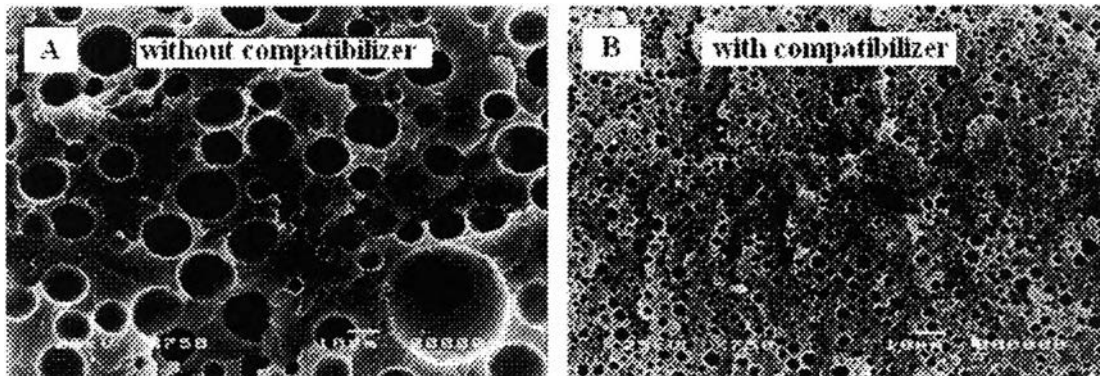




## CHAPTER I INTRODUCTION

To develop new polymeric materials for both scientific and commercial purposes, the blending of two or more different polymers is often used. A major problem, though, is the lack of compatibility between the blended polymers, giving poor interfacial adhesion, and hence poor mechanical properties of the polymer blend which is shown in Figure 1.1A. Reactive compatibilization is often used to improve compatibility, typically via one of the two ways. The first is to graft a functional group onto one or both of the polymers to be blended, so that the two components can react across the interface. Another is to add a third component, which is miscible with one component and can react with the other component. The third component in this case is termed a compatibilizer. Even though the compatibilizer does not cause true miscibility, these types of materials typically reduce domain sizes substantially in the blends and also significantly strengthen interfacial adhesion between the two phases which is shown in Figure 1.1B



**Figure 1.1** Scanning electron microscope for polymer blends, A) without compatibilizer B) with compatibilizer [Lahor *et al.*(2004)].

Polyamide (Nylon) is one of the most widely used engineering plastics. Polyamide 6 is easy to process, is weather and thermally resistant, and has high rigidity, good melt flow, and good barrier properties. Unfortunately, polyamide 6 has low impact strength (particularly below its glass transition temperature), poor

dimensional stability due to high moisture absorption, and is hard to process due to its high moisture absorption. Low-density polyethylene (LDPE) is a type of polyolefin widely used in industries. It acts as a good moisture barrier and has good impact strength. A blend of these two materials could offer a very attractive balance of mechanical and barrier properties. To overcome the incompatibility and poor dispersion of PA6/LDPE blends, a compatibilizer is required.

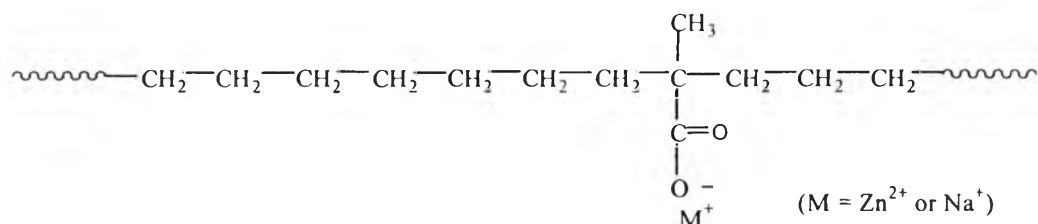
There are four types of compatibilizer which are used in blended PA6/LDPE

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.* (1988)
4. Ionomer such as partial neutralized ethylene methacrylic acid by metal ion (i.e.  $\text{Na}^+$ ,  $\text{Zn}^{2+}$  or  $\text{Li}^+$ ) Willis *et al.* (1988), Armat *et al.* (1993), Yeh *et al.* (1995), Sheng *et al.* (2000), Leewajankul *et al.* (2003) Lahor *et al.* (2004)

All compatibilizers, maleic anhydride, acrylic, acrylate copolymer and ionomer, can improve the compatibility of PA6/LDPE blends with few amount of compatibilizer (0.5-5 phr) required [Macknight *et al.* (1985), Fairley *et al.* (1987), Willis *et al.* (1988) Leewajankul *et al.* (2003), and Lahor *et al.* (2004)]. This is with the exception of maleic anhydride which required a high amount of compatibilizer (10-20 phr).

