

## CHAPTER II

### LITERATURE SURVEY

#### 2.1 Polymer blends

Improving mechanical properties such as toughness is usually the main reason for the development of novel thermoplastic alloys and blends. Other reasons for blending two or more polymers together include: (1) to improve the polymer's processability (2) to enhance the physical and chemical properties of the blend making them more desirable than those of the individual polymers and (3) to meet the market force. Borggreve *et al.* (1989) studied toughening of nylon 6 (PA 6) with a range of modifiers such as ethylene-propylene-diene (EPDM), ethylene-propylene (EPM), low density polyethylene (LDPE), polyether-esters and some functionalized EPDM, EPR and LDPE. They reported an improvement appeared to increase with decreasing modulus of the modifiers except polyether-esters.

Thermoplastic elastomers are materials that possess the excellent processing characteristics of thermoplastic materials at higher temperatures, and the wide range of physical properties of elastomers at service temperature.

Wrocteki *et al.* (1991) studied the effect of particles, which an elastomeric core and a rigid PMMA shell in the toughening of PMMA. They found that the toughness increased with an increasing degree of grafting and increased molecular weight of the shell.

Tinker (1985) studied on PP/NR blend. He found substantial improvement in impact strength for slightly crosslinked NR compared to the uncrosslinked NR phase. Similarly, Dao (1982) found that a slightly crosslinked EPDM rubber is more effective in toughening PP.

Most of the polymer blends are found to be incompatible. These incompatible blends are characterized by a two-phase morphology, poor physical and chemical interactions across the phase boundaries and poor

mechanical properties. These problems can be alleviated by the addition or in situ formation of compatibilizers or interfacial agents.

There are several studies in literature in which the addition of copolymer increases the compatibility of immiscible polymer pairs. Incorporation of a copolymer usually improves the interaction between the constituent homopolymers and thereby slows down the phase separation process. It was reported by Paul (1978) that the copolymer addition provided finer dispersion, improved interfacial adhesion, stabilized against gross segregation and reduced the interfacial tension.

Armat and Moet (1993) investigated the effect of compatibilizing polyethylene and nylon-6 on the morphology and mechanical properties of their blends. A maleic anhydride functionalized styrene (styrene-co-butylene)-styrene block copolymer (MA/SEAB) was added to the blends as a compatibilizer. They reported that the compatibilizer was found to play a dual interfacial function. On the one hand, it reduced the interfacial tension of the system, resulting in reduction of the particle size of the dispersed polyethylene phase. On the other hand, it enhanced the interfacial adhesion through the formation of micro-bridges.

Willis and Favis (1988) investigated the processing-morphology relationships of compatibilized polyolefin/polyamide blends. They reported that the morphology of compatibilized polyolefin/polyamide blends was found to be significantly dependent on the concentration of an ionomer compatibilizer (polyethylene-methacrylic 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 nylon, due to the specific interactions existing between the ionomer and polyamide. These interactions were confirmed by Fourier transform infrared spectroscopy. At high

concentrations of the ionomer, flocculation of the nylon-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 nylon was the matrix and a larger particle size when nylon was the minor phase. The results observed were explained in terms of a speculative model of the interaction occurring across the nylon polyolefin interface.

Jurkowski *et al.* (1998) reported the influence of chemical and mechanical compatibilization on structure and properties of polyethylene/polyamide blends. LDPE/PA 6 binary blends and LDPE/PA 6/compatibilizer ternary blends were prepared in a Brabender extruder, equipped with a prototype static mixer. LDPE grafted with a maleic anhydride (LDPE-g-MA) was used as a compatibilizer. Compatibility of the components was estimated by rheological properties (viscosity and a melt flow index) and observations of the structure were made with the help of scanning electron microscopy and tensile strength. It was found that the blends structure and properties were dependent on the content of the polymer blends and the conditions of their manufacturing. The viscosity of the studied polymer blends reveals positive or negative deviations from the additivity rule depending on the blend content and the deviations are similar for different shear rates. The dependence of the MFI on PA 6 concentration obtained for the blend of LDPE/PA 6 revealed a characteristic deviation from linearity, which suggested that the interphase interactions had increased due to the effect of both the compatibilizer and the applied static mixer. Mechanical and chemical compatibilization affected the improvement of uniformity of the phase structure of polymer blends.

