

CHAPTER II

LITERATURE REVIEW

Blend of polyolefins with condensation polymers are extremely interesting not only from a scientific point of view but also for their possible practical applications. However, since the components of these blends are highly incompatible, a compatibilization step is needed in order to obtain materials with properties suited to practical applications. So, the compatibilization of polyamide/polyolefin blends has gained attention in recent years. Many different compatibilizers that proved useful for blends of PA6/PE have been described in the scientific literature, as showed below.

A commonly used method of including compatibility between polyamides and polyolefins is by chemical modification of the polyolefin to contain pendent carboxyl groups, often by grafting maleic anhydride (MAH) or similar compounds, which form chemical linkages to the polyamide via the terminal amino group. While most commonly exploited in reactive blending, the concept has been employed to produce compatibilizers by grafting maleic anhydride on to polyolefin, and then adding the MAH-g-polyolefin as a third component in PA/PE blends.

2.1 Ternary Blends of Nylon/Polyolefin with Multifunctional Polymers

An early example is reported by Armet *et al.* (1993) who added various levels of maleic anhydride functionalized styrene-(ethylene-co-butylene-styrene) block copolymer (MA/SEBS) as the compatibilizers. The objective of this work was to investigate the morphology, mechanical properties and the effect of compatibilizing of polyethylene and nylon6. The result showed that compatibilizer reduces 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. 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. Its interaction

with nylon6 probably occurs due to hydrogen bonding involving the amide of the nylon and the carboxyl of the anhydride. In 1998, Gadekar *et al.* studied the effect of compatibilization on mechanical and dynamic mechanical behavior of blends of nylon6 with very low density polyethylene (VLDPE) (Nylon6/VLDPE). Since, nylon6/VLDPE blends are immiscible and represent two-phase morphology wherein VLDPE is dispersed in the form of spherical domain in nylon6 matrix and exhibit properties that can be further modified using ethylene based copolymer as a compatibilizer. The mechanical properties and impact strength of these blends were poor due to lack of adhesion at the interface. So, addition of compatibilizer containing MAH group resulted in a significant improve the tensile properties whereas impact testing showed no break confirming better stress transfer across the interface. The modification of dynamic mechanical properties using these compatibilizer has been found presence of micro-heterogeneity resulting into merging of tan delta peak into one peak. In the same year, the effectiveness of the mechanical compatibilization by using of prototype static mixer and chemical compatibilization of PA6/LDPE and PA6/LDPE with LDPE-g-MAH as a compatibilizer is reported by Jurkowski *et al.* All blends were characterized by rheological analysis, SEM and tensile properties. The results of these blend showed that the blends' structure and properties are dependent on the recipe content of polymer blends and the conditions of their manufacturing. The rheological properties of the polymer blends strongly depend on their morphology. Mechanical and chemical compatibilization affects the improvement of uniformity of the properties of polymer blend. Lazzeri *et al.* (1999) studied the effect of the addition of VLDPE functionalized with diethylmaleate (DEM) or maleic anhydride (MA) in blends with PA6 obtained by reactive extrusion. A physical and mechanical characterization of blends of PA6 and VLDPE, functionalized with MA or DEM is reported. The results of this work are reported by morphological, thermal and mechanical analysis, with a particular attention to the relationship between phase dispersion and fracture properties. They found that the ductile-brittle transition temperature of the examined blends depend on the type of functional group and test speed.

2.2 Ternary Blends of Nylon/Polyethylene/ Ionomers

Other approaches to enhancing the properties of polyolefin/polyamide blends, various elastomeric polymers containing acrylates (butyl acrylate, methyl methacrylate, etc.), acrylic acid (AA) copolymer as ionomer have been blended in the melt of polyamide and polyethylene. Early studies of polyamide blends with ionomers mainly dealt with PA6 and polyethylene systems and many examples are given in the patent literature viewed by Fairley and Prud'homme (1987) who studied on blends of PA6 and Surlyn 9950 containing 18 wt% methacrylic acid and 5% of the acid groups converted to the Zinc salt. The thermal, morphology and mechanical properties were investigated using DSC, laser small-angle light scattering and tensile measurement. They found that, the melting and the crystallization of one component of the blend was not affect by the second component, as observed from the results obtained from laser small-angle light scattering and DSC. Tensile properties of PE/EMA binary blends vary linear as a function of composition whereas those of PA6/EMA blends very deviate slightly from linearity. From this results indicated no interaction between the crystalline components of the mixtures and weak interaction in the amorphous phase. In the next year, a poly(ethylene-co-methacrylic acid-co-isobutyl acrylate) ionomer was also used as compatibilizer for blends of polyolefin and polyamide (Willis and Favis, 1998). The presence of ionomer (approximately 0.5% by weight of ionomer) in polyamide/polyolefin blends have improved the adhesion between two phases and decrease in diameters of the dispersed phase when the minor phase was nylon, due to the interaction which exist between the ionomer and the PA. These interactions (H-bonding) have been confirmed by FTIR spectra. The results showed that no evidence of such graft reactions was observed for binary blends of the ionomer and PA. This probably due to the fact that more than 70% of methacrylic acid groups of the ionomer are neutralized by Zinc. The salt form of the acid would thus inhibit the amidation reaction. In the work by Grady *et al.* (1999) a series of Zinc-neutralized ethylene-methacrylic acid ionomers were studied using X-ray absorption spectroscopy. Neutralization methodology, neutralization level and methacrylic acid content were varied to test whether any of these factors affected the local environment of the Zinc cation. 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 content 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. Recently, Sheng *et al.* (2000) investigated dynamic mechanical and thermal properties of binary blend (PA6 with LDPE or Surlyn) and ternary blend (PA6 with LDPE and Surlyn or a graft-copolymer of acrylic acid on to LDPE). The miscibility-immiscibility criterion of these blends were evaluated by dynamic mechanical analysis (DMA), thermally stimulated current (TSC), and small-angle X-ray scattering (SAXS). They found that the glass transition temperature (T_g) of nylon6 and LDPE in the blend of nylon6/LDPE did not change, as compared with the pure components. Thereby, the nylon6 and LDPE in this binary blend are incompatible, but the T_g of nylon6, Surlyn (or LDPE-gAA), and LDPE in nylon6/surlyn and nylon6/LDPE/surlyn (or LDPE-g-AA) change with their composition, indicating that all of these blends are semi-compatible. Clearly, the reaction may take place between the ester groups of the Surlyn ionomer (or AA in LDPE-g-AA) and the terminal amino groups of nylon6 during melt mixing.

