



CHAPTER II

LITERATURE REVIEW

The rate of introduction of new polymers into the market place has decreased in recent years owing to the high cost of research to develop new chemistry and processes compare to the probable return on this investment. As a result, increased attention has focus on blends or alloys of existing polymers to expand the spectrum of properties of established products and to meet new market needs. Most polymer pairs are immiscible and, therefore, form separation phases comprised essentially of the pure components when mixed. Unfortunately, for many polymer pairs there is relatively poor adhesion between these phases. Thus, stress transfer across the interface is not good and hence may poor mechanical properties may obtained. This fact often precludes simple blending of polymer pairs which in principle lead to combinations of interesting properties. This situation has led to interest in blend additives which may somehow alter the interfacial problem mentioned above and circumvent the poor mechanical properties. It may be emphasized here that the function of the third component as a compatibilizer is to reduce the interfacial tension between the two phases, promote adhesion between the phase components and stabilize the dispersed phase morphology

2.1 Literature Work

There are several studies in literature in which the addition of a third component acts as a compatibilizer increases the technological compatibility of immiscible polymer pairs. Incorporation of a compatibilizer usually improves the interaction between the constituent homopolymers and thereby slows down the phase separation process (Thomas, 1995).

George (1987) studied the modification of butadiene-acrylonitrile rubber/poly(vinyl chloride) blend using natural rubber, styrene-butadiene rubber, and polybutadiene rubber. They found that natural rubber, styrene-butadiene rubber, and polybutadiene rubber were used to replace part of the butadiene acrylonitrile rubber in a 70/30 %wt butadiene-acrylonitrile rubber/polyvinyl chloride blend. Such replacement up to 15% of the total weight of the blend improved the mechanical properties, while decreasing the cost of the blend. Styrene butadiene rubber could replace butadiene-acrylonitrile rubber up to 30 % of the total weight of the blend without deterioration in the mechanical properties.

Chuan and coworkers (1990) studied on the compatibilization of NR/LLDPE blends with polyethylene-b-polyisoprene diblock copolymer. They have reported that block copolymers are considered as better interfacial agents than graft copolymers because of less effective penetration of the branches of the latter into homopolymer phases. Molecular weight (MW) of the compatibilizer plays a role in the compatibilizing effect on LLDPE/NR blends. Increase in MW of the compatibilizer favored the penetration of PE and PI block of PE-b-PI into the respective homopolymers. They were also found from the dispersion of LLDPE/NR that the size of LLDPE was reduced on adding PE-b-PI because of the emulsifying effect of the compatibilizer.

Kim and Park (1991) had carried out studies on reactive blending of polyamides to improve mechanical and thermal properties. They examined blends of polyamide with styrene-maleic anhydride copolymer (SMA). One aim of this work was achieved with various addition levels of SMA. For example, an increase in heat distortion temperature (HDT) about 12 °C was obtained with the addition of 15% by weight of SMA to PA. Melt viscosity and elasticity of the PA were also increased on SMA addition. All of these effects were attributed to an anhydride-amine reaction occurring between the two materials.

Bonner *et al* (1992) has investigated the reactive blending of maleic anhydride grafted nitrile rubber (NBR) and polyamide 6. Nitrile rubber provides advantages such as good low-temperature performance and excellent oil/hydrocarbon resistance. Maleic anhydride grafted nitrile rubber (MA-g-NBR) was produced by melt mixing MA with NBR in the presence of a free radical initiator. The impact performance of the nylon 6 was further enhanced when the NBR replaced by MA-g-NBR. It was speculated that this might be due to the presence of a high level of grafted MA coupled with a relatively high degree of crosslinking in the MA-g-NBR.

Ahmad and Abdullah (1992) discussed on the mechanical and thermal properties of TPNR for NR-PP-LNR blends of various compositions. Thermal and mechanical properties indicate that such blends are homogeneous at various compositions of blend. It is observed that the yield stress and modulus increase with the amount of LNR. They also discussed that the data indicate a linear dependence of yield stress on strain rate in agreement with the prediction of the Eyring flow model at room temperature (25 °C).

