

## CHAPTER II

### LITERATURE SURVEY

The term polymer blends may be defined as a mixture of two or more polymers. Polymer blends are growing part of the polymer industry. Polymer blends can provide a product with the best features of all components. Blending also enables polymer producers to produce tailor made products for specific properties or to improve the properties of homopolymer i.e. mechanical properties, processing properties and chemical properties. More recently, polymer blending has been provided a mean for the recycling of the mixed polymer waste. Finally, the production of new materials designed through blending implies lower costs together with a shorter time scale compared to a search for the new material.

A fundamental problem in polymer blends is that different homopolymers are normally incompatible due to structure and thermodynamic limitation. Many researches have showed that only a few polymers are truly miscible blends which can be characterized by a single glass transition temperature ( $T_g$ ) and uniform morphology at the molecular level, e.g. Polyetheretherketone (PEEK) /Polyetherimide (PEI), and Polystyrene (PS)/ Poly(propylene oxide) (PEO) (Folkes and Hope, 1993). Many binary polymer blends are immiscible because of positive energy of mixing arising from either small entropy of mixing or no specific interaction occurred leading to positive enthalpy of mixing. For this reason, phase separation into a distinct macroscopic domain is occurred in immiscible polymer blends and result in poor mechanical properties relative to their components. Then controlling the blend morphology, which can create during blending process, can optimize the properties of polymer blends. Di Lorenao *et.al.* reported that intensive bulk mixing of high molecular weight polymers for few minutes usually produces particle dispersion of 1-20  $\mu\text{m}$  size or larger, whereas 0.3-3  $\mu\text{m}$  particle size

are needed to obtain stable phase morphology and optimum mechanical properties. The dispersed phase size is influenced by the interfacial tension; lowering the interfacial tension results in the reduction of the domain size. Molecular interaction for the immiscible blend is unfavorable and thus it brings about large interfacial tension in the melt (Paul *et al.*, 1978).

In order to improve the interface adhesion between two immiscible polymer domains or obtain the desired properties, the third component is usually added to the mixture. These materials are generally called compatibilizers. The compatibilizer localizes at the interfaces of two components and give lower interfacial tension between incompatible homopolymers leading to smaller domains with better dispersion. The well known compatibilizers are block or graft copolymers which have different polymer species capable to direct specific or chemical interaction with one component in the blends, or both. The influence of the copolymers on the final blends properties contributes to their ability (Folkes and Hope, 1993) (a) to increase the degree of dispersion of one phase into another phase due to the reduction of interfacial tension, (b) to improve the adhesion at the boundaries, thus enhancing stress transfer, and (c) to stabilize the dispersed phase against coalescence. A significant challenge in this research area is to find the copolymers that work as effective compatibilizer. For example, Barentsen and Heikens (1973) found that the LDPE particle size in PS matrix decreased with incorporation of a graft copolymer of PS and LDPE. The blends containing copolymer also possesses higher yield strength, elongation, and breaking strength than unmodified blends, across the whole composition range, as well as having significantly increased impact strength.

Yang *et al.* (1984) described a complex picture when toughening PP blended with HDPE and EPDM. These workers reported that replacing up to 20 % HDPE (in a 20/80 HDPE/PP blend) by EPDM led to improve impact and

tensile properties. In this case EPDM appeared to act as both impact modifier and compatibilizer.

However, synthesis of block and graft copolymers is quite difficult and expensive and the use of the copolymers in industrial process is limited. An alternative way for compatibilized polymer blends has been called reactive blending. Reactive blending provides a useful way to improved physical properties during the preparation of the new polymeric materials from already existing homopolymers. During reactive blending, chemical reactions such as coupling reaction and chain scission reaction between the components in blends can increase miscibility and enhance interface adhesion between polymers. The chemical reaction mechanism may be exploited (Folkes and Hope, 1993):

1. Formation in situ of graft or block copolymer by chemical bonding between reactive groups on component polymers; this may also be stimulated, for example, by addition of free radical initiator during blending.
2. Formation of block copolymer via an interchange reaction in the backbone bonds of the components; this is most likely in condensation polymers.
3. Mechanical scission and recombination of component polymers to form graft or block copolymers. This is generally induced by high shear levels during processing.
4. Promotion of effective reaction by catalysis.

