



CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Polypropylene

PP is a generic name for a family of polypropylenes differing in stereospecificity and common monomer contents. It is commercially produced in isotactic, syndiotactic, and atactic forms with varying degree of tacticity in which the isotactic form being the most common. Further, the chemical composition of PP can be altered via the incorporation of different co-monomers, most notable ethylene, leading to polymers with tailor-made properties.

Generally, PP can be subdivided, based on its chemical composition, into homopolymer, random copolymer and block copolymer. Isotactic PP is characterized into four different crystal forms: α -, β -, γ - and mesomorphic (smectic). Presently, isotactic PP crystallized in its α -form is the most common crystallographic form found in the industry. Although PP can crystallize in several different forms, only two of these can be affected by nucleating agents whose unit cells are illustrated in Figure 2.1. The α - and β -forms can be induced by specific nucleating agents, while the γ - and smectic-forms are the result of fast cooling of the polymer melt. The α -form has a high modulus and high tensile strength but moderate impact strength but β -form has a low tensile strength, high impact and high strain at break [7].



α -form (monoclinic).

β -form (hexagonal).

Figure 2.1: Unit cells of α -form and β -form of PP.

2.2 Polylactide

PLA is a linear aliphatic polyester biodegradable polymer which has a chemical structure as shown in Figure 2.2. It is a biodegradable polymer derived from lactic acid via starch rich products, plant such as corn and sugar through fermentation then polymerized by polycondensation. PLA has similar properties as petroleum-base polymer in terms of transparency and gloss which are comparable with polystyrene. The mechanical properties, i.e., tensile strength, stress at break, strain at break, are comparable with polyethylene terephthalate.

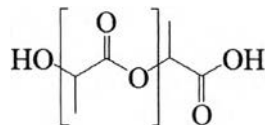


Figure 2.2: Chemical structure of polylactide.

Poly lactide can be fermentation from dextrose, glucose and saccharose by changing lactic acids to dimer or ring-opening polymerization to polylactide as described in Figure 2.3 [8].

Lactide is the cyclic dimer of lactic acid that exists as two optical isomers, D-and L-lactide. The L-lactide is the naturally occurring isomer, and DL-lactide is the synthetic blend of L-lactide and D-lactide. The lactic acid polymerization is illustrated in Figure 2.3. The homopolymer of L-lactide (LPLA) is a semicrystalline polymer which exhibits high tensile strength, low elongation and consequently high modulus that makes it more suitable for load-bearing applications such as orthopedic fixation and sutures. DL-lactide (DLPLA) is an amorphous polymer, exhibiting a random distribution of both isomeric forms of lactic acid, D- and L-forms which accordingly is unable to arrange into an organized crystalline structure. The latter material has lower tensile strength, higher elongation, and typically rapid degradation time, making it more attractive as a drug delivery system. Poly(L-lactide) has

about 37% crystalline, a melting point at 175-178 °C, and a glass-transition temperature at 60-65 °C. The degradation time of LPLA is much slower than that of DLPLA. PLA is fully biodegradable when produced in a large-scale operation with temperature of 60 °C and above. The first state of degradation of PLA (two weeks) is via hydrolysis to water soluble compounds and lactic acid. Rapid metabolism of these products into CO₂, water and biomass by variety of micro organisms occurs after hydrolysis. PLA does not biodegrade readily at temperatures less than 60 °C due to its glass transition temperature being close to 60 °C [9].

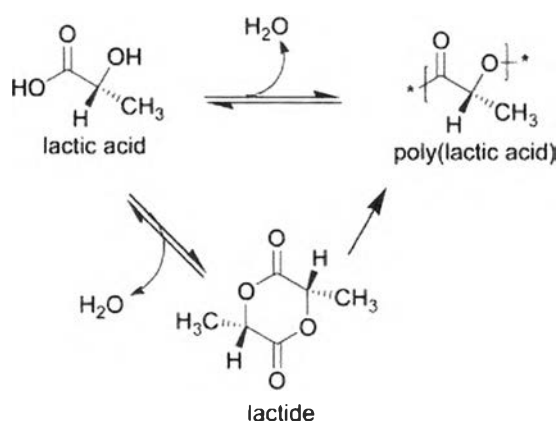


Figure 2.3: Lactic acid polymerization.

2.3 Polymer blend

By definition, any physical mixture of two or more different polymers that are not linked by covalent bonds is a polymer blend. Development of a new polymer to meet a specific need is a costly enterprise. If the desired properties can be realized simply by mixing two or more existing polymers, there is an obvious pecuniary advantage [10].

