

CHAPTER II

LITERATURE REVIEW

2.1 Blends of PA/PE with Compatibilizers

Over recent decades the importance of polymer blends has been studied. One of them was a PA/PE blend. This blend was incompatible, and many researches have been studied to improve the compatibilization of PA/PE blends using the functional reactive groups on the polyolefin chains.

In 1988, Willis and Favis studied the effect of an ionomer compatibilizer on the morphology of polyolefin/polyamide blends. The morphology of compatibilized polyolefin/polyamide blends was found to be significantly dependent on the concentration of an ionomer compatibilizer (polyethylenemethacrylic acid-isobutyl acrylate terpolymer) in the blend. For a dispersed phase content of 10% by weight, a 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 phase size was observed when the minor phase was polyamide, due to interaction, which exists between the ionomer and the polyamide. These interactions have been confirmed by Fourier transform infrared spectroscopy. At high concentrations of the ionomer, flocculation of the polyamide 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 polyamide was the matrix and a larger particle size when polyamide was the minor phase. The results observed were explained in terms of a speculative model of the interactions occurring across the polyamide -polyolefin interface.

Armat and Moet (1993) investigated the effect of compatibilizing polyethylene and polyamide 6 on the morphology and mechanical properties of their blends. 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. It reduced the interfacial tension of the system, resulting in reduction of the particle size of the dispersed polyethylene phase and also enhances the interfacial adhesion through the

formation of micro-bridges. The fine polyethylene phase thus coupled to the matrix in compatibilized blends can carry load and deform co-continuously along with the matrix. This caused 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 drops sharply. This was attributed to flow-induced discontinuities within a large core in the tensile specimens. The lines of instabilities act as large notches within the specimen, causing brittle failure of the otherwise ductile blend.

Silva and Soares (1996) investigate 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 blend, as indicated by the results obtained from DSC studies. The addition of EVASH resulted in a reduced dispersed-phase particle size.

Morphological, calorimetric, rheological, dielectric and mechanical behaviour of blends made with polyamide 6 (PA6) and linear low density polyethylene (PE) were studied by Valenza *et al.* (1997) The PE was functionalized grafting ester and alcohol groups in a Brabender mixer with methacrylic acid derivatives. These groups induced “compatibilization” effects in the blends with respect to blends made with the unfunctionalized polyethylene. The difference effects on the behaviour 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 caused dipolar interactions and hydrogen bonding whereas hydroxyethyl-methacrylate gave rise to condensation reactions with the functional groups of polyamide. This last blend presented the highest increase of the elongation at break.

Jurkowski *et al.* (1998) studied influence of chemical and mechanical compatibilization on 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.

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 scanning electron microscopy and tensile strength. It was found that 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.

Furthermore, 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. The polyethylenes used were grafted with maleic anhydride and, thus, have the potential to react with the amine end groups of polyamide 6 during melt processing. This study focuses 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.

Morphology, thermal behavior, and mechanical properties of PA6/UHMWPE blend with HDPE-g-MAH as a compatibilizing agent was studied

by Yao *et al.* (2000). A functionalized high-density polyethylene (HDPE) with maleic anhydride (MAH) 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). Morphologies of the blends were examined by a scanning electron microscope. This study found that the dimension of UHMWPE and HDPE domains in the PA6 matrix decreased dramatically compared with that of the uncompatibilized blending 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 as high as 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.

Recently, Leewajanakul *et al.* (2003) investigated the use of zinc-neutralized ethylene/methacrylic acid copolymer ionomers as blend compatibilizers for polyamide 6 and low-density polyethylene. The effect of the composition on the morphologies and properties of uncompatibilized and compatibilized blends of polyamide 6 and low-density polyethylene were studied 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 compatibilizers 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 polyamide 6, especially when polyamide 6 was the dispersed phase of the blend.

2.2 Functionalized Polyolefin

Koulouri *et al.* (1997) studied the grafting efficiency on different polyamide (6, 11, 12, 6.10 and 6.12) of ethylene-glycidyl methacrylate copolymer (PE-g-GMA) and ethylene-ethyl acrylate copolymer at a composition of 85/15, when melt-mixed under optimum conditions. Two of this polyamide 6 and 11 were selected to be studied in the complete composition range. Using techniques like dynamic mechanical analysis, tensile testing, differential scanning calorimetry, scanning electron microscopy 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.

Fusion bonding of maleated polyethylene blends to polyamide 6 was investigated by Valdes *et al.* (1998) 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 is also considered. The peel strength of fusion bonded layers of LLDPE/LLDPE-g-MA blends with PA6 strongly depends on bonding time and molecular weight of the maleated polymer. Tensile properties of three-layer 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, infrared (IR) spectroscopy, and thermal analysis (DSC).

Blend of polyamide 6 (PA6) 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 resulting PA6 crystalline structure. 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; (b) PA6 γ crystal polymorph was the major phase present; confirmed and quantitatively evaluated by use of deconvolution computations performed on WAXS spectra of the blends. When PA6 was dispersed in functionalized polyolefin matrix, the weight content of PA6 γ crystals increases up to three times with respect to analogous, non-compatibilized 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 was changed due to the lack of heterogeneous nuclei in most small PA6 droplets, which results in the enhanced γ crystal formation.

In 2001, Sailaja and Chanda studied the use of maleic anhydride-grafted polyethylene as compatibilizer for HDPE-tapioca starch blends. Tapioca starch in both glycerol-plasticized and in unplasticized states was blended with high-density polyethylene (HDPE) using HDPE-g-maleic anhydride as the compatibilizer. The impact and tensile properties of the blends were measured according to ASTM methods. The results reveal that blends containing plasticized starch have 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. Morphologies of the blends was studied by SEM microscopy of impact-fractured specimens of such blends revealed a ductile fracture, unlike blends with unplasticized starch at such high loading, which showed brittle fracture, even with the addition of compatibilizer. In general, blends of HDPE

and plasticized starch with added compatibilizer showed better mechanical properties than similar blend containing unplasticized starch.

Jiang *et al.* (2003) studied reactive compatibilizer precursors for LDPE/PA6 blends. Several home-made and commercially available polyethylene (PE) samples grafted with maleic anhydride (MA) (PE-g-MA) were used as compatibilizer precursors (CPs) for the reactive blending of low density PE (LDPE) with polyamide 6 (PA). Scope of the work was to compare the effectiveness of these CPs with that of a number of ethylene-acrylic acid copolymers (EAA), which had been employed in a previous study for the reactive compatibilization of the same blends, and to get a deeper insight into the coupling reactions producing the PA-g-CP copolymers that are thought to act as the true compatibilizers in these systems. To this end, binary CP/LDPE and CP/PA and ternary LDPE/PA/CP blends were prepared with a Brabender mixer and were characterized by DSC, SEM and solvent fractionation. The results show that the PE-g-MA copolymers react more rapidly with PA than the EAA copolymers and that their CP effectiveness depends critically on the microstructure and the molar mass of their PE backbones. In particular, the CPs produced by functionalization of LDPE was shown to be miscible with this blend component and to be scarcely available at the interface where reaction with PA is expected to occur. Conversely, the CPs prepared from the HDPE grades were immiscible with LDPE and showed better CP 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 succinic 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).