



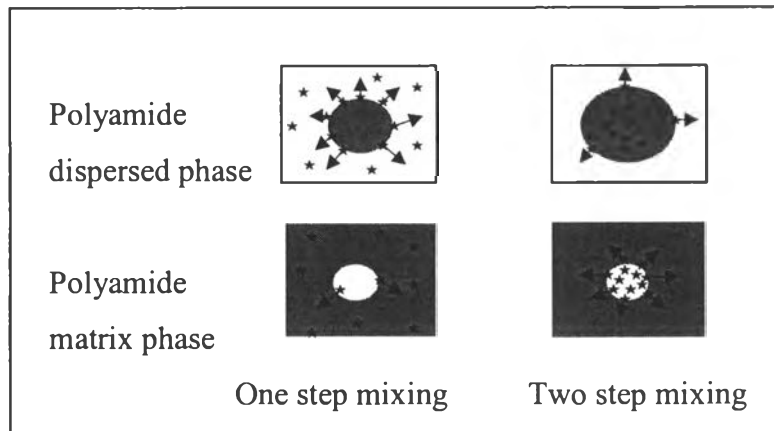
## CHAPTER II LITERATURE SURVEY

### 2.1 Ternary Blends of PA/PE/Compatibilizers

Blends of PA/PE have been studied for almost two decades. Research work showed that PA and PE are incompatible and many attempts have been made to improve the compatibility of the blends by using both chemical and mechanical means. Chemical compatibilization has attracted wide interest, and thus many types of compatibilizers have been studied to improve the compatibility of PA/PE blends.

In 1988, Willis and Favis determined the emulsifying effect of an ionomer (polyethylene-methacrylic acid-isobutyl-acrylate terpolymer) on the morphology of polyolefin/polyamide blends. They found that the concentration of an ionomer compatibilizer strongly influences the morphology of the blends. A maximum reduction in dispersed phase size was observed when only 0.5 % by weight of ionomer was added to the blend. At high concentrations of the ionomer, flocculation of the PA dispersed phase was observed. In comparison to one-step mixing, blends prepared by two-step or batch mixing were characterized by a smaller dispersed phase when PA was used as the matrix. A larger particle size resulted when PA was used as the minor phase. The findings were explained in term of a speculative model (see Figure 2.1) of the interactions occurring at the PA polyolefin interface.

To improve the properties of PA 6, Raval *et al.* (1991) studied blending PA 6 with LDPE. Binary and ternary blends of PA 6/LDPE and PA 6/LDPE/LDPE-g-butyl acrylate were prepared by melt mixing. The blends were characterized for their various mechanical properties and extent of water absorption. Morphology of the prepared blends was studied by scanning electron microscopy (SEM). It was observed that the use of LDPE-g-butyl acrylate as an interfacial agent improves the impact strength of PA 6 and decreases the water absorption remarkably.



**Figure 2.1** Speculative model of the interactions between the ionomer and (a) the matrix and (b) dispersed phase polymer, during one and two step mixing. The stars represent the ionomer, and the arrows represent figuratively the interactions at the PE/PA interface.

Armat and Moet (1993) studied the effect of compatibilizing PE and PA 6 blends on morphology and mechanical properties. A maleic anhydride functionalized styrene-(ethylene-co-butylene)-styrene block copolymer (MA/SEBS) was added to the blends as compatibilizer. This compatibilizer was found to play a dual interfacial function. It reduces the interfacial tension of the system, resulting in reduction of the particle size of the dispersed PE phase and also enhances the interfacial adhesion through the formation of micro-bridges. The fine PE phase thus coupled to the matrix in compatibilized blends can carry a load and deform co-continuously along with the matrix. This causes extensive yielding of the blend prior to its failure and gives high ultimate elongations. Unexpectedly, for MA/SEBS at contents higher than 10 % the ductility of the blends dropped sharply. This was attributed to flow-induced discontinuities within a large core region in the tensile specimens. The lines of instabilities act as large notches within the specimen, causing brittle failure of the otherwise ductile blend.