George *et al.* (1995) investigated morphology and mechanical properties of blends of isotactic polypropylene (PP) and nitrile rubber (NBR) with special reference to the effects of blend ratio. Morphological observations of blends showed a two-phase system, in which the rubber phase

was 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. The mechanical properties of blends were found to depend on the blend ratio. The effect of concentration of maleic-modified polypropylene (MA-PP) and phenolic-modified polypropylene (Ph-PP) as compatibilizer on the morphology and mechanical properties of the blend was also investigated. The compatibilizer concentrations used were 1, 5, 10 and 15wt%. The domain size of the dispersed NBR particles decreased with the addition of a few percents of the compatibilizer followed by a leveling off at higher concentrations. The mechanical properties of the blends were improved by the addition of the compatibilizers. The experimental results were compared with the current compatibilization theories of Noolandi and Hong.

Oommen and Thomas (1993) studied the compatibilizing effect of graft copolymer of natural rubber and poly (methyl methacrylate) (NR-g-PMMA) in natural rubber/poly (methyl methacrylate) (NR/PMMA) blends. They found that the addition of a few percents of the copolymer reduced the size of the dispersed PMMA phase, which leveled off at higher concentrations. SEM analysis of the fracture surfaces of the compatibilized blend showed improved interfacial interaction between the phases. The mechanical properties of the blends were also improved by the addition of the graft copolymer.

Axtell, Phinyocheep and Kriengchieocharn (1996) studied the effect of modified natural rubber compatibilizers on polyamide 6/natural rubber blends. They found that the result of blends had a finer dispersion of natural rubber in the polyamide 6 matrix. The presence of smaller rubber particles gave greater toughness to the blends, with improved mechanical properties including Charpy impact strength, tensile strength and elongation at break. The rheological behavior was affected by the in situ copolymerization during mixing, with mixing torque increasing as the reaction taken place. The

polyamide 6 crystallization was nucleated by both additions of the natural rubber and the compatibilizers.

Asaletha *et al.* (1995) studied compatibility activity of NR-g-PS in heterogeneous NR/PS blends. Both the morphology and mechanical properties of NR/PS blends have been investigated. They suggested that concentration and molecular weight of the copolymer, composition of the blend, mode of addition of compatibilizer, homopolymer molecular weight, and processing condition were the controlling parameters on blend morphology. It was found that the addition of a small percentage of the compatibilizer was enough to decrease the domain size of the dispersed phase, which finally leveled off at higher concentrations. The leveling off could be an indication of interfacial saturation. The experimental results were in agreement with predictions of Noolandi and Hong. The addition of the graft copolymer improved the mechanical properties of the blend and attempts were made to correlate the mechanical properties with the morphology of the system. Different models were discussed to establish the conformation of the compatibilizer at the blend interface. The actual conformation was neither fully extended nor flat. A portion of the copolymer penetrated into the corresponding homopolymer and the rest remained at the interface.