A number of technologies have devised to prepare polymer blend. It often happens that most polymers are not compatible in which they separate into discrete phase during mixing. Thus, an increasing number of completely miscible blends are being developed.

Differences between the two types are manifested in appearances; miscible blends are usually clear, while immiscible blends are opaque, miscible blends exhibit a single T_g intermediate between those of the individual components, whereas immiscible blends exhibit separate T_g characteristic of each component.

Miscible polymer blend is a polymer mixture which is homogenous down to the molecular level. Thermodynamically, this is associated with the negative value of the free energy of mixing, i.e. $\Delta G_m = \Delta H_m < 0$; where ΔG_m is the Gibb's free energy of mixing and ΔH_m is the enthalpy of mixing. In contrast, the thermodynamically immiscible blend is associated with the positive value of the Gibb's free energy of mixing, i.e. $\Delta G_m = \Delta H_m > 0$.

In general, the properties of blend are usually determined by the miscibility of the polymeric constituents. Miscibility implies that a single phase is produced. The most difficult polymer blend category to be clearly described is the partially miscible system. The most common system is one in which two completely immiscible polymer are made compatible with a third organic agent, called a compatibilizer. The compatibilizer usually increases the interfacial force between the two polymer blends [10].

Homogenous polymer blends are more convenient from the standpoint of being able to predict properties of processing characteristics. If additives are used, for example, there are no problems of migration from one phase to another. Physical or mechanical properties usually reflect to a degree, the weighted average of the properties of each component.

The compatibilization can in principle interact in complex ways to influence final blend properties. One effect of compatibilizers is to reduce the interfacial tension in the melt, causing an emulsifying effect and leading to extremely fine dispersion of one phase in another. Another effect is to increase the adhesion at phase boundaries, yielding stress transfer improvement.

Technological definition of compatibilization as modification of blend to produce a desirable set of properties, a number of different lines of approach can be defined which may assist the material developer. Broadly, these are:

- A) Achievement of thermodynamic miscibility
- B) Addition of block and graft copolymers
- C) Addition of functional/reactive polymers
- D) In situ grafting/polymerization (Reactive blending)

The addition of block or graft copolymers represents the most extensive research approach for compatibilization of blends. The block copolymers have been more frequently investigated, than the graft copolymer. The block copolymer containing that block and graft copolymer containing segments chemically identical to the blend component are obvious choices as compatibilizers, miscibility between the copolymer meets certain structural and molecular weight requirement, and that the copolymer locates preferentially at the blend interfaces [10].

Some researchers have described the addition of functional polymer as compatibilizers. Usually, a polymer chemically identical to one of the blend component is modified to contain functional (or reactive) units, which have some affinity for the second blend component; this affinity is usually the ability to chemically react with the second blend component, but other types of interaction are possible. The functional modification may be achieved in a reactor or via an extrusion-modification process [11]. Examples include the grafting of maleic anhydride or similar component to polyolefin, and the resulting pendent carboxyl group having the ability to form a chemical linkage with polyamides via their terminal amino group [12].

2.4 Compatibilizer and addition of functional/reactive polymers

Reactive compatibilization is an alternative method for producing blends in which the components are incompatible. It provides a means for making a stable morphology of a significantly reduced domain size relative to the uncompatibilized blend, primarily by suppressing domain coalescence in the melt, and thus improving interfacial strength. An alternative route for compatibilization is to form the graft copolymerization in situ during the blend preparation via interfacial reaction of functionalized polymeric components addition as illustrated in Figure 2.4.

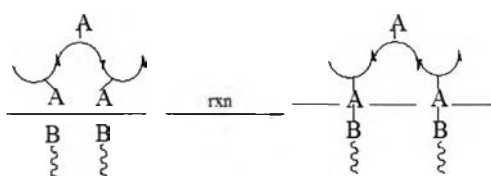


Figure 2.4: A graft copolymer at the interface between two immiscible polymer phases.

