

CHAPTER II

LITERATURE REVIEW



2.1 Binary Blends of Nylon with Multifunctional Polymers

During the past two decades, there have been numerous attempts to improve the compatibility of Nylon and polyethylene blends. Many different compatibilizers that proved useful for blends of polyamide 6 with polyethylene have been described in the following research works, as showed below.

Macknight and Lenz (1985) studied the binary blends of nylon 6 as the major component and ethylene-methacrylic acid copolymer (E-MAA) as the minor component. Increasing the methacrylic acid content in E-MAA, lead to decrease the particle size of the dispersed phase yielded an improvement in the morphology and the mechanical properties of these blends. These behaviors have been attributed to a series of chemical and physico-chemical interactions such as hydrogen bonding taking place between the two components. But the present of the polyethylene component in the polyamide matrix did not affect its thermal properties.

The same system was more thoroughly examined by Fairley and Prud'homme (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. DSC measurements showed that one component of the binary blends does not modify the crystallinity of the other and indicate that 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 and of a mixture of methacrylic acid, zinc methacrylate and isobutylacrylate. The PA/ionomer blends demonstrate a very fine multiphase structure evident only after microtoming/etching of the sample, strong additive behavior in the viscosity/composition curve. Formation of an amide bond was identified by FTIR. This evidence supports the conclusion that there are some interactions exist between the ionomer and the polyamide. DSC data showed that the maximum crystallization temperature of the PA/ionomer blends decreased with ionomer concentration. These concurs with the increase in the half time of the

crystallization and indicates that the ionomer is interfering with the crystallization of the polyamide in these blends.

Addition of small amounts of suitable ionomer (up to 5 wt%) remarkably increase the melt viscosity of polyamide m×D,6 (PA) (Degée *et al.*, 1997). By blend PA with random copolymer of methyl methacrylate-methacrylic acid (P(MMA-co-MAA)) and the related ionomers (P(MMA-co-metal MA)), respectively at 200°C and at low shear rate. The PA melt viscosity increase with the cation as follows: $Ni^{2+} < Ba^{2+} < Mg^{2+} < Li^{+} < Na^{+} < K^{+} < Cs^{+}$. The major effect is believed to occur when polymer compatibility is improved to the point where a finely dispersed two-phase system with low interfacial tension is reached, as a result of strong ion-dipole interaction.

In the same year, Koulouri *et al.* (1997) investigated the grafting efficiency on different nylon (6, 11, 12, 6,10 and 6,12) of ethylene-glycidyl methacrylate copolymer (PE-g-GMA) and ethylene-ethyl acrylate copolymer (PEEA). The most efficient grafting occurred in the case of nylon 11/PE-g-GMA blends, which are semi-compatible because of the long segment of methylene units in the main chain of nylon 11. In case of nylon6/PE-g-GMA blends crystallinity does not vary with blend composition. This blend can be used as compatibilizers for the PA/PE system. This was confirmed in the case of nylon 11/HDPE/PE-g-GMA ternary blends.

A related work dealing with the blends of polyamide 6 (PA6) and linear low-density polyethylene (LLDPE) has been reported by Valenza *et al.* (1997). The LLDPE was functionalized grafting with ethylene-, isobutyl-, and hydroxyethyl-methacrylate. The different functional groups grafted on the LLDPE do not affect the thermal behavior of the polymer, except for the enthalpy values (ΔH_c) when a marked decrease is observed for blend PA6/LLDPE-g-hydroxyethyl-methacrylate. This system shows highest improvement in the compatibilization because it was assumed that in this blends chemical reactions involving hydroxyl groups were occurred during melt mixing, whereas only dipole and hydrogen bonds were believed to be present in the other two blends.

The thermal stability of blends of nylon 6 with polyolefins that contain acrylic acid was studied by Lamas *et al.* (1998). They focus 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 the samples and both qualitative and quantitative analysis were made in order to evaluate the thermal stability of the materials under investigation. The results indicate that when there are strong molecular interactions between the polymers to be mixed (and therefore strong interfacial activity), the thermal stability in the blends can be increased with expected in view of a simple additive rule of mixing and synergistic effects can be produced.

