

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Theoretical background

2.1.1 Miscibility of polymers

The miscibility between polymers is determined by a balance of enthalpic and entropic contributions to the free energy of mixing. While for small molecules, the entropy is high enough to ensure miscibility; for polymers the entropy is almost zero, causing enthalpy to be decisive in determining miscibility. The change in free energy in mixing (ΔG_{mix}) is written as

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}, \quad (2.1)$$

where, ΔH_{mix} is the enthalpy of mixing (J), ΔS_{mix} is the entropy change of mixing (J/K) and T is the absolute temperature (K). Polymers are only miscible when the Gibbs free energy of mixing is negative. Normally, the most polymer blends are immiscible because mixing is endothermic and the entropic contribution is small due to the high molecular weights of the constituent polymers (Brydson, 1998).

2.1.2 Phase morphology of immiscible polymer blends

Most immiscible polymers form coarse mixtures with comparatively large domain sizes and sharp interface, as a result of the high interfacial tension

between the components, which further leads to poor interfacial adhesion. The properties of a blend not only depend on the mechanical behavior of the interface, but also on the size of the respective polymer phases. The phase morphology of immiscible blend from two polymers, for example, when polymer A and polymer B are blended together. In case that there is a lot more of polymer A than polymer B, polymer B separates into little spherical globs. The spheres of polymer B will be separated from each other by the matrix of polymer A, as shown in Figure 2.1. In this case, polymer A is called a major component and polymer B is a minor component. When more polymers B is put into the immiscible blend system, the spheres will get bigger until they become joined together and are the domains of polymer A. In this case, polymer B is called a co-continuous phase or a region of phase inversion. Moreover, the polymer B is put more over than the co-continuous phase until the polymer B becomes the major phase or the matrix phase, and polymer A becomes the minor phase or the disperse phase.

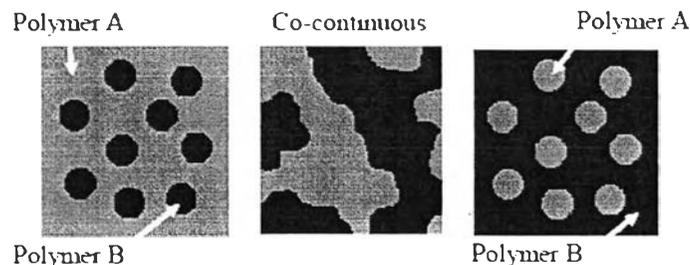


Figure 2.1 Phase morphology of immiscible polymer blends (Fayt, Hadjiandreou and Teyssie, 1998).

It is known that simple blends of two immiscible polymers usually have large discrete dispersed phases and weak interfacial adhesion, resulting in poor mechanical properties coupling between phases. Therefore, compatibilizer is required to enhance interfacial adhesion between the phases of immiscible polymers.

Generally, an effective compatibilizer should reduce the interfacial tension between the two phases leading to a finer dispersion of one phase in another, enhance adhesion by coupling the phases together, and stabilizing the dispersed phase against coalescence (Paul and Newman, 1978). Block and graft copolymers represent the most extensive use as compatibilizers for the stabilization of phase structure. Compatibilizers are usually in a form of block or graft copolymers. They may be added separately or formed during compounding, mastication or polymerization of a monomer in the presence of another polymer. The copolymer compatibilizers often contain segments, which are either chemically similar to those of blend components (non-reactive compatibilizers) or miscible or adhered to one of the components in the blend (reactive compatibilizers). In case of reactive copolymer compatibilizers, the segments of the copolymer are capable of forming strong bonds (covalent or ionic) with at least one of components in the blend. In the non-reactive copolymer compatibilizers, the segments of the copolymer are miscible with each of blend components. The proposed conformations of compatibilizers molecules at the interface of a heterogeneous polymer blend are shown in Figure 2.2.

