes and increased the uptake of the dye from a bath. Results showed that the dye uptake of blend PP/PES fibers modified by PET and PBT, dyed by disperse dye C.I. Disperse Blue 56, increased with the dyeing temperature and time. The highest dye uptake was measured in blend PP/PES fibers modified by PBT. The diffusion coefficients and the constant dyeing rate increased with an increase in dyeing

temperature. The most significant increase was achieved in blend PP/PES fibres modified by PET.

2.10.4 Blend of Polypropylene with Organoclay

Infusing nanoclays modified with quaternary ammonium salt into polypropylene to create dye sites for acid and dispersed dyeing was investigated by Fan *et al.* (2004). Color yield was dependent on the amount of nanoclay, while dyeing levelness depended on the uniformity of nanoparticle distribution in the PP matrix and on the homogenizing time. Quaternary ammonium salts in the PP nanocomposites acted as effective dye sites for acid dyes because they attracted electric charges, while disperse dye-ability was possible mainly because of the van der Waals forces and hydrophobic interaction between the disperse dyes and the clay particles.

Toshniwal *et al.* (2007) prepared polypropylene nanocomposites with three different clay loadings by solution mixing. Solution-mixed nanocomposites were extruded to fibers using a single screw extruder. PP nanocomposite fibers were uniformly dyed with three distinct dispersed dyes at different shade levels. As compared with neat PP fibers, improved and uniformly disperse-dyed nanocomposite fibers were observed. Tensile testing of neat PP and nanocomposite fibers showed that the modification of PP with quaternary ammonium-treated clay increased the modulus and the strength of the resultant fibers. However, the nanocomposite fibers showed a reduction in the breaking elongation as compared to neat PP fibers.