The area of reactive blending is one in which there is currently a great deal of development activity and research. For example, Ballegoie and Rudin (1988) compared melt blend of PS/PE and reaction extruded blend with dicumyl peroxide and triallyl isocyanurate coupling agents. They found that the reaction extruded blend method has improved mechanical properties and

morphology at a certain level of coupling agent. They attribute the improvement to the formation of grafted copolymer during reactive extrusion.

Recently, reactive extrusion of PP and natural rubber was studied by Yoon *et al.* (1995). The presence of peroxide [1,3-bis (t-butylperoxy) benzene] and coagent (trimethylolpropanetriacrylate, TMPTA) acted to decrease the rubber domain sizes and enhance the mechanical properties of the final blends.

Polyethylene (PE) and poly(vinyl chloride) (PVC) are the most widely used plastics materials for packaging, electronics, and other applications. When these polymer are blended it may offer an attractive balance of mechanical, barrier, and chemical properties. Due to the difference in chemical structures of these two polymers, the blend of PE and PVC are immiscible blends and lead to poor properties. To improve the miscibility of these blends the use of a compatibilizer is an established process.

Many researchers have reported compatibilized blends of PE/PVC. Boutevin *et al.* (1985) used polyethylene grafted methyl methacrylate as a compatibilizer in LDPE/PVC blends. They concluded that the presence of this compatibilizer improved the mechanical properties in term of modulus, elongation at break, and stress at break.

A different compatibilizer, chlorinated polyethylene (CPE) which prepared by solid state polymerization, was used in LLDPE/PVC blend by He *et al.* (1997). The result showed that the compatibility of PVC/LLDPE blends were improved with addition of CPE. Also, adhesion strength between two phases and the mechanical properties of the blends were improved.

Benedetti *et al.* (1986) preformed compatibilized PE/PVC blends by using polyolefin grafted diethyl maleate as compatibilizing agent. The presence of the compatibilizer resulted in reducing the interfacial tension and further improving the blends morphology and their processibility

The reactive blending technique was used in PE/PVC blend by Nakamura *et al.* (1987). They successfully performed compatibilized PE/PVC blends through a partial co-crosslinking reaction with peroxide to give a uniform dispersion of small PE particles and with improved mechanical properties.

From many research works, it was found that the presence of carboxylated polyethylene, i.e. polyethylene grafted with methyl methacrylate, polyethylene grafted with maleic anhydride or ethyl maleate, improved the compatibility. This was due to the interaction between carbonyl group on PE chain and the  $\alpha$ -hydrogen atom on PVC chain.

The *in situ* formed carboxylated polyethylene by blending polyethylene with carboxylated monomer was disclosed by a number of workers. In an early example, Gallucci *et al.* (1982) modified the chemical reactivity of polyolefin especially polyethylene by grafting with various functionalized monomers, i.e. glycidyl methacrylate, glycidyl acrylate, buthyl methacrylate and maleic anhydride. In summary, modified polyolefin were prepared successfully in the melt by free radical grafting of monomers. The products had a high level of functionalization depending on type of monomer and initiator.

Simmons and Baker (1989) studied grafting of dimethylamino ethylmethacrylate (DMAEMA) to LDPE in the Brabender mixer. A grafting product contained nearly 3 % wt DMAEMA grafted LDPE was prepared and showed better stability in thermal properties than that of the starting material.

Nowadays, many researchers pay attention to new blending process, called one-step reactive blending, which can combined both grafting step and blending step in the same equipment. For example, grafting can be carried out first, followed by subsequent interfacial reaction between the grafted polymer and another polymer. This process has many advantages especially equipment cost and time saving. The commercial compatibilized polymer blends by one

step reactive blending was performed by Hu *et al.* (1996). They prepared PP/PBT blends by one-step reactive blending in a co-rotating intermeshing twin screw extruder using glycidyl methacrylate as a grafting monomer. The final blends did not have different properties compared with the blends obtained by two step reactive blending. The effects of processing parameters were also studied in this work. In summary, the processing parameters, i.e., feed rate, screw speed, and specific throughput, strongly affected the properties of the blends.

#### Abbreviation List

LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
HDPE	High Density Polyethylene
EPDM	Ethylene-Propylene-Diene-Monomer (rubber)
PP	Polypropylene
PBT	Poly(butylene terephthalate)