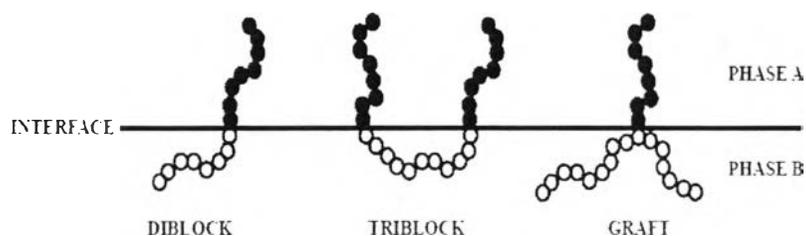


Figure 2.2 Location of block and graft copolymers at phase interfaces (Cor, Martin, Christophe and Robert, 1998).

2.1.3 Log additivity rule model

Generally, the flow behavior of a homopolymer depends on the flow geometry and processing conditions such as the temperature, shear rate, time of flow, etc. Contrary to the polymer blends where the flow behavior becomes more complex and is influenced by additional factors like the miscibility of the system, the morphology, interfacial adhesion, and interfacial thickness. The melt viscosity of polymer blends shows three types of behavior as follows (Utracki, 1989).

- (1) Positive deviation behavior (PDB) where blend viscosities show a higher value than the log additivity value.
- (2) Negative deviation behavior (NDB) where blend viscosities show a lower value than the log additivity value.
- (3) Positive-negative deviation behavior (PNDB) where the same blend exhibits both positive and negative deviation behavior, depending on the composition, morphology and processing conditions.

$$\log (\eta_{blend}) = \sum_i x_i \log (\eta_i), \quad (2.2)$$

where η_{blend} and η_i are the shear viscosity of the blend and that of the phase i and x_i is the weight fraction of the phase i .

The log additivity rule is an indication of strong or weak interactions between the phases of the blend. The immiscible blends show a negative deviation

behavior due to the heterogeneous nature of components. Thus, the observed negative deviation is due to the incompatibility between the phases and interlayer slip as a result of the decreasing viscosity of the system. Also, the compatible blends lead to a positive deviation in rheological properties, such as the increasing viscosity.

2.1.4 Graft copolymerization

For graft copolymerization, side chains of the backbone polymer are formed by attachment of macromolecules with different chemical compositions. The simplest case of graft copolymer can be represented by the model as shown in Figure 2.3 where a sequence of monomer units (A) is referred as the main chain or backbone, a sequence of B units is the side chain of a graft and X is the grafting position on the polymeric backbone (Bayer, 1992). Graft copolymerization can thus be defined as a post polymerization. The vinyl monomers, such as styrene, acrylonitrile, and maleic anhydride are normally used to graft on the backbone.

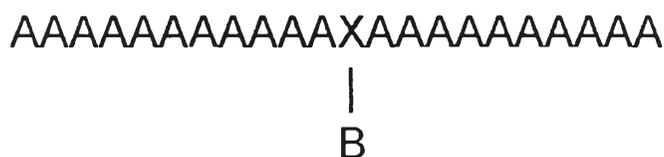


Figure 2.3 Model of graft copolymer (Bayer, 1992).

2.1.5 Reactive extrusion

Reactive extrusion involves the synthesis of materials by a melt phase reaction in an extruder. The advantages of synthesizing polyethylene-graft-MAH by reactive extrusion as opposed to alternative technologies include little or no use of

solvents, a simple product isolation, short reaction times, a continuous process and relatively low infrastructure costs. Some potential disadvantages with reactive extrusion are the high reaction temperatures necessary to form a polymer melt and the extent of polymer degradation or crosslinking that may accompany processing (Moad, 1999). An additional problem is often that unreacted grafting component must be removed during of post-grafting process.

2.2 Literature reviews

Wulin, Takashi and Takahiro, 2005 studied a mechanochemical method of preparation of maleic anhydride-grafted-polypropylene. The preparation was performed by ball milling of polypropylene powder with maleic anhydride (MAH) in the presence of benzoyl peroxide. The FT-IR spectra, the grafting degree and the morphology were investigated. It was found that the ball-mill method induced MAH grafting on the backbone of PP chains. The new absorptions which appeared at 1863 cm^{-1} (asymmetric C=O stretching) and 1786 cm^{-1} (symmetric C=O stretching) in the spectra of the resultant samples are the characteristics of maleic anhydride-grafted-polyethylene. The grafting degree increased fast within the MAH concentration of 1 phr, beyond which it increased slowly, and showed a maximum at 3 phr. The ball mill changed the PP powder to a flake morphology, and some particles were smaller while some other were much larger.