2.3 Ternary Blends of Nylon/Polyethylene/ Acrylate Copolymer

In the work of Macknight and Lenz (1985). The detailed study was carried out on the morphology and mechanical properties of binary blend of PA6, as the major component and ethylene methacrylic acid copolymer (E-MAA), as the minor component. They found that, with increasing the methacrylic acid content of the copolymer used as the second component lead to decrease in the particle size of the E-MAA disperse phase in PA6 matrix while the morphology and mechanical properties of these blend increased regularly; however, the presence of the polyolefin component in the PA matrix did not affect its thermal properties. These behavior have been attributed to a series of chemical and physico-chemical interaction such as

hydrogen bonding taking place between the two components. A details infrared spectrometric investigation of these blends showed that the enhanced compatibility at higher acid concentration was attributed to amidation reaction occurring between the terminal amine group of the polyamide and the carboxylic acid groups of the copolymer.

Blends of PA6 and LDPE with butyl acrylate grafted LDPE as a compatibilizer were studied by Raval *et al.* (1991). The reaction of the ester groups of butyl acrylate with terminal NH₂ group of the PA6 was detected and as a result a grafted copolymers, which locates at the interface between PA6 and LDPE was formed. The blends were characterized for their various mechanical properties and extent of water absorption. Morphology of prepared blends was studied by SEM. They found that in PA6/LDPE/LDPE-g-BuA blends improve the impact strength. Moreover, water absorption and dispersed phase size decreased when the compatibilizer was added.

The characterization of blends with polyamide6 and ethylene acrylic acid copolymers at different acrylic acid content were studied by Valenza *et al.* (2002). The morphological, calorimetric, rheological, mechanical behavior and fourier transmission infrared analysis of blend were investigated. The results of these analyzes showed that the acrylic acid act as a compatibilizer cause a compatibilizing effect between polyethylene and polyamide component with modification of blends morphology and mechanical behavior. The effect of compatibilization with increase of acrylic acid content in the copolymer presence in the blend is improvement of the morphological, rheological and mechanical properties of the studied materials and they were attributed generally to hydrogen bond interaction among the acrylic acid group and the functional group of the polyamide.

Hallden *et al.* (2000) studied blend of LDPE and PA6 with PE as a matrix and using poly(ethylene-graft-polyethylene oxide)(PE-PEO) as a compatibilizer which is synthesized from poly(ethylene-co-acrylic acid)(PEAA) (backbone) and poly(ethylene oxide) monomethyl ether (MPEO) (grafts). As a comparison, the unmodified backbone polymer, PEAA, was used. These blends were prepared by melt mixing the polymers in a co-rotating, intermeshing twin-screw extruder and were characterized by differential scanning calorimetry (DSC), scanning electron

microscopy and tensile testing. They found that 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 a morphology characterized by small PA-spheres agglomerated to larger structures. Both compatibilized PA/PE blends had much improved mechanical properties compared with the uncompatibilized blend, with the elongation at break increasing up to 200%. Furthermore, Hallden *et al.* (2001) also investigated the morphology and thermal properties of blend of LDPE and PA6 with two PE-PEO as compatibilizers. The copolymers were grafted with molecular weights of 750 and 2000 g/mol, respectively, and with similar total PEO contents (40 and 37%, respectively). The results showed that the PE-PEO2000 graft copolymer was effective as compatibilizer for PE/PA6 blends. The average size of the dispersed phase decreased 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 polymers formed two continuous interpenetrating phases. The addition of 4% PE-PEO2000 to this blend improved the adhesion between the two phases significantly.