CHAPTER II

THEORY AND LITERATURE REVIEW

Different polymers blend when together may be miscible, partially miscible, or completely immiscible. General classification of polymer blends are given in Figure 2.1. The methods of blending may be by polymerization blending, latex blending, fine powder mixing and melt blending [2]. The melt blending were employed in this study, which was simply by melting polymers together while blending. Detailed consideration of the rheology of melt blending is given in Section 2.1.
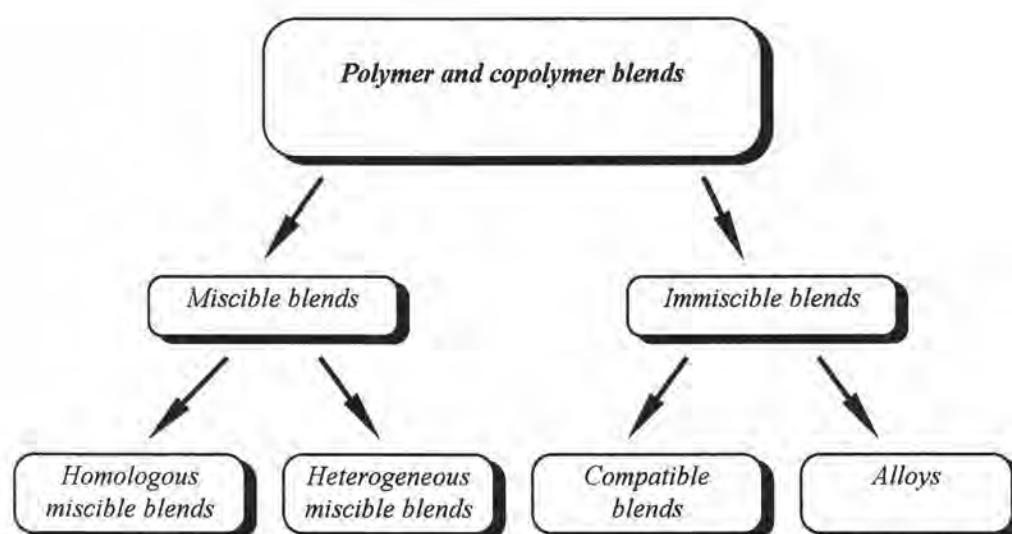
Figure 2.1 Classification of polymer blends [2].

2.1 Melt Blending Process and Morphology of Polyblend

Thermodynamic predicts the temperature and concentration at which phase separation occurs under equilibrium condition. Rheological properties of polymer melts affect the conditions of phase separation. The system with low interfacial tension tends to form compatible blends, examples of these are polyolefin blends such as PE/PP [21] and LDPE/HDPE. Polymer pair with high interfacial tensions, such as PE/PS, will benefit considerably from compatibilization [2].

During melt processing, droplet of polymer will be deformed by hydrodynamic forces leading to elongated and distorted structures. When the mixing process is stopped, e.g. when the polymer melt exits in an extruder, the system is driven thermodynamically to reduce the interfacial tension of the blend by lowering the surface area between the two phases. This process involves motion of the liquid polymers until solidification occurs. As no external forces are driving the process, it is said to be a spontaneous change, full minimisation of the interfacial area does not occur, since the density difference between the two phases is low, and the viscosities are high. The effect upon morphology is that the elongated structures tend to form spheres, or in the case of co-continuous morphologies a coalescing of the structure followed by the formation of large spherical particles. The implications of these are (a) control of the blend system by choice of components and mixing conditions will be hampered by the spontaneous morphological changes that occur after the mixing process has finished, and (b) determination of the effect of mixing conditions upon morphology by analysis of the final article is limited by the spontaneous morphological changes occured upon cessation of the mixing [2].