The functional groups can be placed along the chain of polymer by copolymerization or by grafting (e.g., maleic anhydride). Reactive grafting is used to be the method for attaching maleic anhydride groups to several polymers including polyolefins. For polyolefins, grafting is achieved by mixing the polymer with maleic anhydride (MA) and an initiator, such as a suitable peroxide, in an extruder at elevated temperatures. Various mechanisms have been used for grafting of maleic anhydride to both unsaturated and saturated polyolefins. The MA is attached to polyolefins through a variety of mechanisms. When the polyolefin contains only methylene carbon, MA is attached in the form of single succinic anhydride rings as well as short oligomers as illustrated in Figure 2.5. When there are tertiary hydrogen atoms, as in polypropylene and ethylene-propylene copolymers, the MA grafts onto the polymer backbone primarily in the form of single succinic anhydride groups, and chain scission often occurs, so that the anhydride unit is attached to the end of a short chain as shown in Figure 2.5 [13].

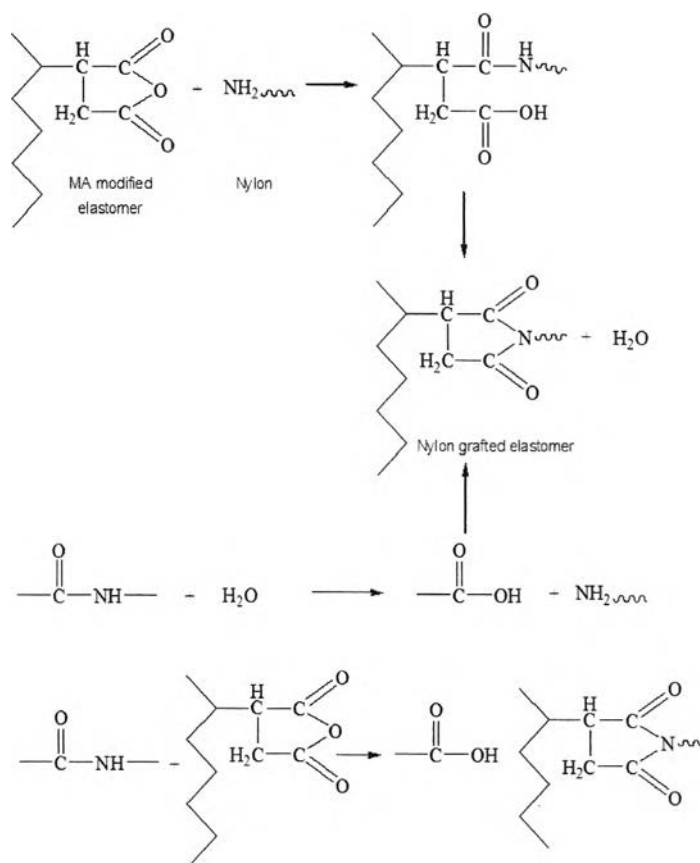


Figure 2.5: Principal reactions that occur during melt blending of polyamides with maleated elastomers or other polymers with anhydride functionality [13].

2.5 Determination of polymer blend miscibility

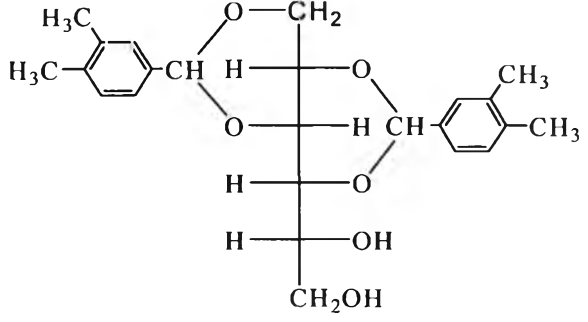
There are several techniques that can determine the compatibility of polymer blend; each technique has its own limitation. A variety of experimental techniques has been used to determine the compatibility of polymer blends. Some techniques, such as calorimetry, thermodynamical, dynamic mechanical procedures, are based on the determination of the number and location of glass transition temperature; T_g . The determination of T_g is easily detected in amorphous polymers. A narrow T_g is typically obtained from a miscible system, whereas an immiscible system exhibits a broad glass transition temperature. Other techniques are based on scattering techniques [14].