Furthermore, the effects of different types of compatibilizer precursors (CP) upon the barrier properties and morphology of PE/PA blends were investigated by Yeh *et al.* (1995). Three alkyl carboxyl-substituted polyolefins, which were 40 % zinc neutralized ethylene/acrylic acid (89/11) copolymer, HDPE grafted with 0.4 %

of maleic anhydride and 70 % zinc neutralized ethylene/methylacrylic acid (96/4) copolymer, were selected to modify PA in a twin screw extruder by “the reactive extrusion” process. The barrier properties of the modified PA, (MPA) were better than pure PA, and the amount of barrier improvement of the blend of PE and MPA depended significantly on the barrier properties of the MPA prepared. The extent of mixing PE and MPA had a significant effect on the barrier properties of blow molded products. Further analysis of the fracture surfaces indicated that a more demarcated laminar structure of MPA dispersed in PE matrix is essential for better barrier properties of PE/MPA blends. It was not completely clear how the type of CP affected the barrier properties of MPAs. However, it was suggested that long PA sequences with shorter grafted CP chains and high normalized grafting efficiency of MPA are essential for preparing a clear laminar structure of MPA with good barrier properties of the PE/MPA blends.

In 1997, Koulouri *et al.* studied the grafting efficiency on different PAs (6, 11, 12, 6,10 and 6,12) of ethylene-glycidyl methacrylate copolymer (PE-g-GMA) and ethylene-ethyl acrylate copolymer with a composition of 85/15 when melt mixed under optimum conditions. Two of these PAs (PA 6 and 11) were selected to be studied in the complete composition range. The blends were characterized using dynamic mechanical analysis, tensile testing, DSC, SEM and FTIR techniques. The results showed that efficient grafting occurred in the case of PA 11/PE-g-GMA blends. The formation of a copolymer was confirmed using solvent extraction techniques. The existence of both polymers in the isolated copolymers was proved by FTIR and thermal analysis. Overall, they confirmed the concept of the compatibilization of PA/PE system in the case of PA 11/HDPE compatibilized by PE-g-GMA.

To compare the influence of chemical and mechanical compatibilization on the structure and properties of PE/PA blends, Jurkowski *et al.* (1998) prepared LDPE/PA 6 binary blends and LDPE/PA 6/compatibilizer ternary blends in a Brabender extruder equipped with a prototype static mixer. Compatibility of the components was assessed from rheological properties (viscosity and melt flow index) and observations of the structure were made by viewing fractured tensile specimens. They found that the blends' structure and properties were dependent on the recipe

content of the polymer blends and the manufacturing conditions. Uniformity 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.

Recently, Sheng *et al.* (2000) studied the compatibility of the two phases (matrix and dispersed phase) in blends of PA with LDPE and ionomer. They examined pressed films of binary blends (PA with LDPE or Surlyn<sup>®</sup>) and ternary blends (PA with LDPE and Surlyn<sup>®</sup> or a graft copolymer of acrylic acid onto LDPE) using dynamic mechanical analysis (DMA), thermally stimulated current (TSC), and small angle X-ray scattering (SAXS). The variation of glass transition temperature for two phases in the blends was studied using DMA and TSC. X-ray scattering from the relation of the phases was analyzed using Porod’s law and led to values of the interface layers in the blends.

In the same year, Hallden *et al.* studied poly(ethylene-graft-ethylene oxide), (PE-PEO) and poly(ethylene-co-acrylic acid), (PEAA) as compatibilizers in blends of LDPE and PA 6. They prepared blends by melt mixing the polymers in a co-rotating, intermeshing twin-screw extruder. The morphology of the blends was studied by SEM. Melting and crystallization behavior of the blends were investigated using DSC, and mechanical properties by tensile testing. The compatibilizing mechanisms were different for the two copolymers and generated two different blend morphologies. Addition of PE-PEO gave a material with small, well-dispersed PA spheres having good adhesion to the PE matrix, whereas PEAA generated morphology characterized by small PA-spheres agglomerated into larger structures. Both compatibilized PE/PA blends had much improved mechanical properties compared with the uncompatibilized blend. Elongation at break increased up to 200 %. Addition of compatibilizer to the PE/PA blends stabilized the morphology against coalescence and significantly reduced the size of the dispersed phase domains.