Abdullah *et al.* (1995) investigated the blending of natural rubber with linear low-density polyethylene and the effect of liquid natural rubber (LNR) as the compatibilizer on the properties of NR-LLDPE blends. The LNR with some active terminals like -OH was expected to react with the plastic particles and thereby bonded the plastic particles to the NR matrix. The blends were prepared by melt blending of the materials in a Brabender mixer at various temperatures and mixing rates. The optimum processing conditions were at a temperature of about 130°C and a mixing rate of 55 rpm. And they observed the mixing process, which had a third rise in torque, very broad, where more LNR was added in the blend system. By adding LNR, the interaction between

the various phases, chemical and physical was expected to be more extensive and resulting in a higher degree of material curing. The tensile properties, stress and strain, of the blends improved significantly with the addition of LNR into the blend. For blends with composition around 50% NR, about 10-15% LNR produced the most significant improvement in the physical properties. SEM of the samples also indicated an increase in the homogeneity of the mixers with addition of LNR. A single glass transition temperature of about  $-55^{\circ}\text{C}$  for the blend was observed via dynamic mechanical analysis (DMA). Interfacial linking between the NR and LLDPE phase was attributed to the presence of active groups on the polyisoprene chain of LNR, which induced the interphase reaction between the NR and LLDPE phases.

## 2.2 Rheology

A study of the flow behavior of thermoplastic elastomers is necessary for optimizing the processing conditions and for developing suitable equipment.

Huang and Chang (1997) investigated rheological and thermal properties of reactive compatibilization of polymer blends of PBT and PA66. They found that processability improvement has been achieved by reducing die swell and melt fracture during blending extrusion.

Micic *et al.* (1996) studied the melt strength and elastic behavior of LLDPE/LDPE blends. Differences in processability between linear low-density polyethylene and low density polyethylene as well as for their blends subjected to extensional flow were assessed in terms of melt strength and elastic parameters from shear flow such as storage modulus ( $G'$ ) and first normal stress difference ( $N_{11}-N_{22}$ ). The results from the LDPE rich blends revealed similar synergistic effects on these parameters.

Rheological behavior of polymer blends has been studied by several workers. During processing of polymer blends several factors have to be

optimized. Akhtar *et al.* (1987) studied the rheological behavior of blends of high-density polyethylene and natural rubber (NR) as a function of blend ratio, dynamic crosslinking of rubber phase and carbon black filler. The shear viscosity of these blends was found to be influenced by shear rate rather than by temperature. Morphology was found to depend on the blend ratio and shear rate.

Thomas *et al.* (1986) studied on the rheological behavior of plasticized poly (vinyl chloride)-thermoplastic copolyester elastomer blends. The rheological behavior of plasticized PVC-HYTREL 40D blends had been evaluated with specific reference to the effects of blend ratio and temperature on viscosity, flow behavior index and die swell. The proportion of the thermoplastic rubber in the blend was found to have a profound influence on viscosity at higher shear stresses. The die swell of the extrudates was found to decrease with increase in Hytrel content.

Gupta *et al.* (1989) studied on the melt rheological behavior of binary PP/ABS and ternary PP, ABS and LDPE blends. Data obtained in capillary rheometer are presented to describe the effect of blending ratio, shear stress and shear rate on flow properties, melt viscosity and melt elasticity. At a blend composition corresponding to 10 wt % ABS content, both binary and ternary blends showed maximum in melt viscosity accompanied by minimum in melt elasticity. Pseudoplasticity of the melt decreased with increasing ABS content. In ternary blends, LDPE facilitated the flow at low LDPE contents and obstructed the flow at high LDPE contents. Scanning electron microscopic studies were also presented to illustrate the state of dispersion and its variation with blend composition.

Kim and Lee (1996) studied the effect of PS-GMA as an in situ compatibilizer on the morphology and rheological properties of the immiscible PBT/PS blend. Rheological behavior of blends having in situ compatibilizer was investigated by dynamic oscillatory shearing measurement. It was shown

that as the amount of graft copolymer formed during blending increased, the viscosity at low shear rates increased but the degree of shear thinning was not pronounced. For polymer alloys prepared at the setting temperature of 230°C, the finer morphology was obtained when more than 5 phr PS-GMA was added to PBT/PS blend, but this amount of PS-GMA decreased to 3 phr when setting temperature in the mixer was increased to 240°C since at higher temperature more graft copolymer could be formed.