2.2 Impact Modifiers

The toughness or impact strength of a material depends upon the type of test, specimen fabrication method, temperature, specimen geometry and presence of stress concentration. The presence of an impact modifier enhances the deformation of the metric and promotes yielding, thereby reducing the local stress at the crack tip. Elastomeric materials form the basis of the majority of impact modifier systems [2].
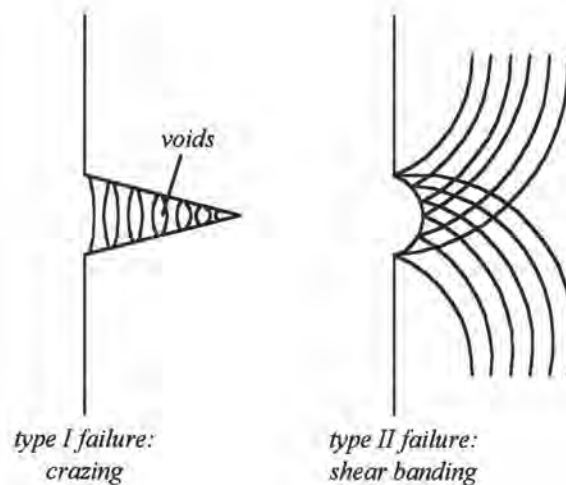

type I failure:
crazing

type II failure:
shear banding

Figure 2.2 Failure mechanisms in polymeric materials[2].

Polymer matrices fail by two different failure mechanisms, shear banding and crazing (see Figure 2.2). Often a combination of the two occurs. The contribution of each mechanism is related to the shear rate as well as the material type. The rubber inclusions modify the way in which the polymeric article fails by creating shear stress at the matrix/modifier boundary that promotes either crazing or shear banding. Since the impact modifier is distributed throughout the matrix, the stress is delocalized and large amount of energy are dissipated. If the impact modifier creates a large amount of crazing, a plastic article may fail. To terminate the failure the modifier must terminate these crazes; if not a large void can form that leads to the formation of a crack and hence failure. The ability of an impact modifier to initiate and terminate crazes is related to the size of its particles when distributed in the base resin. They must be

roughly the same size as the crazes for effectively termination. There must be a large number of distributed particles, i.e. at a fixed volume fraction of impact modifier many small particles. These are required to promote a sufficiently large amount of crazing. A material fail primarily by shear banding it is required that a large amount of democratization of matrix shear yielding occurs, i.e. a large number of particles are required, and hence a small particle size is employed for a given impact modifier loading [2].

2.3 Phase Stabilization

The immiscible blends with stabilized phase structure can be prepared by three techniques including mechanical, physical and chemical compatibilizations. The physical compatibilization is the most widely employed; the methods in this category includes (a) modification of the polymer structure to enhance miscibility by the introduction of groups capable of participating in van der Waal's or hydrogen bonding, (b) controlled crystallisation to "lock-in" the developed morphology, and (c) addition of compatibilizing agents. Copolymers and grafted copolymers as well as functionalised polymers and copolymers can be used as a compatibilizer for the stabilization of phase structures by the method of physical compatibilization. Details of each of the compatibilizer are given subsequently.

2.3.1 Copolymer and Grafted Copolymer

In this approach a blend comprising polymers A and B is modified with a block copolymer of polymers A and B. The polymer A component of the copolymer is soluble in phase A of the blend, whilst the component B is soluble in phase B. The copolymer reduces the interfacial tension, and the size of the dispersed phase will decrease, whilst the thickness of the interphase region will increase. It should be noted that the finest dispersions do not necessarily give the best physical properties to the blend. There appears to be the optimum size that must be related to the requirements

of end use of the article made from the blend. When the blend cools from the melt the two ends of the copolymer will be physically held in the relevant phase, with the copolymer chain acting as a chemical link between the two regions. Grafted copolymers have similar mode. It get the best performance from a block copolymer, its structure must be optimized in term of structure and molecular weight [2].

