CHAPTER II
LITERATURE SURVEY

2.1 Miscibility of Polymer Blends having Acrylic Acid

Polymer blends have recently seen a tremendous surge in industrial applications because they offer an inexpensive route for new polymeric materials. There are many research works showing interest in the miscibility of polymer blends. In 1988 Agarwal P.K. and Horrion, J. investigated thermal and mechanical properties of blends of a low density polyethylene (LDPE) and ethylene-acrylic acid copolymers (EAA) with vary acrylic acid content and zinc ionomer form. Thermal and mechanical characteristics indicate that such are immiscible at all proportions for acrylic acid contents above 5% mol. It was observed that compatible blends could be achieved when the acrylic acid content of the copolymer did not exceed ~ 5mol% and the effect of degree of neutralization and type of counter ion were not reflected in these measurements.

Roy *et al.* (1993) studied blending of epoxidized natural rubber (ENR) and ethylene-acrylic acid (EAA) that contained 6% acrylic acid. The blending of ENR/EAA produced a graft polymer like EAA-*g*-ENR. The proportion of ENR/EAA blends were studied was 90/10. The results were shown some improvement in processability of ENR on grafting. In 1995, Mohanty *et al.* studied miscibility of blends of epoxidized natural rubber (ENR) and poly(ethylene-acrylic acid) (PEA) (6% wt of acrylic acid). These blends were partially miscible up to 50% by weight of PEA and completely miscible beyond this composition, as confirmed by DSC study, which exhibited a single second-order transition (T_g). The miscibility was assigned to the esterification reaction between –OH groups formed *in situ* during melt blending of ENR and –COOH groups of PEA which were confirmed by UV and IR spectroscopy. The existence of a single phase of the blends beyond 50% wt of PEA was confirmed by SEM studies.

These three poly(ethylene-*ran*-acrylic acid)s (PE-AAs) with different amounts of acrylic acid but exhibiting similar rheology properties were studied to investigate the effect of acrylic content in PE-AAs on the morphology and

mechanical properties of PE-AAs/polystyrene (PS) blend compatibilized by poly(styrene-*ran*-glycidyl methacrylate) (PS-GMA) (Kim *et al.,*1996). From morphological observations, there appeared to be an optimum amount of acrylic acid in PE-AA that effectively reduced the dispersed domain size in PE-AA/PS blend systems. The tensile strength (σ_b) and elongation at break (ε_b) for these blend systems steadily increased with an increasing in amount of acrylic acid in PE-AAs. Impact strength of blend systems was investigated by varying amount of acrylic acid in PE-AA. Moreover Eguiburu *et al.* (1996) observed the blend of amorphous and crystalline polylactides (PDLA and PLLA) with poly(methyl methacrylate) (PMMA) and poly(methyl acrylate) (PMA) via thermal behavior using differential scanning calorimetry (DSC). The results were compared with those obtained by dynamic mechanical analysis (DMTA). It was proposed that only one T_g was found in PDLA/PMA and PDLA/PMMA blends, indicating a high degree of miscibility over entire composition range.

Xu *et al.* (1998) reported the compatibilization effect of poly(styrene-*b*-2-ethyl-2-oxazoline) diblock copolymer,P(S-*b*-Eox), on immiscible blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and poly(ethylene-*ran*-acrylic acid) (EAA). The blends exhibited a more regular in terms of phase structure and thermal, rheological and mechanical properties. These blends also exhibited a more regular and finer dispersion on addition of a small amount of P(S-*b*-Eox) which was determined by scanning electron microgaph (SEM). The interfacial tension was also estimated by rheological measurement. The tensile strength and elongation at break increased with the addition of the diblock copolymer for PPO-rich blends, whereas the tensile strength increased but the elongation at break decreased for EAA-rich blends.

Erro et al. (1999) studied effects of the chemical structure on the miscibility level and properties of phenoxy(Ph)/polymethacrylate(PMMA) blends. The observed miscibility showed that the change in component of miscible blend of some pendant units that gave rise to miscibility, by forming a different second component, which gave rise to immiscibility was less important. The change in the nature of the side chain had considerable effect on short-term mechanical properties such as modulus of elasticity and yield stress.

Psarski *et al.* (1999) studied blends of nylon (Ny6) and polyolefins functionalized with poly(ethylene-acrylic acid) (PE-AA), poly(propylene-acrylic acid) (PP-AA). These blends were investigated in terms of crystallization behavior and resulting Ny6 crystalline structure. It demonstrated that reduction of size of Ny6 dispersed particles was caused by the interaction between the functional groups of polyolefin and the polar groups in polyamide chain. The nucleation mechanism was changed due to the lack of heterogenous nuclei in most small Ny6 droplets, which results in enchanced crystal formation.

