



CHAPTER II

LITERATURE REVIEW

Over recent decades, the importance of polymer blends has increased tremendously. As the need for new and more advanced plastics has been continuously growing, many researchers tried to develop new materials by combining well-known polymers together. Polyamides and polyethylene are two important classes of well-known polymers. PA/PE blends are prepared in an attempt to retain the most desirable properties of both polymers. A number of research works showed that PA/PE form immiscible blends. An attractive way to improve compatibility of these blends is to add a third component as a compatibilizer. The thermal properties, crystallization behavior, and morphology of the PA/PE blends are of great importance in polymer processing and applications. Thus, much of the related research works studied the influence of interfacial modification on thermal properties, crystallization behavior, and morphology of the immiscible blends.

Macknight and Lenz (1985) analyzed the morphology of binary blends of PA6, as the major component, and ethylene-methacrylic acid copolymer (EMA), as the minor component. They found that by increasing the methacrylic acid content, the size of the domains of the ethylene-methacrylic acid copolymer in the PA6 matrix decreased. This behavior was attributed to a series of chemical and physio-chemical interactions taking place between the two components. The interactions were due to the presence of acid functionality on the copolymer during the blending process.

To study interactions between blends, Gary and Robert (1987) studied PE/EMA, and EMA/PA6 blends with the intent that the role of EMA as a compatibilizer in PE/EMA/PA6 ternary blends might be better understood. Differential scanning calorimetric (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 changed under similar conditions. These results indicated that no interaction took place between the crystalline components of the mixtures, but that there were weak interactions in the amorphous phase.

Eisaku *et al.* (1989) investigated the formation of ionic crystallites and their effect on the modulus of ethylene ionomers. Modulus, thermal properties, and dynamic mechanical properties were studied for Zn (II) salts, complex Zn (II) salts with 1,3-bis(aminomethyl) cyclohexane (BAC), and BAC salts of EMA. There was an outstanding increase in modulus as the degree of neutralization increased with aging at room temperature. The increase in modulus with aging was explained as being due to the formation and development of ionic crystallites in ionic clusters in a relaxation process. They found that the dramatic increase in modulus on ionomerization was due to cross-linking of the ionic crystallites. The formation and nature of the ionic crystallites depends on the type of salts predominantly governing the stiffness of the ethylene ionomer. In the same year, Kenji *et al.* (1989) observed order-disorder transitions of ionic clusters in ionomers. Thermal expansion and DSC tests were made for the complex Zn (II) salts with The BAC of EMA to clarify the structure and transition of the ionic clusters. It was found that the ionic clusters were ordered assemblies of ionic groups (ionic crystallites) and showed an order-disorder transition of first order near 330 K below the melting point of the crystallites of the polyethylene regions. The transition of ionic clusters underwent a thermal hysteresis, which was explained by a relaxational process from an ordered state to a disordered state.

Byung *et al.* (1991) investigated the thermal properties and morphologies of melt blends of PE/PA6, PE/PA6/maleic anhydride-g-polyethylene (g-PE) and g-PE/nylon. It was found that g-PE is an effective compatibilizer for the PE/PA6 blends, especially in PE-rich compositions. Compatibility was greatly improved in g-PE/nylon blends, and the results were interpreted in terms of possible chemical reactions between g-PE and nylon.

The effect of compatibilizing PE and PA6 on the morphology and mechanical properties of their blends was investigated in order to get a better understanding of the function of the compatibilizer. Rahim *et al.* (1993) prepared blends of PA6/PE. A maleic anhydride 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. On the one hand it reduced the interfacial tension of the system, resulting in a reduction

in particle size of the dispersed PE phase. On the other hand it enhanced the interfacial adhesion through the formation of micro-bridges. The fine PE phase thus coupled to the matrices in the compatibilized blends could carry load, resulting in deformation of the co-continuous phase along the matrix phase. This cause extensive yielding of the blend prior to its failure and high ultimate elongations. Unexpectedly, at MA/SEBS contents higher than 10%, the ductility of the blends dropped sharply. This was attributed to flow-induced discontinuities within large areas in the tensile specimens. The regions of instabilities acted as large notches within the specimen, causing brittle failure of the otherwise ductile blend.

Willis *et al.* (1993) studied the influence of interfacial modification in PA/ionomer/polypropylene (PP) ternary blends. Two binary blends were chosen, PP/ionomer and PA/ionomer, where the ionomer was a copolymer of PE and of a mixture of methacrylic acid, zinc methacrylate and isobutylacrylate. The PP/ionomer blend was an incompatible system and displayed a high degree of interfacial voiding as seen in SEM fracture surfaces. There was a strong negative deviation from additivity in the viscosity/composition relationship and an important coalescence effect on increasing the dispersed phase concentration. This blend exhibited increased nucleation and crystallization rate compared to PP. The second blend, PA/ionomer, gave 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 Fourier transform-infrared spectroscopy. This evidence supported the conclusion that much stronger interactions exist between the ionomer and polyamide than between ionomer and the PP due to chemical bonding via amine groups and carboxylic groups.