2.3.2 Functionalized Polymers and Copolymers

Other compatibilizers include functionatized polyolefins or thermoplastic rubbers, such as PP-g-MA [5,6,7,8] and EPR. The polymer may be functionalized with an unsaturated acid or anhydride via a free radical mechanism in the presence of a peroxide initiator. The reaction may take place either in a chemical batch reaction or in a modified extrusion process. The latter has advantages in better temperature control, continuous production and allowing the removal of unwanted reaction products by devolatilization. The grafted acid or anhydride interacts either physically or chemically with groups on the chain of one polymer, whilst the remainder of the macromolecule is miscible with the second. For example a PP/Polyamide 6,6 (PA6,6) blend can be compatibilized with PP-g-MA through the interaction of the anhydride group with the amide structure of the nylon.

2.4 T_g-composition Analysis of Miscible Polymer Blend

The T_g represents the temperature at which the polymeric chains have a combination of energy (i.e., vibrational, translational, and rotational forces) equal to the forces of attraction (i.e., despersive forces, polar interactions, and specific interactions). Below this temperature, the polymer chains are locked into a random network with motion restricted to vibrational, rotational, and short-order translational movement of small units of the polymer chain. Above this point, translatinal movement of the entire chain is possible, and diffusion therefore occurs as might be required, for example, by a crystallization process which approaches a negligible rate at the T_g. The

observed T_g is affected by the frequency of the observed test method, pressure, crystallinity, and crosslinking.

Heterogeneous blends will exhibit distinctly different T_g's as opposed to a homogeneous blend with a single T_g. For miscible polymer blends, T_g versus composition is not a universally similar relationship, but has many variations, similar to those observed with random copolymers. For polymer blends exhibiting miscibility over the entire composition range, three generalized curves (illustrated in Figure 2.3) are possible: the linear relationship and the minimum and maximum deviations from linearity.
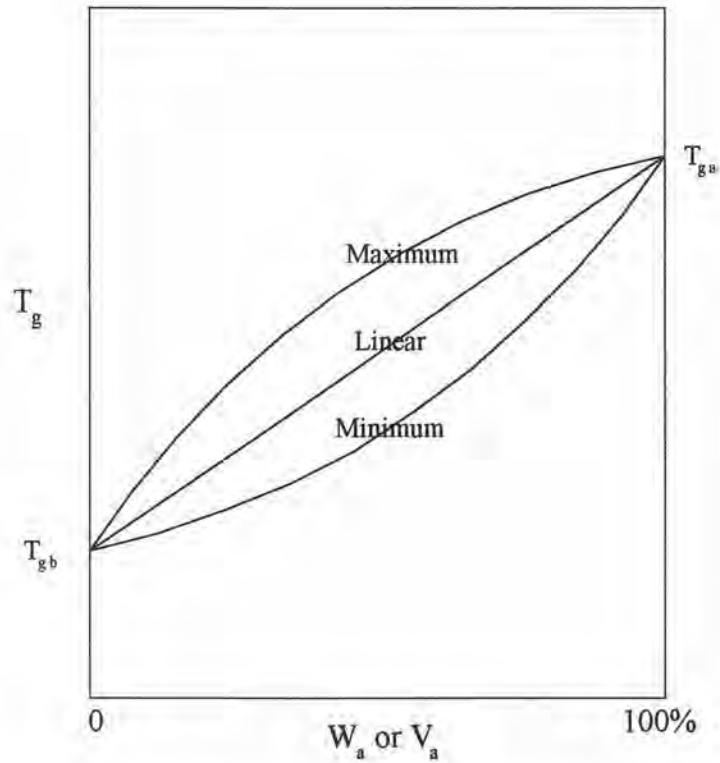

Figure 2.3 Generalized behavior of T_g relationships for miscible polymer blends [3].

Examples of a minimum variation from linearity are quite common. In many of these cases, data fit relationships commonly used for random copolymers of for polymer-diluent blends (e.g., plasticized PVC), namely, the Fox equation,

$$1/T = (W_a/T_{ga}) + (W_b/T_{gb}) \qquad (2.1)$$

and the Gordon-Taylor equation,

$$T_g = [W_a T_{ga} + k(1 - W_a)T_{gb}]/[W_a + k(1 - W_a)] \qquad (2.2)$$

where T_{ga} and T_{gb} represent the glass transitions of the undiluted polymer components, W_a and W_b are the weight fractions of the blend, and k is the ratio of the thermal expansion coefficients between the rubber and glass states of the component polymers, $(\alpha_{1b} - \alpha_{gb})/(\alpha_{1a} - \alpha_{ga})$.