Hongbo, Weibing, Hanyang, Zhengfa, Shijun and Qiusheng, 2004 studied the preparation and characterization of polyethylene modified with grafting MAH monomer on its backbone at first. Then two kinds of nanocomposites, polyethylene (PE)/organic montmorillonite (Org-MMT) and maleic anhydride-grafted-polyethylene

(PE-g-MAH)/Org-MMT nanocomposites were prepared. The FT-IR spectroscopy, X-ray diffractometry (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of the nanocomposites were investigated. It was found that the FT-IR spectra of PE-g-MAH showed the characteristic bands of succinyl anhydride rings bonded to PE which proved the successful grafting reaction. The XRD and TEM micrographs showed that an intercalated structure would be acquired on mixing the PE and Org-MMT and an almost exfoliated system would be obtained by mixing the PE-g-MAH and Org-MMT. The DSC and TGA thermogram showed that both nanocomposites had a higher thermal decomposition temperature and a higher crystallization temperature when compared to the original matrix.

Machado, Covas and Van Duin, 2001 studied the effect of polyolefin structure on maleic anhydride grafting. A series of polyolefin with different ethene/propene ratios was grafted with MAH. The MAH graft content and the degree of branching/crosslinking or degradation were determined by FT-IR and rheometry. It was found that the MAH graft content was low for polyolefin with a high propene content and high when the propene content was below 50 wt%. The branching/crosslinking occurred for polyolefin with the low propene content, while degradation was the main side reaction for polyolefin with the high propene content.

Nakason, Kaesaman and Supaasanthitikul, 2004 studied the grafting of maleic anhydride onto natural rubber (NR). Graft copolymers of NR and MAH were prepared in a toluene solution and benzoyl peroxide was used to initiate the free radical graft copolymerization. Effects of the monomer and initiator concentrations

together with the influence of reaction temperature and time of the grafting reaction were studied. The quantification of the grafted MAH on the NR molecules were determined by titration with the standard KOH solution and the estimation of the grafted MAH level was performed using IR absorbance ratio of the peaks at 1780-1784 cm^{-1} plus 1854 cm^{-1} to 835 cm^{-1} . It was found that quantities of the grafted MAH on NR molecules increased with the increasing monomer and initiator concentrations. The increases of reaction time and reaction temperature also caused the increasing level of grafted MAH. The T_g values also increased with increasing the monomer concentrations in the grafting reaction.

Chaoqin, Yong and Yinxi, 2003 studied the grafting of maleic anhydride onto low-density polyethylene/propylene blends by melt extruding in the presence of dicumyl peroxide. The melt viscosities of the grafted blends were measured by a capillary rheometer and the grafting degrees were determined by a back titration method. The characteristic groups of MAH in the grafted products were measured by FT-IR. It was found that the melt viscosities of MAH grafted LDPE/PP decreased with increasing PP content while the grafting degree was little changed. The characteristic bands of MAH in the MAH grafted LDPE/PP were located between that of the MAH grafted LDPE and MAH grafted PP.

Haiyun, Zhangbin, Lifang, Aiguan and Zhengping, 2006 studied morphology, thermal stability and flammability properties of ABS-g-MAH/clay nanocomposites by melt blending. It was found that FTIR spectra confirmed that the MAH was successfully grafted onto butadiene chains of the ABS backbone in the molten state using dicumyl peroxide as an initiator and styrene as the comonomer and

the relative grafting degree increased with increasing loading of MAH. TEM images indicated that the size of the dispersed rubber domains of ABS-*g*-MAH increased and the dispersion was more uniform than the neat ABS resin. XRD and TEM showed that intercalated/exfoliated structure was formed in ABS-*g*-MAH/OMT nanocomposites and the rubber phase intercalated into the clay layers. TGA showed that the intercalated/exfoliated structure of ABS-*g*-MAH/OMT nanocomposites had better barrier properties and thermal stability than did the intercalated ones of ABS/OMT nanocomposites. The T_g of ABS-*g*-MAH resin was unchanged compared to the neat ABS but the addition of clay could improve T_g of ABS-*g*-MAH/OMT and the T_g of ABS-*g*-MAH/OMT nanocomposites was higher than that of the neat ABS/OMT nanocomposites. The cone calorimetric measurement showed that ABS-*g*-MAH/OMT nanocomposites exhibit reduced flammability compared to ABS/OMT nanocomposites at the same clay content. The chars of ABS-*g*-MAH/OMT nanocomposites were tighter, denser, more integrated and fewer surface microcracks than those of the ABS/OMT nanocomposites.