Haipeng *et al.* (1998) investigated the phase morphology and thermal stability of PA1010/polystyrene (PS) blends compatibilized by sulfonated polystyrene (HSPS) and their zinc salt (ZnSPS). It was found that the addition of ionomer had an improved effect on phase morphology of the resulting blends. The HSPS was a more effective compatibilizer than the ZnSPS due to its low melt viscosity and less self-agglomeration in the PA matrix. DSC results showed that with increasing ionomer content the amount of the less perfect crystals of PA

increased in the blends and, hence, led to only a small increase in crystallinity of the PA phase. The crystallization rate of PA in the resulting blends increased slightly by the ZnSPS but decreased by the HSPS, which was probably due to the nucleation effect of ZnSPS for PA but no nucleation with HSPS.

The effect of ionic aggregates was analyzed by Prince Antony (1999). Ionomeric polyblends based on a zinc salt of maleated EPDM rubber (Zn-mEPDM) and a zinc salt of poly(ethylene-co-acrylic acid) (Zn-PEA) in the composition range 90/10, 80/20, 70/30, 60/40, and 50/50 parts by weight were studied. It was found that the ionomeric polyblends showed synergism in tensile strength, tear strength, and hardness, which was believed to be due to the formation of intermolecular ionic crosslinks, facilitating compatibilization of the blends. The ionomeric polyblends exhibited better physical properties than the corresponding nonionomeric polyblends. Dynamic mechanical thermal analysis showed a high temperature transition due to the presence of a rigid phase arising out of the restricted mobility regions of the polymer chains adjacent to the ionic aggregates.

In order to gain an understanding of the chemical interactions occurring between components, Lamas *et al.* (1998) studied the effect of interfacial interactions on the thermal stability of PA6 blended with (i) polypropylene (iPP), (ii) polypropylene grafted with 6% by weight acrylic acid (iPP-AA), and (iii) a random copolymer of ethylene and acrylic acid with 8% by weight acrylic acid (iPP-AA). The results indicated that when there were strong intermolecular interactions between the polymers being mixed (and therefore strong interfacial activity) the thermal stability in the blends could be increased with respect to the values expected from a simple additive rule of mixing, i.e. synergism was observed.

Albano *et al.* (2001) studied the thermal decomposition of PA66/high-density polyethylene (HDPE) blends using dynamic thermogravimetry. The results for activation energy showed that PA66/HDPE blends had similar thermodegradative properties to that of PA. These blends would represent an economically viable alternative way to obtain materials having good thermal properties at low cost.

Psarski *et al.* (2000) determined crystal phases and crystallinity of PA 6/functionalized polyolefin blends of PA6 and polyolefins functionalized with acrylic acid (polyethylene-PE-AA, polypropylene-PP-AA). Crystallization behavior and the

resulting PA6 crystalline structures were evaluated. Thermal analysis showed that in the case of blends with functionalized polyolefin as a matrix: (a) PA6 crystallization dramatically shifted toward lower temperatures, approaching that of the polyolefin component, i.e. towards 125-132 °C and (b) PA6 γ crystal polymorph was the major phase present (confirmed and quantitatively evaluated using deconvolution computations performed on WAXS spectra of the blends). When PA6 was dispersed in a functionalized polyolefin matrix, the weight content of PA6 γ crystals increased up to three times with respect to analogous, non-compatibilized blends and up to ~ 16 times with respect to PA6 homopolymer. These phenomena were explained by the reduction in size of the PA6 dispersed particles, caused by the interactions between the functional groups of polyolefin and the polar groups in the polyamide chain. The nucleation mechanism changed due to the lack of heterogeneous nuclei in most small PA6 droplets, resulting in enhanced γ crystal formation.

Recently, Angélica *et al.* (2001) studied the compatibility promoted in PA6 and ultra low-density polyethylene (ULDPE) blends by grafting polar groups onto the ULDPE. Several blend compositions were prepared in a twin-screw extruder. The grafting agent was diethylmaleate. Compatibility was evaluated by studying the morphology and thermal properties of the blends. Thermal properties showed changes due to compatibilization. For instance, fractionated crystallization of the PA6 component was observed when it formed the dispersed phase in reactive blends due to enhanced dispersion. Nucleation of the ULDPE component by PA6 component was observed for both reactive and non-reactive blends. DSC tests showed the presence of two crystalline forms of PA6 in the blends. These were the less stable γ -form (more predominant) and the more stable α -form in reactive blends, especially for the 20/80 and 50/50 wt % blend compositions. Dynamic rheometric tests showed T_g depression, which could be due to the plasticization effect resulting from the substitution of intramolecular PA6 hydrogen bonds with water molecules, or by physical interactions across the interphases.