The Kelley-Bueche equation is similar to the Gordon-Taylor equation expect that the volume fraction, ϕ_i, is used instead of the weight fraction:

$$T_g = [\phi_a T_{ga} + k(1 - \phi_a)T_{gb}]/[\phi_a + k(1 - \phi_a)] \qquad (2.3)$$

As $\alpha_1 - \alpha_g$ has been proposed to be constant for all polymers, k = 1.0 and the Gordon-Taylor and Kelley-Bueche equations reduce to the linear form:

$$T_g = W_a T_{ga} + W_b T_{gb} \qquad (2.4)$$

$$T_g = \phi_a T_{ga} + \phi_b T_{gb} \qquad (2.5)$$

The above equations, commonly used to express the T_g-composition relationships for copolymers and plasticizer-polymer compositions, are quite useful for miscible polymer blends [3].

2.5 Polypropylene Polyblends

The major practical development of polypropylene polyblends has been the addition of ethylene-propylene rubber (EPR) to improve impact strength at room and especially low temperatures, environmental stress-crack resistance, and filler tolerance. Approximately 10% or more utilized 10-20% by weight of EPR in the blend. The major application is in the automobile industry, but other uses include appliances, signs, sport equipments, and tool handles.

A number of studies have aimed to achieve an understanding of these improvements. Optimum rubber domain size was variously estimated from 0.4 to 2 μm, or even bimodal distributions, to produce ductility through crazing and shear yielding. PP blocks in the EPR nucleated crystallization of the PP matrix producing smaller spherulites, while the mobility of EPR promoted higher crystallization of the PP matrix.

2.6 Ethylene Vinyl Acetate Copolymer Polyblends

The full ranges of EVA copolymer runs from crystalline to amorphous and from nonpolar to polar, so it is not surprising that this polymer has been proved interesting and useful in blending with a variety of other polymers.

Paraffin wax was flexibilized and strengthened by blending with EVA. Crosslinkable polyethylene and EVA at polyblend ratios near 50:50 form two continuous phases, which crosslinking between them minimized the phase separation. LLDPE heat-sealability, toughness and environmental stress-crack resistance were improved by adding 5-25% EVA. LDPE is miscible with some EVA, so that the polyblend improves puncture resistance, toughness, low temperature flexibility and environmental stress-crack resistance. EPDM is miscible with copolymers having a high ratio of ethylene to vinyl acetate (VA). PP/EVA blend morphology and its properties show complex dependence upon composition. At the best their flexibility and impact strength are useful in cable, footwear and automotive applications.

Poly-1-butene blends with EVA could be coextruded on packaging to form heat-seal adhesives. Phase separation made it easy to open the seal later by cohesive failure.

The blend of polystyrene with EVA forms two-phase systems [4]. Increasing VA content improves interfacial adhesion and impact strength. Styrene-maleic anhydride copolymer has been blended with EVA grafting glycidyl methacrylate onto the EVA using reactive processing technique. Methyl methacrylate-acrylonitrile-butadiene-styrene (MABS) grafted copolymer was incompatible with EVA, showing severe losses of mechanical properties. Increasing VA content of the EVA narrowed the difference in polarity, but was not sufficient to produce compatibility.

The miscibility of chlorinated rubber with EVA has been reported to be limited. In contrast, PVC/EVA blends form a series of interesting and useful polyblends. Thermodynamic miscibility increases with the increase of VA content and polarity, or by incorporating CO or SO_2 into the EVA. At low to medium VA content, the copolymer are rather immiscible with PVC, but the microphases are strongly bonded to each other. The EVA domains provide high impact strength in the rigid PVC matrix. Grafting PVC to EVA may also help. At high VA content, or with CO or SO_2 termonomers, miscibility increases, and the EVA becomes a polymeric plasticizer, sometimes even forming the continuous matrix phase. These blends shows an application as a promising UV stabilizer [4].