Ahmad *et al.* (1994) had studied NR/HDPE blends at various composition of HDPE with liquid natural rubber as a compatibilizer. They found that the tensile properties and hardness of TPNR improved significantly with the addition of LNR to the blend. The degree of cross-linking also increased with increasing amount of LNR added. They also found that the interphase properties of TPNR could be tailored by varying the composition of the blend and the optimum content of LNR was between 10 and 27%.

Abdullah and Ahmad (1995) investigated the effect of liquid natural rubber (LNR) as a compatibilizer on the physical properties of LLDPE/NR blends. They had found that the optimum processing conditions were a temperature of 135 °C and a mixing of 55 rpm in Brabender internal mixer. The tensile properties, stress and strain, of the blend had improved significantly with the addition of LNR about 10-15 % into the blends. SEM of

the samples also indicated an increase in the homogeneity of the mixtures with the addition of LNR. They further found that a single T_g of about $-55\text{ }^\circ\text{C}$ for the blend was observed via dynamic mechanical analysis (DMA).

Axtell *et al.* (1996) studied on the effect of modified NR compatibilisers on polyamide 6/NR blends. This blend was compatibilised with maleic anhydride modified NR as a third component in the blends. They had found that the blend compatibilization occurred by physical interaction and by chemical formation of in situ copolymers. This chemical compatibilising copolymer (CCC) was verified by the observations from the Molau test and the increased mixing torque. Addition of the compatibilizer gave a higher degree of dispersion, resulting in smaller particle size of the rubber phase. They further concluded that the smaller rubber particles present gave greater toughness to the blends, with improved mechanical properties including Charpy impact strength, tensile strength and elongation at break.

Micic *et al* (1996) studied on the melt strength and elastic behavior of LLDPE and low density polyethylene (LDPE) blends. Melt strength is defined as the force at the break point and is indicative of the relative extensional performance of polymer melts. It is inversely related to the draw-down or extensibility of the melt, i.e. the ability of the melt to be drawn down to thin gauge. They had reported that the melt strength of LLDPE/LDPE blends was dependent on the different molecular structure of parent polymers. It was observed to be related to the melt morphology in such a way that the good melt strength property of a polymer blend was associated with the immiscibility of the blend components. The melt strength test proved to be sensitive enough to verify the melt structure. They also reported that the polymer response to extensional deformation was much more sensitive to differences in molecular structure, or in the case of polymer blends to the differences in melt miscibility, than the polymer response to shear deformation.

Hellmann et al (1996) studied on the effect of block-graft copolymers as compatibilizer in polymer blends. They found that block copolymers could be good compatibilizers in polymer blends, if tailored carefully. However, they were produced by anionic polymerization which was not a versatile technique and, moreover, was expensive. Suitable alternatives were block-graft copolymers, which could be prepared by radical grafting from readily available block copolymers, in particular from S-b-B (S, styrene; B, butadiene). The efficiency of two block-graft copolymers, S-b-B-g-CHMA and S-b-B-g-MMACHMA, cyclohexylmethacrylate; MMA, methyl methacrylate), as compatibilizers in PS/PVC blends of polystyrene (PS) and poly (vinyl chloride) (PVC). Their blend morphologies were investigated by electron microscopy. Both copolymers refine the coarse morphologies of the PS/PVC blends excellently, covering the interfaces between the phase domains of PS and PVC with monolayers. This was accorded to their commonly assumed model of the compatibilizer effect of block copolymers. However, the phase structures were, in fact, even finer than that predicted by the model. This inferred that perfectly compatibilized phase domains were torn apart during mixing in the kneader, whereby the morphology was further refined.