The melt-mixed of polyester-type polyurethane (PU) with the Zn^{2+} ionomer of poly(ethylene-co-methacrylic acid-co-isobutylate) terpolymer (Ion, Zn^{2+}) blends are compatible throughout their composition range (Papadoulou and Kalfoglou, 1998). DMA and DSC results support the view that the amorphous components of the blend are miscible. Miscibility seems to be less favoured at rich PU compositions and it may be mostly attributed to dipole-dipole and hydrogen bonding interactions.

Kudva *et al.* (1999) investigated the blends of polyamide and polyethylene grafted with maleic anhydride (PE-g-MA), thus have the potential to react with the amine end groups of PA6 during melt processing. The mechanical properties of PA6/PE-g-MA blends are improved when uses polyethylene materials containing a very low degree of anhydride functionality, which is the high viscosity PE-g-MA. A brief portion of this study focused on ternary blends of PA6/PE-g-MA/PE; in general, the impact properties of these blends improved as the PA6 molecular weight increased and as the ratio of PE-g-MA to PE increased.

Crystallization behavior and 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 is spread and dramatically shifted toward lower temperatures, approaching that of the polyolefin component 125-132°C; (b) PA6 γ crystal polymorph is the major phase present; confirmed and quantitatively

evaluated by use of deconvolution computations performed on WAXS spectra of the blends.

When PA6 is dispersed in functionalized polyolefin matrix, the weight content of PA6 γ crystal increases up to three times respect to analogous, non-compatible blends and up to ≈ 16 times with respect to PA6 homopolymer. These phenomena are 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 polyamide chain. The nucleation mechanism is changed due to the lack of the heterogeneous nuclei in most small PA6 droplets, which results in the enhanced γ crystal formation.

By DSC and WAXS tests Minkova *et al.* (2002) have revealed 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) (Escor) and ethylene-glycidylmethacrylate copolymer (Lotader) blends. The fine dispersed compatibilizer particles in PA6/compatibilizer blends crystallize at large supercooling exhibiting low degree of crystallinity and perfectness. PA6 or LDPE in the presence of the compatibilizer crystallize into spherulites with dimensions smaller than those of the corresponding neat polymers. The X-ray measurements demonstrate that there are no interactions in the crystal phase or no co-crystallization occurs between the components in the PA6/compatibilizer blends. The functionalized polyethylenes Escor/Lotader interact with the polar groups of polyamide chain giving rise to the formation of a copolymer, the Escor has higher compatibilization efficiency than Lotader, which can act as a compatibilizer for the matrix PA6 phase. On the contrary, only physical interactions proceed between LDPE and the compatibilizers.

More recently, many behaviors of the blends made with PA6 and ethylene acrylic acid copolymer (EAA) containing different amount of acrylic acid were investigated by Valenza *et al.* (2002). Acrylic acid causes a compatibilizing effect between polyamide and polyethylene components with modifications of blend morphology and mechanical behavior. These effects are enhanced with increase of the acrylic acid content in the copolymer and they are attributed generally to

hydrogen bond interactions among the acrylic acid groups and the functional groups of polyamide.

2.2 Ternary Blends of Nylon/Ionomers/Polyethylene

Willis and favis (1988) reported on the application of polyethylene-methacrylic acid-isobutyl acrylate terpolymer as an ionomer compatibilizer for polyolefin/polyamide blends. The maximum reduction in phase size was observed when only 0.5% by weight of 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, hydrogen bonding, which exist between the ionomer and polyamide. FTIR spectra showed that no evidence of such graft reactions, as a result of amidation reactions taking place during melt mixing, was observed for binary blends of the ionomer and nylon. This is probably due to the fact that the ionomers are neutralized by zinc, the salt form of the acid would thus inhibit the amidation reaction.