2.7 Polypropylene Grafted Maleic Anhydride

Effort to produce peroxide grafting of maleic anhydride on polyolefins was initiated in 1960s. It been found to be a successful compatibilizing agent in blends of polyolefins and polyamides [5]. PP-g-MA has been prepared mostly by peroxide induced thermal maleation of PP.

Let's I represents a peroxide compound. Being subjected to thermal treatment, it cleaves to give the peroxide radicals $R^\bullet$,

$$I \rightarrow 2\,R^\bullet \qquad (2.6)$$

then the radicals transfer to polymer chain (P-P) to give the polymer radicals $(P^\bullet\text{-}P')$ and non-radical R,

$$R^\bullet + P\text{-}P \rightarrow P^\bullet\text{-}P' + R \qquad (2.7)$$

in the presence of MA, it reacts with $P^\bullet$-P' to obtain PP-g-MA.

$$P^\bullet\text{-}P' + MA \rightarrow PP\text{-}g\text{-}MA \qquad (2.8)$$

Reactions (2.7) and (2.8) requires migrations of both peroxide and maleic anhydride to polymer [6].

2.8 Literature Reviews

Gupta, A. K. et at [9] studied the potential to utilize EVA as an impact modifier for PP. PP/EVA blend were prepared in the ranges of 0-40 wt % EVA employed in their study contained 9, 12 and19% by weight of VA. Izod impact toughening effect as a function of blending ratio both at low and above ambient temperatures upto 60°C was measured and compared with that of various reported blends of PP with other elastomers. Morphological studies using scanning electron microscopy on the etched impact-fractured surfaces were carried out as well as a correlation of morphology and impact properties at various blending ratios. The impact strength was simultaneously dependent upon two variables including the blending ratio and temperature as simulated mathematically. Relevant contour diagrams, based on the second order polynomial regression, for optimization of those properties were also presented.

Gupta, A. K. at el [10] studied of melt-rheological properties of the binary blend of isotactic polypropylene (i-PP) and EVA with the variation of the weight fraction of EVA ranging from 0 to 40%. Three grades of EVA used contained different VA contents of 9, 12 and 19%. A capillary rheometer was employed to reveal the effects of blend composition and shear stress on the flow curves, melt viscosity and melt elasticity at three different temperature (210, 220 and 230°C) under shear stress in the ranges of 10^4-10^6 Pa (shear rate 10^1-10^4 s^{-1}). Morphology of the blend was studied using a technique of scanning electron microscopy. Distinct differences in average size and number of density of the dispersed EVA droplets were found as a function of the blend composition and the shear stress.

Blow, H. P. et al [21] studied the modification of isotactic PP/HDPE blend with EPDM and EVA. An addition of high-density polyethylene (HDPE) to PP resulted in a significant reduction in the elongation at break and in the gate-region impact strength of injection molded articles. The compatibilizers employed in their study were ethylene/propylene/diene monomer (EPDM) or EVA copolymers. The former improved effectively the impact strength and gate puncture resistance of the PP/HDPE blend weight ratio of 90/10. EVA, on the other hand, imporved effectively

the impact strength and the elongation at break of the polyblend. It was also found that EVA was a better impact modifier for PP than EPDM. DSC analysis indicated that EPDM blended with PP caused a significant reduction in the degree of crystallinity of the PP. This was not observed in the case of EVA/PP blends.

Moon, H. S. et al [7] studied the nonisothermal crystallization of molten blends of two semicrystalline polymers, namely PP and Nylon-6 (N6). The effect of the concentration of the compatibilizing agent, PP-g-MA, on the crystallization behavior was studied. The crystallization thermograms showed one or two crystallization peaks, which were significantly affected by the presence of the compatibilizer. The crystallization temperature of N6 leveled off down as the concentration of PP-g-MA increased, whereas that of PP stayed at a roughly constant temperature. These blends containing the compatibilizing agent exhibited concurrent crystallization at the crystallization temperature of PP. The crystallization behavior was also studied using the technique of optical microscopy under crossed polarizers.