## 2.2 Binary Blends of PA with Multifunctional Polymers

Much work has been carried out on blends of PA with multifunctional polymers because the chemical reaction or interactions between the amide group and the multifunctional group were expected to enhance the miscibility of blend systems.

Macknight and Lenz (1985) studied the morphological and mechanical properties of binary blends of PA 6, (major component) and ethylene-methacrylic acid copolymers (E-MAA), the minor component. They found that the methacrylic acid content of the copolymer used as the minor component had a profound effect on the properties of the resulting blends. In particular, with increasing methacrylic acid content, the size of the domains of the E-MAA dispersed phase in PA 6 matrix decreased in a regular fashion while the ultimate tensile properties increased regularly. This behavior has been attributed to a series of chemical and physico-chemical interactions taking place between the two components. The interactions are due to the presence of acid functionality of the copolymer and do not occur when this functionality is absent. Chemical analysis of the blends confirmed that chemical modification took place during the blending process.

In the same year, the blends of PA 6 with an ethylene-based multifunctional polymer (CXA 3101, DuPont Co., Ltd.) were studied by Han and Chuang (1985) in terms of rheology-structure relationships. The thermal and thermomechanical behavior of the blends was investigated using DSC and DMA. The chemical structure of the functional groups present in the CXA 3101 was identified using FTIR. Furthermore, optical and scanning electron microscopy was used to investigate the state of the dispersion of the constituent compounds in each of the blends. They found that during melt blending, chemical reactions had taken place between carboxyl or anhydride groups present in the CXA 3101 resin and the amino end groups of PA 6, forming a graft copolymer which acted as an “interfacial agent”.

Fairley and Prud'homme (1987) studied the binary polyethylene/EMA and EMA/PA 6 blends with the hope that the role of EMA, poly(ethylene-co-methacrylic acid containing between 4 and 15 % of methacrylic acid units, as compatibilizer in polyethylene/EMA/PA 6 ternary blends might be better understood. DSC, laser small-angle light scattering, and mechanical property results were discussed. DSC

measurements showed that one component of the binary blends did not modify the crystallinity of the other. However, laser small-angle light scattering showed that the morphology of the mixtures changes under similar condition. Tensile properties of polyethylene/EMA binary blends varied linearly as a function of composition, whereas those of EMA/PA 6 blends deviated slightly from linearity. These results indicated no interaction between the crystalline components of the mixtures, and weak interactions in the amorphous phase.

In order to understand the influence of interfacial modification in PA/ionomer/PP ternary blends, Willis *et al.* (1993) investigated the binary blends of PP/ionomer and PA/ionomer. The ionomer used was a copolymer of polyethylene and of a mixture of methacrylic acid, zinc methacrylate and isobutylacrylate. They found that the PP/ionomer blend is a classic example of an incompatible system which displays a high degree of interfacial voiding, as observed in SEM fracture surfaces, a strong negative deviation from additivity in viscosity/composition relationship and an important coalescence effect on increasing dispersed phase concentration. This blend demonstrated increased nucleation and crystallization rate, compared to pure polypropylene. The second blend, PA/ionomer, demonstrated a very fine multiphase structure evident only after microtoming/etching of the sample, and a strong additive behavior in the viscosity/composition curve. Formation of an amide bond was identified by FTIR. This evidence supports the conclusion that much stronger interactions exist between ionomer and PA than between ionomer and PP.

Furthermore, Molnar and Eisenberg (1993) studied the miscibility of carboxylated and sulfonated polystyrene ionomer with PA 66, PA 610 and PA 11. DSC thermograms of blends of polystyrene ionomers and PA 66 show that lithium sulfonated groups are more effective than lithium or sodium carboxylated groups in enhancing the miscibility between the PA and PS. The miscibility between aliphatic polyamides and the polystyrene ionomer containing 9.8 mol % lithium sulfonate groups decreased as the amide content of PA decreased. Thus, while blends of this ionomer with PA 66 and PA 610 appear miscible by DSC, the blends with PA 11 show evidence of some phase separation. Dynamic mechanical measurements of 50:50 blends of this ionomer with PA 610 and PA 11 confirm the one-phase and two-phase behavior of these blends, respectively.