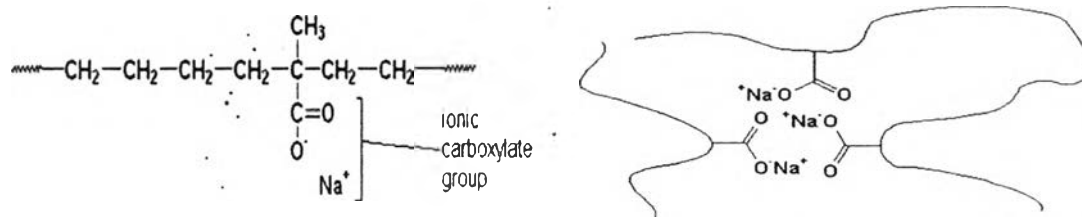
Among acrylic acid copolymer, acrylate copolymer and ionomer, ionomer is the most suitable type of compatibilizer for PA6/LDPE blends because ionomer not only interact with carboxylic group in polyamide by hydrogen bonding but also interact with carboxylic group in polyamide by ionic bonding. Therefore using ionomer as a compatibilizer in the PA6/LDPE blend can achieve better mechanical, morphology and thermal properties than acrylic acid and acrylate copolymer.

The most commercial ionomer is Surlyn<sup>®</sup> which is produced by DuPont and its structure is shown in the Figure 1.2.



**Figure 1.2** Structure of Surlyn<sup>®</sup> ionomer [www.psrc.usm.edu/mauritz/surlyn.html].

Surlyn<sup>®</sup> is a family of ethylene methacrylic acid (EMAA) copolymers in which a part of the methacrylic acid is neutralized with metal ions such as zinc ( $\text{Zn}^{2+}$ ) or lithium ( $\text{Li}^+$ ) or sodium ( $\text{Na}^+$ ). Interaction between ion pairs, and the nonpolar nature of the backbone, will cause the ions to aggregate together, which act as “ionic crosslink” which is shown in Figure 1.3. However, ionomers are not crosslinked polymers because, when heated, the ionic groups weaken enough to allow the melt-processing of this material on standard processing equipment. [www.psrc.usm.edu/mauritz/surlyn.html]



**Figure 1.3** Ionic crosslink of ionomer [Nishioka *et al.*(2002)].

The Surlyn<sup>®</sup> ionomer has excellent heat sealability, good hot tack, and can be sealed through contaminants. Surlyn<sup>®</sup> is used as a premium heat seal layer for packaging films, especially recommended for high speed packaging machines. Two of the most common neutralizing cations are sodium ( $\text{Na}^+$ ) and zinc ( $\text{Zn}^{2+}$ ). The properties of sodium-neutralization and zinc-neutralization are different; sodium ionomer absorb significantly more water and tend to have higher fractional crystallinities than zinc ionomers.

Zinc-neutralized [Leewajanakul *et al.* (2003)] and sodium-neutralized [Lahor *et al.* (2004)] ionomers have been extensively studied in previous work as blend compatibilizers for the polyamide-PE system. It has been repeatedly shown that the addition of compatibilizers increase compatibility between the two components, including improvements in mechanical properties, barrier properties, as well as smaller dispersed domain size.

Another polymer widely used is polypropylene (PP). As a textile fiber, PP has outstanding physical, chemical, and mechanical properties. However, the fiber is not dye-able with existing classes of dyes because of the lack of polar sites in the molecular structure. One recent method for producing dye-able polypropylene fiber is by adding nanoparticles into the polymer, to act as dye sorbers. Preference is given to nanoclay (sodium bentonite) rather than other nanoparticles because of its common availability at good quality and low price. Moreover, nanoparticles can enhance the physical and thermal properties of polymer.

This research deals with the compatibility of PA6/LDPE blends, induced by hydrogen bonding and ionic bonding, between polyamide6 (PA6) and sodium-, zinc-, or lithium-neutralized ethylene-co-methacrylic acid. Two systems are investigated: PA6 high content is PA6 80: LDPE 20 and LDPE high content is PA6 20: LDPE 80. For PA6 high content, this phase has many PA6 functional groups to react with the ionomer functional groups and for LDPE high content, this phase has fewer PA6 functional groups to react with the ionomer functional groups. It is interesting to understand the effect of neutralization and content level on the improvement of compatibility between blends of PA6 and LDPE. Therefore, ionomers have been added into the PA6/LDPE blends and the compatibility of the PA6/LDPE blends is determined by scanning electron microscopy, dynamic mechanical thermal analysis, differential scanning calorimetry, mechanical testing, and rheology. This study expands significantly what was done in a previous study because different neutralization levels are investigated, and the starting copolymer resins are identical. After that the sodium ionomer will be used to enhance the compatibility between the polypropylene and organomodified clay.

For the first step, blends of polyamide 6 and low-density polyethylene compatibilized with sodium-, zinc-, and lithium-neutralized ethylene-methacrylic

acid ionomers were investigated for their thermomechanical, mechanical, morphological and crystallization properties at 11, 33, 55 wt% neutralization of the ionomer.

For the second part, the melt properties (e.g. shear viscosity, power law index and elongational viscosity) were determined. The viscosity should be a measure of the amount of reaction between the PA6 and the ionomer. The relationships among flow activation energy, die swell, and blend compatibility were also investigated

In the third step, the sodium ionomer was selected as a compatibilizer for the nanocomposite of polypropylene and an organoclay. The effect of draw ratio on mechanical properties and dye ability of the polypropylene-organoclay nanocomposite fiber was studied.