Martin Van Duin (1997) studied the graft formation and chain scission in blends of Polyamide 6 (PA6) and Polyamide 6,6 (PA-6,6) with maleic anhydride containing polymers. They studied four blends, containing PA-6 or PA-6,6 and Ethylene Propylene diene monomer-maleic anhydride (EPDM-g-MA) or poly (styrene-co-maleic anhydride) (SMA, 28 wt% MA) which were prepared and characterized. Chemical analysis showed that the amount of PA graft was independent of the blend composition. For EPDM-g-MA and SMA the MA content of the original MA-containing polymer increased, which corresponded to the blend results which showed an increase in the number of PA grafts and a decrease in the length of the PA grafts. In the SMA blends the

number averaged molecular weight of the grafted PA is only about 200 g/mol. It is postulated that the water molecules, released upon imide formation at the interface of PA/MA-containing polymer were hydrolysed from a PA's amide group, resulting in a new amine end group. The amine group reacted further with the MA-containing polymer and so on. Differential scanning calorimetry showed that the degree of crystallinity of the PA phase was decreased only when the size of the PA phase between the MA-containing polymer domains approaches the PA crystalline lamellar thickness.

Martuscelli (1958) studied the crystallization, morphology, structure and thermal behaviour of nylon-6/rubber blends. An experimental study was carried out in order to investigate the morphological, kinetic, structural and thermodynamic properties of nylon-6/rubber (namely ethylene-propylene copolymer (EPM) and ethylene-propylene copolymer functionalized by, inserting along its backbone, succinic anhydride groups (EPM-g-SA) blends. The morphology and the overall kinetics of crystallization of the blends strongly depended on the type of copolymer added to nylon and on the blend composition. The EPM-g-SA acted as a nucleating agent for the Nylon spherulites and at the same time caused a drastic depression of the overall kinetic rate constant. This decrease related to the increase of the melt viscosity observed in Nylon/EPM-g-SA blends. The crystalline lamellar thickness of the Nylon phase in the blends was lower than that of pure Nylon crystallized at the same T_c suggesting that the presence in the melt of an elastomeric phase disturb the growth of the Nylon crystalline. The rubber did not influence the thermal behavior of the nylon. The results found led to the conclusion that nylon-6 was incompatible with both EPM and EPM-g-SA copolymers.

Lee *at el.* (1995) reported that reactive extrusion of polypropylene (PP)/natural rubber (NR) (90/10) blends was conducted in the presence of a peroxide and coagent (trimethylolpropanetriacrylate, TMPTA).

Effects of peroxide and coagent content were studied in terms of melt index (MI), melt viscosity, morphology, thermal, and mechanical properties. At a constant content of the coagent, melt viscosity increased at a low and decreased at a high content of the peroxide. On the other hand, melt viscosity increased monotonically with the coagent concentration at constant peroxide content. The increases and decreases of viscosity were interpreted in terms of crosslinking and chain scission of PP, which governed the rubber domain size and mechanical properties of the reactive blends.

Nikos (1996) studied the blends of poly (ethylene terephthalate) with unmodified and maleic anhydride grafted acrylonitrile-butadiene-styrene terpolymer. They found that tensile, dynamic mechanical, thermal properties and morphology features of poly (ethylene terephthalate) (PET) blends with the acrylonitrile-butadiene-styrene (ABS) terpolymer were examined up to 25 %wt content of ABS. Both unmodified and maleic anhydride grafted ABS (ABS-g-MA) were used. PET/ABS blends quenched from the melt and tested shortly showed good mechanical properties. The result of component miscibility in melt predicted by the theory provided temporal component adhesion in the solid state. After storage, properties hence deteriorated due to ABS particles debonding and the polymer alloy possessed poor tensile properties. This property deterioration was not observed in PET/ABS-g-MA blends due to the grafting of the modified ABS particles onto the PET matrix. These findings were supported by the optical and mainly by the scanning electron microscopy examination of cryofractured and etched blends.