In 2001 Shiao Wei Kuo and Feng Chih Chang observed the miscible blend via hydrogen bonding of poly(vinylphenol-co-methyl methacrylate) (PVPh-co-PMMA) with poly(ethylene oxide) by using differential scanning calorimetry (DSC), Fourier transform infared spectroscopy (FTIR) and solid-state nuclear magnetic resonance (NMR). The experimental results indicated that the blends of PEO and PVPh-co-PMMA were completely miscible in amorphous phase over the entire composition range. In the same year, Valenza *et al* studied the morphological, calorimetric, rheology and mechanical behavior and fourier transmission infrared analysis of blends made with polyamide 6 (PA6) and ethylene-acrylic acid copolymers (EAA) containing different amount of acrylic acid were investigated. The result observed from the sample characterizations evidenced as acrylic acid caused a compatibilizing effect between polyethylene and polyamide components with modifications of blends morphology and mechanical behavior. These effects were enchanced with increase of the acrylic acid content in the copolymer and they were attributed generally to hydrogen bond interactions among the acrylic acid group and the functional group of polyamide. A more significant compatibilization phenomenon was obtained in blends containing higher amino terminal groups of the copolymer than the carboxylic ones.

ESCOR™ acid terpolymer are a novel polymer that has similar structure as EAA copolymer. Therefore in theory, polymer blend between ESCOR™320 terpolymer and EAA copolymer might be miscible blends. Worakanya *et al.*, (2001) studied and indicated that only blends of ESCOR™320/EAA1 at 80% wt of EAA1, ESCOR™320/EAA2 at 90% and 95% wt of EAA2, ESCOR™320/EAA4 at 80% wt of EAA4, and ESCOR™320/EAA5 at 80% wt of EAA5 that showed single

glass transition temperature resulting from dynamic mechanical properties, suggesting completely miscibility. The mechanical properties of these blends increased with increasing EAA content, but the gloss of most blends dropped upon blending, which indicated phase separation. ESCOR^{TM}320 with EAA2 at 60% wt of EAA content was considered the most suitable for used as the dampener material due to its high tan δ and good mechanical properties.

2.2 Vibration Damping

Application of poly(ethylene-co acrylic acid) (PEA) as a material for dampener of vibrations was studied. PEA was used to laminate steel sheet and the laminate was expected to serve as a vibration dampener. The theoretical analysis of dampening efficiency was based on a model proposed by Ungar. The frequency analyzer was used to measure the loss factor of the laminates. The results showed that the loss factor of the laminate increased monotonically with increasing thickness of the viscoelastic layer. Ungar's theory predicted a higher loss factor than the experimental data. This might have resulted from interfacial adhesive bonding, a nonuniform viscoelastic layer thickness, and the extrapolation of the rheological data from low to high frequencies. The loss factor of the laminate increased with increasing temperature. Compared to the laminates using pure resin, the maximum dampening peak of the laminates become broader, and occurred at a temperature between the T_g's of the individual components of the polymer blend. (Chen Y.S. and coworker., 1991)

2.3 Crystallization Characteristic in Other Polymers

It is well known that molecular weight, molecular weight distribution, stereoregularity and regioregularity greatly influence the crystallization behavior. Therefore, It is important to understand the basic crystallization characteristic of the interested polymer before further studies are carried out.

Gupta and coworkers (1994) studied the nonisothermal crystallization exotherm of high-density polyethylene (HDPE)/ linear-low density polyethylene

(LLDPE) blend obtained by differential scanning calorimetry (DSC) and analyzed the effect of cocrystallization on kinetic parameters, namely the Avarami exponent and activation energy. They reported that The Avarami exponent and activation energy for crystallization of HDPE symstematically decreased with increasing LLDPE content of the blend from 2.94 to 1.72 for the Avarami exponent and from 30 to 11 kcal/mol for activation energy.

In 1999, Supaphol and Spruiell studied the isothermal crystallization of five samples of syndiotactic polypropylene. Crystallization studies were carried out in the temperature range of 60°C to 97.5°C using a differential scanning calorimeter (DSC). The results showed that double melting endotherms. The low-melting endoterms corresponded to melting of primary crystalline aggregates formed at the specified crystallization temperature, whereas the high-melting one was a result of the melting of crystalline aggregates formed by recrystallization of unstable crystals during the reheating process. Comparison with some other polymers revealed that s-PP crystallizes much slower than Nylon 6, I-PP, and Nylon 66, while it crystallizes faster than isotactic polystyrene

In 1999, Supapol analyzed the non-isothermal crystallization of five s-PP samples by using three macrokinetic models, namely the Avrami, the Tobin, and the Ozawa models. Both Avrami and Tobin models were shown to provide a fair description of the experiment data, whereas The Ozawa model was found to describe the non-isothermal crystallization kinetic of s-PP very well. For each s-PP sample, s-PP crystallized faster with increasing cooling rate.

Next year, Yongsok (2000) presented the crystallization kinetics of polytetrafluoroethylene (PTFE) under nonisothermal conditions by using the Avarami theory. The Avarami exponent of PTFE was obtained as ~1.49, which indicated the formation of one-dimensional crystallites (fibrillar type) after thermal nucleation or two dimensional crystallites (disc) athermal nucleation. The activation energy was also obtained as 34 kcal/mol. This value is much smaller than those of PEEK and PET, indicating a very fast crystallization of PTFE.

In 2001, Feller *et al* studied the crystalline characteristic of carbon black/poly(ethylene-co-alkyl acrylate) blend. The results were shown the acrylate comonomer is affected on the crystalline characteristic parameter of polymer blends.