Kuriakose and De (1985) studied on the melt flow behavior of thermoplastic elastomers from polypropylene-natural rubber blends with reference to the effects of blend ratio, extent of dynamic crosslinking of the rubber phase and temperature on viscosity, flow behavior index, and deformation of the extrudate. The proportion of rubber in the blend and the extent of dynamic crosslinking of the rubber phase were found to have profound influence on the viscosity of the blends at lower shear stresses. But at higher shear stress, the effect of blend ratio on the viscosity was comparatively less for the uncrosslinked blends than that for the crosslinked blends. At lower shear stress, the viscosity of the blend increased with increase in degree of crosslinking but at higher shear stress, the effect of crosslinking on viscosity was found to vary depending on the ratio of the plastic and rubber components in the blend. The deformation of the extrudates was also very much dependent on both blend ratio and degree of crosslinking.

Varghese *et al.* (1993) studied the melt rheological behavior of acetylated sisal fiber reinforced natural rubber composites using a capillary rheometer. The results illustrated the effect of fiber concentration and shear stress/shear rate on melt viscosity and melt elasticity of the composites. The melt showed pseudoplasticity which increased with fiber loading. Incorporation of acetylated sisal fiber into natural rubber resulted in an increase in its melt viscosity and a decrease in its melt elasticity.



Das (1987) studied the rheological behavior of polymer blends consisting of crosslinkable polyethylene (XLPE) and crosslinked butyl rubber (XL-20) with the help of a capillary rheometer at four shear rates and three temperatures. The viscosity of the blends increased with increasing elastomer content. The rubber microgel was broken down at high shear rate with consequent viscosity decrease, which was predominant at higher XL-20, content. The flow activation energy showed inversion above 50% XLPE and decreased with the shear rate. Recoverable deformation and the Weissenberg number related linearly to the swelling ratio. The stored elastic energy and relaxation time increased with the increase in XL-20 content. Phase inversion seemed to occur at the 50:50 ratio.

Friedrich *et al.* (1996) studied the rheological and thermodynamic properties of the miscible blend polystyrene/poly (cyclohexyl methacrylate). The viscoelastic properties of the blend components and the blends had been studied in a wide range of temperatures. The investigations of the isotherms of the storage and loss modulus of the blends showed that individual relaxation of the blend components was observed to a certain degree. Nevertheless, the deviations from a master curve are small, and comparable with other miscible polymer blends supporting the idea that time-temperature superposition hold approximately. Material parameters like the Newtonian viscosity,  $\eta_0$ , the plateau modulus,  $G_p$ , and the terminal relaxation time,  $\lambda_0$ , were determined from the material functions.

Two polyethylene resins (LDPE and HDPE) and their blends were characterized for dynamic shear rheology, extrudate swell from a capillary rheometer, and recoverable strain measured by melt elasticity indexer in attempts to compare parameters related to the so-called "melt elasticity". Xanthos *et al.* (1997) found that extrudate swell data were found to correlate reasonably well with equilibrium recoverable strain data. With respect to blends, complex viscosity and storage modulus versus composition curves

showed positive deviations from linearity, similar to those observed in melt heterogeneous blends. Similarities between the short time recoverable strain vs. composition and the storage modulus vs. composition curves suggested that similar morphological states might exist in the melt over the experimental times and conditions applicable to these different experimental techniques.

Varughese (1990) studied the melt rheology of plasticized poly (vinyl chloride)/epoxidized natural rubber miscible blends. Melt viscosity of plasticized PVC increased with ENR content at higher processing temperatures. The melt elasticity parameters such as die swell ratio, principal normal stress difference and recoverable shear strain at a particular shear stress increased with temperature up to a 50 wt % composition of ENR in blends. For high ENR blends the die swell ratio and recoverable shear strain decreased with temperature and the principal normal stress difference and elastic shear modulus remained independent of temperature for all values of shear stress. It was noted that the nature of deformation in the surface layer was linear for a smooth extrudate and nonlinear for a distorted extrudate. Moreover, recoverable shear strain was found to have a correlation with the extrudate distortion of the melts.