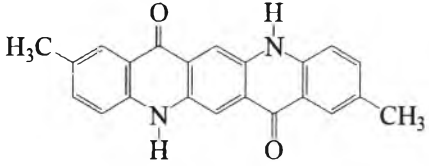
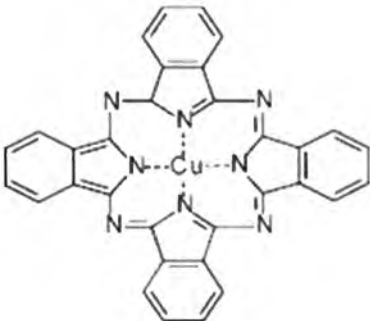
2.6 Nucleating agents

Most of polymers are semi-crystalline in which the degree of crystallinity depends on molecular weight, chemical structure, and tertiary bonding between polymer chains. Mechanical stretching helps an increase in crystallinity, whereas quenching reduces the crystallinity. First, the most commonly used nucleating agents inducing the crystallization of the α -form (i.e., α -nucleators), are discussed. A large number of studies exist on α -nucleators for PP and their effects on the mechanical and optical properties of the final part [7].

It is known that nucleating agents are added to the polymer systems to increase the rate of crystallization and temperature of crystallization [15]. The additives function by providing a large number of stable nuclei on which crystallization of the polymer may take place. Typically, the nucleating agents are added to improve the mechanical properties of the system or to increase the clarity of semi-crystalline polymers. At the same time, the decrease in spherulite size is obtained through the modified crystallization process. Crystallization is an important feature in the morphology development of the polymer blends. The chemical structures of nucleating agents are listed in Table 2.1.

Table 2.1 Name and structure of nucleating agents [15].

Chemical Name	Structure
1,2,3,4-bis(3,4-dimethyl-benzylidene sorbitol) ; DMDBS	

Chemical Name	Structure
Quinacridone Red Pigment, Color index pigment red 122 (73915)	
Phthalocyanine Blue Pigment, Color index pigment blue 15:3 (74160)	

2.7 Crystallization behavior

The crystallization process is a first-order transition that takes place when the polymeric material is cooled from the molten state to a temperature range located between the glass transition temperature and the melting temperature, at relatively large under cooling, and is due to the formation of crystalline nuclei and their subsequent growth. In homogeneous nucleation, stable crystalline nuclei are generated by the existence of statistical fluctuations in the melt, and the nucleation rate is constant. In the case of heterogeneous nucleation, the rate is variable, because it is the presence of heterogeneities in the system that induces the development of crystalline material. In any case, the nuclei present in the system at the start of the crystallization process include heterogeneous nuclei formed by particles chemically different from the crystallizable polymer, such as catalysts, pigments, impurities, nucleating agents and the homogeneous or athermal nuclei. Given that the rate of crystallization depends on the thermal history, melt-phase memory effects must be considered when studying polymer crystallization. In this regard, although the role of the heterogeneous nuclei can be regarded as surface defects and as such practically insensitive to the thermal history of the melt, the concentration of a thermal nuclei (i.e., preexisting crystallite structures in the melt),

with the same chemical structure as the matrix, is strongly conditioned by the melting temperature and the residence time at that temperature in the molten phase. For this reason, and to select the thermal history prior to crystallization required for good reproducibility of the crystallization process of the melting conditions prior to crystallization on the crystallization rate was analyzed, and the temperature of 210 °C and a residence time of 10 min were determined to erase any melt-phase memory of the previous three-dimensional structure. In the α -form, the isotactic polypropylene (iPP) chains are arranged parallel in a monoclinic unit cell with a fiber axis of 6.5 Å and alternate between layers of right-handed and left-handed helices. This polymorph is the most stable thermodynamically and dominant in the crystallization of iPP under normal processing conditions and is encountered in the majority of industrial applications of polypropylene [16].

The crystallization of iPP is controlled by the nucleation stage, and in the high temperature region where heterogeneous nucleation is predominant, the formation of crystalline nuclei can be accelerated by the presence of discrete particles that act as foreign nuclei in the polymer melt. These particles act as nucleating agents by reducing the induction time for crystallization, because the polymer melt does not need to form its own nuclei to initiate the crystallization process. They provide surfaces or nuclei that reduce the free energy barrier of the process, modify the size and density of the spherulites formed, and, consequently, alter the optical and mechanical properties of the material. In this respect, the control of the crystallization rate from the melt provides an important method for the modification of the solid-state properties of the material, allowing the design of materials for new applications. Furthermore, by using nucleating agents, the cycle times can be considerably reduced, especially in injection molding, which can have a decisive influence on the processing costs [16].