2.2 Microstructure

Microstructure of materials must be understood in order to develop relationships between the structure and properties of materials. A wide range of electron microscope techniques determines the morphology of polymers. In

polymer blend systems, the micrographs can illustrate the dispersion of dispersed phase and the adhesion between dispersed phase and continuous phase.

Machado (1994) studied the compatibilization of immiscible blends with a mutually miscible third polymer. They four immiscible blend systems, styrene-maleic anhydride/styrene-acrylonitrile(SMA/SAN), styrene-maleic anhydride/acrylonitrile-butadiene-styrene(SMA/ABS), poly(vinylidene fluoride)/SAN (PVF2/SAN), and PVF2/ABS, were investigated. The effect of adding up to about 10 wt%, of a third polymer that is miscible with each blend component, poly(methylmethacrylate)(PMMA), was determined. In every case, the addition of PMMA led to the improvement of properties such as tensile strength, tensile elongation, and notched impact strength. Furthermore, the addition of PMMA resulted in finer, more uniform dispersions of the primary blend components. The experimental results were interpreted in terms of interfacial activity of the common phase component, PMMA.

Chris (1995) studied the processing and morphology of polystyrene/ethylene-propylene rubber reactive and nonreactive blends. The difference between reactive and nonreactive polymer blends, in terms of processing and morphology, had been investigated. The glassy phases for the blends were oxazoline functional polystyrene (PS-Ox) and polystyrene (PS). The rubbery phases were ethylene-propylene rubber (EP) and ethylene-propylene rubber(EP-MA) with 0.7%wt grafted maleic anhydride. In the case of PS-Ox/EP-MA blends, the oxazoline group might react with the grafted rubber functionality at the interface between the two immiscible components during blending to form an *in situ* compatibilizing agent. The nonreactive blend systems of PS-Ox/EP and PS/EP-MA were used for comparison to the reactive system. The blend components were rheologically matched to simplify the interpretation of the process and morphological data. The blends were prepared in a batch mixer with roller blades. The torque required for

mixing was measured during the blending process. The torque traces for the reactive blends exhibited a peak in torque, attributed to the chemical reaction at the interface. The weight fraction of gel in the blends was used to measure the extent of reaction. It correlates well with the mixing torque and rheological properties. The nonreactive PS-Ox/EP and PS/EP-MA blends showed poor interfacial adhesion between the two phases. In contrast, the reactive PS-Ox/EP-MA blends showed excellent adhesion and smaller dispersed domain sizes. The stability of the morphology during annealing is also much greater for the reactive blends. Varying the functionality concentration in the PS phase show that increasing the concentration of oxazoline in the matrix reduced rubber particle size. Blends with no or small amounts of functionality in the PS phase exhibited yield behavior in tension. However, level of concentration of reactive functionality might be reached when the material became brittle.

Zachariah Oommen (1996) studied the compatibilizing effect of natural rubber-g-poly(methyl methacrylate) in heterogeneous natural rubber/poly (methyl methacrylate) blends. They found that the morphology and properties of heterogeneous poly(methyl methacrylate)/natural rubber blends could be by the addition of a graft copolymer of a natural rubber and poly (methyl methacrylate) (NR-g-PMMA). The morphology had been studied as a function of copolymer concentration. A sharp decrease in the dispersed domain size was observed by the addition of a few percent of the copolymer followed by leveling off at higher concentrations. The compatibilizer increases the interfacial adhesion by the formation of micro-bridges between dispersed phase and the matrix. The effects of homopolymer molecular weights, processing conditions, and mode of addition on the morphology of the dispersed phase had been investigated. The experimental results are compared with the theoretical predictions of Noolandi and Hong. Attempts had been made to explain the conformation of the graft copolymer at

the interface. The changes in mechanical properties of the blends as a result of the addition of the compatibilizer were related to the morphology of the blends.