Oommen *et al.* (1997) studied the melt rheological behavior of natural rubber (NR) and poly (methyl methacrylate) (PMMA) blends with reference to the effect of blend ratio, processing conditions and graft copolymer concentration as a function of shear stress and temperature. The viscosity of the blend increased as the amount of NR increased. The observed values of viscosity were found to be higher than that calculated from additivity rule. In the case of solution cast samples the melt viscosity increased as the percentage of graft copolymer increased and the blend became more sensitive to temperature in the presence of graft copolymers. The influence of dynamic vulcanization of the rubber phase on the flow behavior of the blends had been analyzed. The die swell of the NR/PMMA blends was also evaluated in the

presence and absence of graft copolymers. The morphology of extrudates had been analyzed as a function of composition, graft copolymer concentration and shear stress conditions. Addition of compatibilizer reduced the domain size of the dispersed phase and stabilized the morphology. It was also noted that state of dispersion was affected by conditions of blend preparation and extrusion. A shear rate-temperature superposition master curve was constructed to predict the melt viscosity of the system as a function of temperature. The rheograms of 50/50 NR/PMMA with varying graft copolymer concentrations were found to coalesce into a master curve using modified viscosity and shear rate functions.

Valenza and Acierno studied the effects of adding modified polypropylenes, one functionalized with maleic anhydride ( $PP_{mal}$ ) and the other with acrylic ( $PP_{acr}$ ) acid, to blends of nylon 12 (Ny12) and polypropylene (PP) by considering morphological, thermal, mechanical and rheological properties. The rheological results indicated that the blend without compatibilizer exhibited viscosity values slightly higher than the matrix at low frequency and slightly lower than the matrix at high frequency. Greater differences appeared in the blends with compatibilizers, especially when reported in the form of Cole-Cole plots, an indicating  $PP_{mal}$  giving the most homogeneous structure.

Utracki and Sammut studied the dynamic shear behavior at 200°C of low-density polyethylene (LDPE), polystyrene (PS) and their blends in 1988. The LDPE/PS system was immiscible with relatively large values of the apparent stress in storage and loss moduli. Addition of poly (styrene-*b*-isoprene) di-block copolymer (SEB) decreased the yield stresses. For most blends a change of morphology at higher frequency was observed. This instability of structure, accentuated by lowering the temperature, precluded time-temperature superposition. The horizontal shift factor,  $a_T$ , was found to

depend on both time and temperature. A compositional dissymmetry of blend morphology was observed.

The rheological behavior of a series of blends of poly (vinyl chloride) (PVC) with different contents of styrene-butadiene rubber (SBR) have been studied by Zhou Pu and Sun Zaijian (1987). The results showed that SBR/PVC blends have better processability for injection molding. The rheological model has been constructed for SBR/PVC blends using regression analysis.

Mohanty *et al.* (1998) have been studied the flow behavior of blends of poly(ethylene-co-acrylic acid) (PEA) and epoxidised natural rubber (ENR) by a Monsanto processibility tester (MPT). The blends were found to be miscible during reactive processing due to chemical interaction via esterification reaction at higher proportion of PEA. The rheological properties were studied at three different temperatures, five different shear rates in the range from  $122 \text{ s}^{-1}$  to  $2452 \text{ s}^{-1}$  and at three different shear stresses. The melt viscosity of the blends at  $120^\circ\text{C}$  and  $130^\circ\text{C}$  showed a positive deviation at lower shear rates and shear stress and at higher proportions of PEA and a negative deviation at higher shear rates and shear stress and lower proportion of PEA, where as at higher temperature of melt processing the viscosity showed positive deviation (at all shear rates for all the blends) with respect to that calculated by additivity rule. This variation in melt viscosity has been explained on the basis of chemical reaction via esterification leading to grafted structure i.e. PEA-g-ENR.