The other type of compatibilizer which is used with polyethylene/polyamide blend is a maleic anhydride functionalized styrene-(ethylene-co-butylene)-styrene block copolymer (MA/SEBS). Armat and Moet (1993) found that this compatibilizer stabilizes the cold-drawing of the blends by coupling the deformation phase through “micro-bridging” mechanism. Formation of these micro-bridges, as well as the fine PE particles, is suggested to be due to the reduced interfacial tension and also enhances the interfacial adhesion upon addition of MA/SEBS. DSC analysis showed that the crystallinity of these blend decrease with an increasing amount of compatibilizer. In the melt, the MA/SEBS interaction with the evolving PE droplets through van der Waals bonding between the PE chain and the ethylenic segment of the MA/SEBS. The interaction with nylon probably occurs due to hydrogen bonding involving the amide of the nylon and the carbonyl of the anhydride.

Yeh *et al.* (1995) reported a systematic investigation on the effects of type of compatibilizer precursors (CP) 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 “reactive extrusion” process. The barrier property of the modified PA (MPA) was better than pure PA, and 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 has a significant effect on its corresponding barrier properties. 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 is not completely clear how the type of CP added affects the barrier properties of MPAs. However, it is suggested that long PA sequence with shorter grafted CP chain and high normalized grafting efficiency of MPA are essential for preparing a clear laminar structure of MPA, and a good barrier properties of PE/MPA blends.

Sheng *et al.* (2000) prepared binary blends (PA/LDPE or Surlyn[®]) and ternary blends (PA/LDPE/Surlyn[®] or LDPE-g-AA). Dynamic mechanical analysis (DMA) and thermally stimulated current (TSC) indicated the incompatible of PA6/LDPE binary blends but for the binary blends of PA6/Surlyn[®] and the ternary blends of PA6/LDPE/LDPE-g-AA are semi-compatible. Clearly, the reaction may take place between the ester groups of the ionomer Surlyn[®] (or AA in LDPE-g-AA) and the terminal amino groups of PA6 during melt mixing (shown in figure 3.). It has been proved at the interface range and the interface layer thickness (σ_b) of the two phases in the semi-compatible blends was calculated by small-angle X-ray scattering (SAXS).

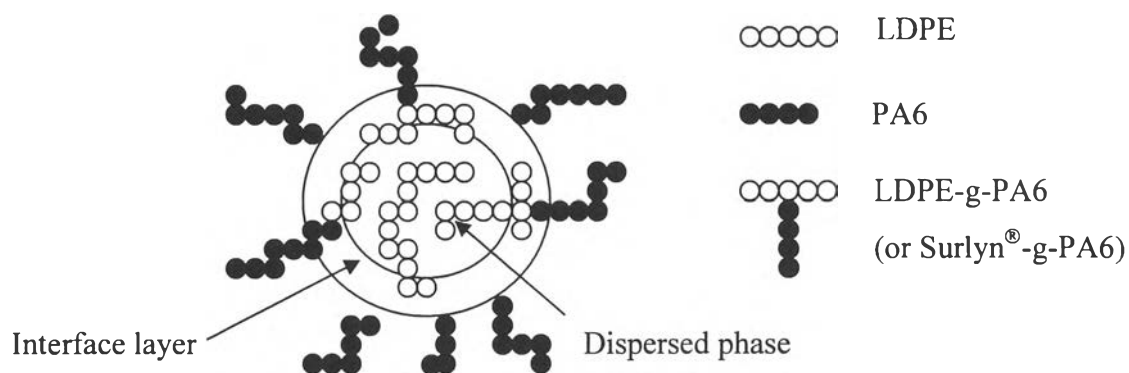


Figure 2.1 Surlyn[®]-g-PA6 (or LDPE-g-PA6) acts as an interfacial agent for the PA6/LDPE blend system.