Mei-ling, Yong-liang, Hoe, John, Kim and Lee, 2007 studied the miscibility and compatibilization of poly(trimethylene terephthalate)/acrylonitrile-butadiene-styrene (PTT/ABS) blends by melt processing with and without epoxy or styrene-butadiene-maleic anhydride copolymer (SBM) as a reactive compatibilizer. They were investigated by DSC, dynamic mechanical analysis (DMA), capillary rheometer, and scanning electron microscopy (SEM). It was found that the PTT was partially miscible with ABS. Both epoxy and SBM showed compatibilization effects on the PTT/ABS blends, which led to a shift in the cold crystallization and glass transition temperatures of the PTT phase to higher temperatures. The PTT/ABS

blends exhibited typical pseudoplastic flow behavior. The rheological behavior of the epoxy compatibilized PTT/ABS blends showed an epoxy content-dependence. In contrast, when the SBM content was increased from 1 wt% to 5 wt%, the shear viscosities of the blends increased and exhibited much clearer shear thinning behavior at the higher shear rates. The SEM showed a finer morphology which supports their compatibilization.

Nikos, Dimitrios and Joannis, 1996 studied the blends of poly(ethylene terephthalate) (PET) with unmodified and maleic anhydride grafted acrylonitrile-butadiene-styrene terpolymer by melt blending. The blends were examined at up to 25wt% content of ABS, tensile, dynamic mechanical, thermal properties, and morphology were investigated. It was found that PET/ABS blends quenched from the melt showed good tensile properties at low ABS contents, which were deteriorated during storage at room temperature. At elevated melt temperatures, miscibility at the component interface was predicted. However, at ambient temperature, the phase separation was predicted by solubility parameter theory, and the mismatch of components expansively led to poor adhesion and particle debonding during storage. The grafting of ABS-g-MAH onto PET stabilized the blend morphology and mechanical properties due to the anchoring of ABS-g-MAH onto the matrix. The optimum content of the modified ABS was 5wt%.

Tiganis, Burn, Davis and Hill, 2002 studied the thermal degradation of acrylonitrile-butadiene-styrene due to aging at elevated temperatures (>80 °C). It was found that the degradation of the bulk polymer did not occur due to the limited oxygen diffusion. For the aged ABS under an imposed stress, microcracks were

initiated from the existing flaws in the degraded polymer surface layer. When the degraded layer reached a depth of 0.08 mm, the cracks were sufficiently large enough to propagate into the bulk of the polymer causing an abrupt mechanical failure. The microindentation measurements suggested that an increased in Young's modulus in this layer promoted brittle behavior. The degradation of the elastomeric polybutadiene (PB) phase was initiated by hydrogen abstraction from the carbon attached to the unsaturated bonds. Thermo-oxidative degradation in the PB phase at the surface caused an increased in polymer density, stress hardening and modulus. The thermal degradation of the styrene-acrylonitrile (SAN) phase also occurred by physical aging and thermo-oxidative degradation, but had only a minor contribution to the deterioration of mechanical properties in ABS. The most critical degradation process in ABS was thermo-oxidative degradation of the PB phase; performance was dependent on adequate levels and distributions of the stabilizers for the specific temperature applications.

Marilda and Leni, 2008 studied the morphology and environmental resistance of HDPE/LDPE and HDPE/LLDPE blends. The measurements of crystallinity and dynamical mechanical studies were investigated. It was found that a significant improvement in the stress cracking resistance of HDPE based materials could be achieved by blending with LDPE and LLDPE. The best results were found for the combination of HDPE with LLDPE due to the cocrystallization and the degree of mobility in the amorphous phase, as measured by $\tan \delta$, indicator of the polymer resistance to stress cracking.