Han *et al.* (1995) studied the effect of flow geometry on the rheology of dispersed two-phase blends of polystyrene and poly (methyl methacrylate). For the PS/PMMA blends, they found that logarithmic plots of steady shear viscosity versus shear rate obtained by a cone-and-plate rheometer did not overlap those obtained by a capillary rheometer, whereas for the homopolymers PS and PMMA there is a good agreement between the two.

This observation was explained in terms of the differences in the morphological states of the blends between the uniform shear flow in a cone-and-plate rheometer and the non-uniform shear flow in a capillary rheometer, which involved the entrance and exit effects. They had also pointed out that the Cox Merz rule does not hold for dispersed two-phase polymer blends, because the morphology of a dispersed two-phase blend in oscillatory shear flow would not be the same as that in steady shear flow. In terminal region, logarithmic plots of dynamic storage modulus ( $G'$ ) versus dynamic loss modulus ( $G''$ ) showed curvature for the PS/PMMA blends but a straight line for the constituent components, leading to conclude that such plots are very sensitive to variations in the morphological state of the blends.

The effects of sample preparation and flow geometry on the rheological behavior and morphology of microphase-separated block copolymers have been studied by Han *et al.* The steady shear viscosities of two microphase-separated triblock copolymers, a polystyrene-block-polybutadiene-block-polystyrene copolymer (Kraton 1102) and a polystyrene-block-polyisoprene-block-polystyrene copolymer (Kraton 1107) were measured at various temperatures, using a cone-and-plate rheometer at low shear rates and a capillary rheometer at high shear rates. They found that for compression-molded specimens the shear viscosities obtained from a cone-and-plate rheometer did not overlap those obtained from a capillary rheometer, while for solvent-cast specimens there was a reasonably good agreement between the two. The viscosities of solvent-cast specimens were much lower than those of compression-molded specimens. They found from transmission electron micrographs that the application of steady shear flow affected greatly the morphology of Kraton 1102 to have cylindrical microdomains of polystyrene phase. It had little effect to the morphology of Kraton 1107 to have spherical microdomains of polystyrene phase. The complex shear viscosities of the two block copolymers at various temperatures were measured. They have shown

that neither time-temperature superposition nor the Cox-Merz rule is applicable to microphase-separated block copolymers.

Sharma *et al.* (1988) studied the effect of fillers on the rheological behavior of thermoplastic and 1, 2 polybutadiene rubber. The influence of fillers like clay, silica, and carbon black on the rheological properties of polybutadiene has been investigated by using capillary rheometer. Silica filled compound exhibited the highest viscosity and clay filled compound showed the lowest viscosity at all shear rates. The effect of filler loading and temperature on the rheological behavior had also been studied. Smooth extrudates were obtained in most of the cases and die swell was lower for silica and carbon black filled compounds than for clay filled compounds. Rheograms of different 1, 2 polybutadiene systems had been found to merge into a master curve using modified viscosity and shear rate functions that contained melt flow index as a parameter.

Silerstein *et al.* (1994) examined the effects of various calcium carbonate filler types on the ductility of filled amorphous copolyester. One of the calcium carbonate fillers had received a surface treatment. For all filler types, the Young's modulus increased with increasing filler content and was satisfactorily described by Kerner's equation. The only filler to affect the yield stress was the surface-treated calcium carbonate; in this case, the decrease in yield stress was attributed to cracking and splitting of aggregated particles. A sharp drop in fracture strain was observed with increasing filler content.



### **2.3 Research Objectives**

1) Study the effect of blend composition, shear rate (shear stress), temperature, and concentration of maleic anhydride and filler on the rheological behavior of the blends.

2) Study the dynamic mechanical properties and morphology of LLDPE/NR blends at different composition and various percentages of maleic anhydrides.

3) Construct storage and loss modulus master curves by using time-temperature superposition.