Marco (1997) studied rheological properties, crystallization, and morphology of compatibilized blends of isotactic polypropylene and polyamide. The blends of isotactic polypropylene (iPP) with the polyamide nylon-6 (N6), prepared by extrusion, were studied with a composition of up to 30 % by weight polyamide. In the case of a 70/30 iPP/N6 blend, the influence of a compatibilizing agent based on polypropylene functionalized with maleic anhydride (PP-g-MA), with compositions of 1,3,5, and 10% by weight in polypropylene, was followed. The influence of the concentration of N6 and the compatibilizing agent on the rheological and thermal properties were investigated. And the morphology of the blends, was analyzed by monitoring the melt viscosity at different shear rates; differential scanning calorimetry; and polarized light microscopy. Vibrational spectroscopy was used to characterize the blends and to study the effect of the compatibilizing agent. The viscosity-composition curves for the iPP/N6 blends, in the composition and shear rate ranges analyzed, showed a negative deviation from the additive rule, while that opposite trend is observed for the blends compatibilized with PP-g-MA. Important variations in the spectroscopic behavior was observed between compatibilized and noncompatibilized blends, which varied as a function of the compatibilizing agent concentration. The crystallization rates of iPP in the iPP/N6 blends, under both dynamic and isothermal conditions, were much greater than were those observed for pure iPP and were directly related to the nucleating activity of the polyamide. This effect was reduced in the presence of the compatibilizing agent. The isothermal crystallization of the N6 in compatibilized blends was affected by the presence of iPP; i.e. causing reduction of the crystallization rate of N 6 due to the diluent effect of the polypropylene.

Kroeze (1997) investigated the compatibilization of blends of low density polyethylene and poly (vinyl chloride) by segmented EB(SAN- *block*-E_B)_n block copolymers. They found that hydrogenated segmented poly (butadiene-*block*-((styrene-co-acrylonitrile)-*block*-butadiene))*block* copolymers, which were developed by use of the polymeric iniferter technique, were tested for its compatibilizing capacity for 10/90 %wt LDPE PVC blends. The acrylonitrile content of the SAN blocks of the block copolymers was, as expected, found to be an extremely important factor for their miscibility with the poly(vinyl chloride) phase. When the SAN blocks of the block copolymers had the proper composition. They were excellent agents for the dispersion of the polyethylene phase in the blend into smaller domains. Addition of one percent of block copolymer proved to be sufficient to give a large improvement of the mechanical properties of the blend. These compatibilized blends showed toughness comparable to the virgin poly(vinyl chloride). Scanning electron micrographs showed improved adhesion between the dispersed polyethylene phase and the poly(vinyl chloride) matrix.

Sang Young Lee (1997) investigated the effect of the compatibilizer on the crystallization, rheological, and tensile properties of low-density polyethylene (LDPE)/ethylene vinyl alcohol (EVOH) 70/30 %wt blends. Maleic anhydride-grafted linear low-density polyethylene (LLDPE-g-MA) was used as the compatibilizer in various concentrations (from 1 to 12 phr). Morphological analysis showed that the blends exhibited a regular and finer dispersion of the EVOH phase when LLDPE-g-MA was added. Nonisothermal crystallization exotherms of the compatibilized LDPE/EVOH blends showed the retarded crystallization of the dispersed EVOH phase, which probably resulted from the constraint effect of the grafted EVOH (EVOH-g-LLD) as well as the size reduction of the EVOH domains. The blends exhibited increased melt viscosity and storage modulus and also enhanced tensile properties with the addition of LLD-g-MAH, which seemed

to be attributable to both dispersed particle-size reduction and improved interfacial adhesion.

2.3 Research Objectives

The objectives of this research are:

- To study the effect of NR composition on thermal, morphological, mechanical, flow and heat stability of LLDPE/NR blends
- To study the effect of molecular weight of NR on thermal, morphological, mechanical, flow and heat stability of LLDPE/NR blends
- To study the effect of compatibilizer composition on thermal, morphological, mechanical, flow and heat stability of LLDPE/NR blends
- To study the effect of molecular weight of NR and compatibilizer composition on the compatibility and related properties of LLDPE/NR blends