George, S. et al [11] studied the morphology and mechanical properties of blends of PP with nitrile rubber (NBR) with specific focus to the effects of blend ratios. Morphological observations of the blends showed a two-phase system, in which the rubber phase dispersed as domains in the continuous PP matrix at lower proportions of NBR ($\leq 50\%$). The 30/70 PP/NBR blend was found to exist as a co-continuous system. Attempts were made to correlate the changes in morphology with properties. The mechanical properties of the blends were found to depend on the blend ratios. Various composite models, such as the series model, the parallel model, the Halpin-Tsai equation, and Coran's model, were used to fit the experimental mechanical properties. The effect of concentration of PP-g-MA and phenolic-modified polypropylene (Ph-PP) as compatibilizers on the morphology and mechanical properties of the blends was also investigated. The compatibilizer concentrations used were 1, 5, 10 and 15 wt %. The domain size of the disperesed NBR particles decreased with the addition to a few percent of the compatibilizer followed by a levelling off at higher concentrations, which was the indication of interfacial saturation. The mechanical properties of the blends were improved by the addition of the compatibilizer followed by a levelling off at higher concentrations

which was an indication of interfacial saturation. The experimental results were compared with the compatibilization theories of Noolandi and Hong.

Li, H. et al [12] studied the polymer-polymer interface in polypropylene/poly amide blends by reactive processing. The reactive blending of PP with amorphous polyamide (aPA) was carried out using a gram-scale mixer. PP-g-MA was used as a reactive compatibilizer. Time-resolved light scattering analysis showed that fine particles of submicron was obtained via a faster size reduction process which exhibited better stability of the dispersed particles for static annealing, suggesting the emulsifying effect of in situ formed PP-aPA graft copolymer. Both illipsometry and transmission electron microscopy (TEM) showed that the interface established in the reactive system was very thick (~ 40 nm); it was several times the coil size of the component polymer. The thick interface was assumed to be a layer of accumulated micelles of the in situ formed grafted copolymer. In the thick interface, instead of the cross-hatched lamellar crystallites, long lamellar crystals were found to develop.

Duvall, J. [8] studied interfacial effect produced by crystallization in PP/Nylon-6 using PP-g-MA as a compatibilizing agent. Two PP-g-MA compatibilizers, including high-anhydride compatibilizer (HAC, 2.7% by weight grafted MA) and low-anhydride compatibilizer (LAC, 0.2% by weight MA), in comparison to the PP rich blends with polyamide-66 (25% by weight). LAC imparted a much higher fracture strain than did HAC at similar anhydride concentrations. LAC was capable of cocrystallization with PP, while HAC was not. However, HAC crystallized as a second phase in the binary PP/HAC blends as obtained by DSC and hot-stage microscopic techniques. A cocrystallization model was proposed to explain the higher fracture strain of PP/LAC/PA blends. The separate phase crystallization model was proposed for PP/HAC/PA blends. The peel tests demonstrated the greater adhesion of PP with LAC than with HAC.

Samay, G. [13] studied the process of grafting MA onto high-density polyethylene in the presence of various comonomers in an intermeshing corotating twin screw extruders. Three types of comonomers were investigated: (a) vinyl monomers, including styrene and methacrylic acid; (b) esters of dicarboxylic acids forming succinic groups after grafting, such as fumaric acid, (c) esters of fumaric and

maleic acid and ethylenically unsaturated cyclic dicarboxylic anhydrides, such as Diels-Alder adducts of MA, and (d) dienes and dodecenyl succinic anhydride.

Garcia-Martinez, J. M. et al [14] studied the chemical modification process of atactic PP by MA. The modified polymer was useful as an interfacial agent. This polymer had a higher level of modification than the stereoregular isotactic PP, despite the lower processing temperature used, that caused a decrease in the initiator activity. A mechanism of chemisorption and some considerations about the fractal nature of the reaction kinetics were proposed to explain the results obtained.