2.8 Literature reviews

Felgeman and Guthrie [4] studied the effect of C.I. Pigment blue 15:4 and C.I. Pigment red 122 on the properties of a pigmented Xenoy blend. The pigments were incorporated into the blend during extrusion. Both pigments acted as nucleating agents, increased the crystallinity of pigmented Xenoy in comparison with those of the unpigmented blends. Of the two pigments studied, C.I. Pigment red 122 has a greater effect on the properties than the C.I. Pigment blue 15:4. The effect that the pigments have on a polymer depends upon the level of interaction that occurs between the polymer matrix and the pigments. Factors influencing the final properties and mechanical properties of the polymer included the chemical composition and surface energy of the pigment, together with its particle size and particle size distribution. The inclusion of the carbonyl group is able to interact with the pigment surface.

Marks et al. [17] observed that isotactic polypropylene films that were pigmented with copper phthalocyanine had higher values of tensile modulus and crystallinity than did the unpigmented polypropylene films. The spherulite size for pigmented films was significantly smaller than those of the unpigmented film.

Suzuki and Mizuguchi [18] studied a mold shrinkage of the colored plastics based on a partial crystalline polymer assumed to be caused by pigment induced crystallization of polymers, polypropylene, and high density polyethylene. As a result, the mold shrinkage is found to become more significant, the onset temperature was higher, and crystallization rate was faster.

Silberman et al. [19] examined the effect of C.I. Pigment Red 122, a quinacridone, and C.I. Pigment green 7, a halogenated copper phthalocyanine, on the properties of isotactic polypropylene. The strong nucleation with the quinacridone was observed, yielding the

polymer with a very high chemical absorption occurring with low pigment concentrations, whereas physical absorption at high concentrations. For the phthalocyanine pigment, the symmetry of nitrogen atoms resulted in the physical adsorption of the polypropylene on the pigment surface.

Van de Velde et al. [20] observed that C.I. Pigment blue 15:1 acted as a nucleating agent for spin-dyed polypropylene. The crystallization temperature and enthalpy of the blue yarns were increased relative to those of the uncolored yarn. In addition, the smaller crystallites were observed in the blue yarns compared to those of the uncolored yarn.

Broda and Wlochowicz [21] investigated the structure of natural polypropylene fibers and colored polypropylene fibers. In the presence of a phthalocyanine, well formed α -crystallites were formed. In the presence of a quinacridone, structure with a large content of β -crystallites was formed. At higher take-up velocities, the nucleating action of the fibers were observed to be more perfect for the colored fibers compared to the structures of the uncolored fibers.

Takahashi et al. [22] prepared poly(L-lactic acid) film consisting of highly oriented α crystal was uniaxial by tensile force. The effects of the draw ratio, draw temperature, and draw stress on the crystal/crystal transform from α -form to β -form crystal were studied. At the initial stage of drawing, the highly oriented α crystals of the starting film transformed into a broader orientation distribution, and a significant crystal disorder was introduced. Upon further drawing, the α crystal steadily transformed into β crystals with increasing the draw ratio.

Peesan et al. [23] studied a hexanoyl chitosan/polylactide blend thin film. The blend films were obtained with a high degree of crystallinity, low tensile at break and modulus on the blend with increasing a hexanoyl chitosan content.

Papadopoulou and Kalfoglou [24] studied the compatibilization efficiency for poly(ethylene terephthalate)/polypropylene blends, in which maleic anhydride modification, offers some advantages over the pure components. Poly(ethylene terephthalate) may enhance the stiffness of polypropylene at higher temperatures while the polypropylene could facilitate crystallization of poly(ethylene terephthalate) by heterogenous nucleation further raising blend stiffness.

Broda [25] studied the efficiency of quinacridone and phthalocyanine in PP nucleation process. The study compared the crystallization temperature of pigmented and unpigmented PP. Both pigments created good nucleating activity. In the presence of pigments, the increment of the crystallization temperature, nucleation rate and nucleation efficiency were obtained.

Verga et al. [26] found that most nucleating agents nucleate the monoclinic alpha-form of PP, thermodynamically stable crystalline modification usually obtained under common processing conditions. Several nucleating agents are unable to nucleate the more rarely encountered β -form.

Wojciechowska et al. [27] studied the manufacturing and the structure of polypropylene (iPP) blends with fibre-grade poly(L-lactide). On the basis of thermal investigations, a method of iPP/PLA fibre melt-spinning was developed. By selecting optimum processing temperatures, blend fibres were obtained of good quality within the whole range of component concentrations. The supermolecular structure of the fibres obtained was investigated by wide-angle and small-angle X-ray scattering methods. It was stated that the structure was dominated by the smectic phase of iPP. The long period of this structure decreased as the PLA content in the mixture increased.