Dynamic viscoelastic properties of blends of alkali metals salts of sulfonated polystyrene ionomers with PA 6 in the melt were studied by Yoshikawa *et al.* (1994). The blends of lithium-sulfonated polystyrene (10 mol % sulfonation) with PA 6 (LiSPS/PA 6) behaved as a homogeneous viscoelastic fluid over most of the blend composition range, since blending with PA 6 disrupted the ionic network of the LiSPS. Specific interactions between the lithium sulfonate group and the amide group are believed to be responsible for the behavior. By contrast, blends of sodium-sulfonated polystyrene with PA 6 (NaSPS/PA 6) showed typical behavior of immiscible systems in that they exhibited large positive deviations from the log-additivity rule for complex viscosity. This implies that sodium sulfonate groups did not interact strongly with amide groups, in contrast to the behavior with lithium sulfonate groups. Oldroyd's emulsion model (Graebing and Muller, 1990) was applied to the results of dynamic viscoelastic studies of both the immiscible ionomer/PA 6 blends and the PS/PA 6 blends. The fits for the latter blends were much better than for the former. This difference in behavior might be due to partial miscibility or to the presence of an indistinct phase boundary in the "immiscible" ionomer-based systems.

In 1997, Valenza *et al.* studied blends of PA 6 and LDPE functionalized with methacrylic acid derivatives. The PE was functionalized by grafting ester and alcohol groups in a Brabender mixer with methacrylic acid derivatives. These groups induce "compatibilization" effects in the blends with respect to blends made with the unfunctionalized PE. The different effects of morphological, calorimetric, rheological, dielectric and mechanical behavior of the blends of the various functional groups were shown. In particular, the interactions at the interface change depending on the chemical nature of the grafted groups. Ethyl and isobutyl-methacrylate essentially cause dipolar interactions and H bonding whereas hydroxyethyl-methacrylate gives rise to condensation reactions with the functional groups of PA. This blend presents the highest increase in elongation at break.

Kudva *et al.* (1999) investigated blends of PA 6 and polyethylene over a range of compositions. The polyethylenes used were grafted with maleic anhydride and thus had the potential to react with the amine end groups of PA 6 during melt mixing. This study focused on the effects of concentration, viscosity and

functionality of the maleated polyethylenes (PE-g-MA) on the rheological, morphological, and mechanical properties of PA 6/PE-g-MA blends. The impact properties of these blends were strongly influenced by the amount and type of maleated PE used. A low viscosity maleated PE was shown to be ineffective in toughening PA 6; this was because of the propensity of PE to become continuous even when PA 6 was the majority component. Two higher viscosity maleated PEs were able to produce blends with high impact strength and excellent low temperature toughness over a range of compositions.

Recently, blends of PA 6 and polyolefins functionalized with acrylic acid (polyethylene-PE-AA, polypropylene-PP-AA) were investigated by Psarski *et al.* (2000) in terms of crystallization behavior and PA 6 crystalline structure. Thermal analysis showed that in the case of blends with functionalized polyolefin as a matrix: (a) PA 6 crystallization is spread and dramatically shifted toward lower temperatures, approaching that of the olefin component, 125-132 °C; (b) PA 6  $\gamma$  crystal polymorph is the major phase present as confirmed and quantitatively evaluated using of deconvolution computations performed on WAXS spectra of the blends.

When PA 6 is dispersed in a functionalized polyolefin matrix, the weight content of PA 6  $\gamma$  crystals increases up to three times with respect to analogous, non-compatible blends, and up to  $\approx 16$  times with respect to PA 6 homopolymer. These phenomena are explained by the reduction of size of PA 6 dispersed particles, caused by the interactions between the functional groups of polyolefin and the polar groups in the PA chain. The nucleation mechanism is changed due to the lack of heterogeneous nuclei in most small PA 6 droplets, which results in enhanced  $\gamma$  crystal formation.