The morphology and thermal properties of blends of LDPE and PA6 with two poly(ethylene-graft-ethylene oxide)s (PE-PEO) as compatibilisers were investigated by Halldén *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. The morphology of the blends was studied by SEM. Addition of PE-PEO2000 to the PE/PA6 blends decreased the size of the dispersed phase domains significantly 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, the blend formed a morphology with two continuous phases. Addition of 4% PE-PEO2000 to this blend improved the adhesion between the phases significantly.

More recently, Leewajanakul *et al.* (2003) studied the effect of the composition on the morphologies and properties of uncompatibilized and compatibilized blends of nylon 6 and low-density polyethylene over a wide range of weight fractions. The uncompatibilized blends had substantially reduced mechanical properties after mixing, and this was almost certainly due to poor interfacial adhesion between the two polymers. The addition of a zinc-neutralized poly(ethylene-co-methacrylic acid) ionomer (Surlyn[®] 9020) as a compatibilizer improved the mechanical properties in comparison with those of the material blended without the compatibilizer. The clearest evidence of this improvement came from dynamic mechanical studies; 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 due to the interaction between the ionic part of the ionomer and the amide groups of nylon 6, especially when nylon 6 was the dispersed phase of the blend.

2.3 Ionomers

Ionomers are the thermoplastic polymers containing a small mole fraction of ionic groups. The most common commercial type of ionomer is marketed by DuPont

under the trademark Na-EMAA[®]. Na-EMAA[®] is a family of ethylene methacrylic acid (E-MAA) copolymer, in which part of the methacrylic acid is neutralized with metal ions such as zinc (Zn^{2+}) or sodium (Na^+). The resulting polymer structure has three regions: amorphous polymer, crystalline polymer, and ionic clusters. This resultant ionic groups tend to aggregate to form domains which act as physical crosslinks for the polyethylene. However, the domains break down on heating (shown in Figure 2.2.), so the material may be melt processed as other thermoplastics.

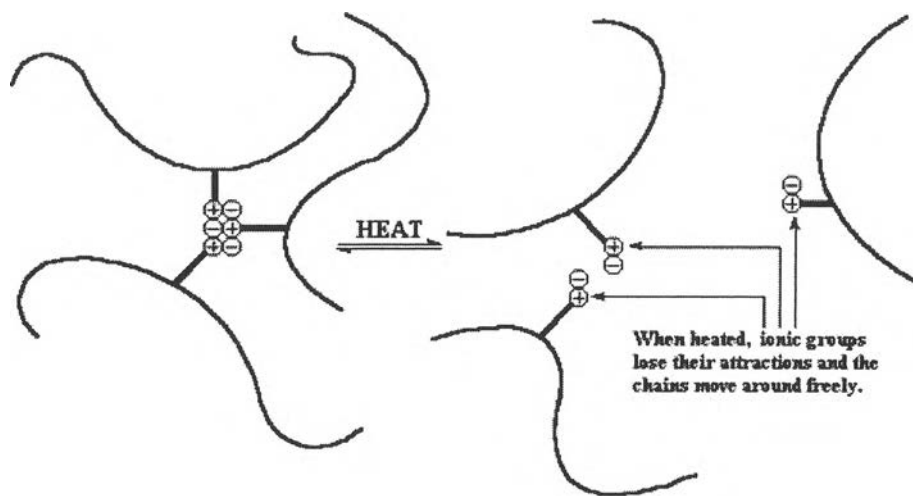


Figure 2.2 Reversibility of the crosslinks of ionomers.

Commercial grades of Na-EMAA[®] are available in approximately 25 different grades. They vary in ion type, molecular weight, crystallinity, and acid content. The structure of this ionomer is shown in Figure 2.3.

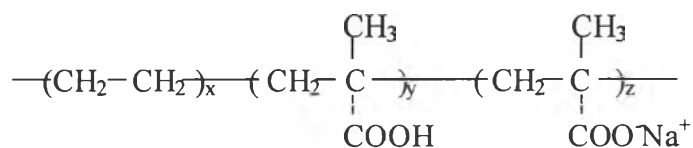


Figure 2.3 Structure of sodium-neutralized ethylene-methacrylic acid (Na-EMAA) ionomers.