### 2.3 Binary Blends of Ionomer with Other Polymers

Papadopoulou and Kalfoglou (1998) studied the compatibility behavior of melt-mixed blends of a polyester-type polyurethane (PU) with the  $\text{Zn}^{2+}$  ionomer of poly(ethylene-co-methacrylic acid-co-isobutylacrylate) terpolymer in the complete composition range. The analytic techniques applied were tensile testing, DMA, DSC,



FTIR and optical microscopy. Tensile properties were typical of a compatible system and DMA results indicated a miscible blend. FTIR results failed to reveal the nature of the specific forces involved in bringing about compatibilization. Analysis of the thermal data obtained allowed the determination of a polymer-polymer interaction parameter which had a near zero value at the elevated temperature at which it was determined.

## 2.4 Studies for More Understanding on Ionomer Properties

In 1993, Tachino *et al.* studied the dynamic mechanical properties of ionomers based on metal salts (Li, Mg, Na, and Zn) of poly(ethylene-co-methacrylic acid) (EMAA) using a dynamic viscoelastometer. The study reproduced the previous observation (Tadano *et al.*, 1989) that the mechanical relaxation behavior clearly responded to ionic cluster formation and its phase separation from the hydrocarbon matrix. The Li, Mg, and Na ionomer formed ionic clusters at a neutralization of ~ 35 % or higher, and the Zn ionomer did not form ionic clusters at neutralization up to 60 %. However, this work has revealed clear evidence that even the Zn ionomer forms regions of microphase separated ionic clusters at a neutralization of 80 % or higher. A peak, designated as the  $\alpha'$  peak, appeared at ~ 325 K on the loss modulus curve of all EMAA ionomers that form ionic clusters, and the temperature exhibiting this peak proved to be independent of frequency. The order/disorder transition temperature ( $T_i$ ) of the ionic clusters of EMAA ionomers, measured by DSC, agreed with the  $\alpha'$  peak temperature. It was proposed that the  $\alpha'$  peak be regarded as a first-order transition at  $T_i$  and represent the existence of the order/disorder transition in the ionic clusters.

The melt rheology of a series of ethylene-methacrylic acid (E/MAA) ionomers, all based on the same E/MAA copolymer, with emphasis on the low shear rate Newtonian region were examined by Vanhoorne and Register (1996). They found that ionomers show Newtonian behavior at sufficiently low shear rates. The zero-shear rate viscosity,  $\eta_0$ , was found to be a strong function of neutralization level and was significantly higher for Zn ionomers than for Na ionomers at the

temperatures and neutralization level studied, indicating that the ionic associations bear no stress during steady flow in the terminal region. Therefore, the individual ionic associations have lifetimes much shorter than the terminal relaxation times of the polymer chains. They probed the effect of unneutralized acid groups on  $\eta_0$  by removing these groups through esterification. Unneutralized acid groups substantially lowered the viscosity of Na ionomers but had no discernable effect with Zn ionomers. An “acid/cation exchange” mechanism was proposed to explain these findings.

Recently, a series of zinc-neutralized ethylene/methacrylic acid ionomers were studied using X-ray absorption spectroscopy by Grady *et al.* (1999). Neutralization methodology, neutralization level and methacrylic acid content were varied to test whether any of these factors affected the local environment of the zinc cations. Three different neutralization methods were investigated: melt neutralization with zinc oxide, melt neutralization with zinc acetate, and solution neutralization with zinc acetate. Neutralization levels varied between 25 and 100 % stoichiometrically, and methacrylic acid contents were varied between 10 and 20 % by weight. Samples were prepared and handled to rigorously exclude water. Despite the substantial differences in sample preparation procedures, the local environments around the zinc atoms were found to be identical for all materials, resembling the arrangement of the atoms in the crystal structure of monoclinic anhydrous zinc acetate. In this compound, four oxygen atoms surround the zinc atom with distances ranging from 1.950 to 1.965 Å .