CHAPTER II

THEORETICAL BACKGROUND AND LITERATITRE REVIEW REFERENCES

2.1 Polycarbonate (PC)

Polycarbonate (PC) is an engineering thermoplastic, it has several properties such as excellent transparency, dimensional stability, excellent mechanical properties, flame retardant, high heat distortion temperature, and high impact strength. However, PC is known to exhibit poor solvent resistance, high processability, and notch sensitivity. PC can be prepared by reaction of bisphenol A and phosgene or diphenyl carbonate as shown in Fig. 2.1 and also by non-phosgene process. Applications of PC are bottle, lens, mirror, roof and automotive part.

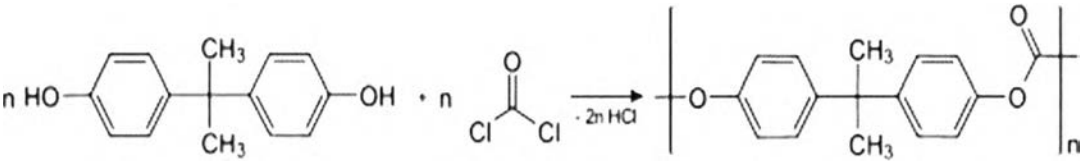


Fig. 2.1 Reaction of Polycarbonate PC.

PC/PLA blends are a good balance of these properties, high toughness, more green composition, high tensile strength, high heat resistance and flow properties.

2.2 Polylactic Acid (PLA)

Polylactic acid (PLA) is a thermoplastic aliphatic polyester which is derived from renewable resources such as corn starch or sugarcanes. Polymerization of PLA has been produced by either a direct polycondensation or a ring-opening reaction of lactide (Fig. 2.2). The advantages of PLA are high biodegradability and good mechanical properties. However, PLA has been limited for some application because of brittleness, poor impact strength, processability and low heat distortion temperature. Therefore, polymer blending is efficient and economical method to tailor new materials with an advantageous combination of end-use properties. Applications of PLA are food packaging, plastic bag, cup or glass.

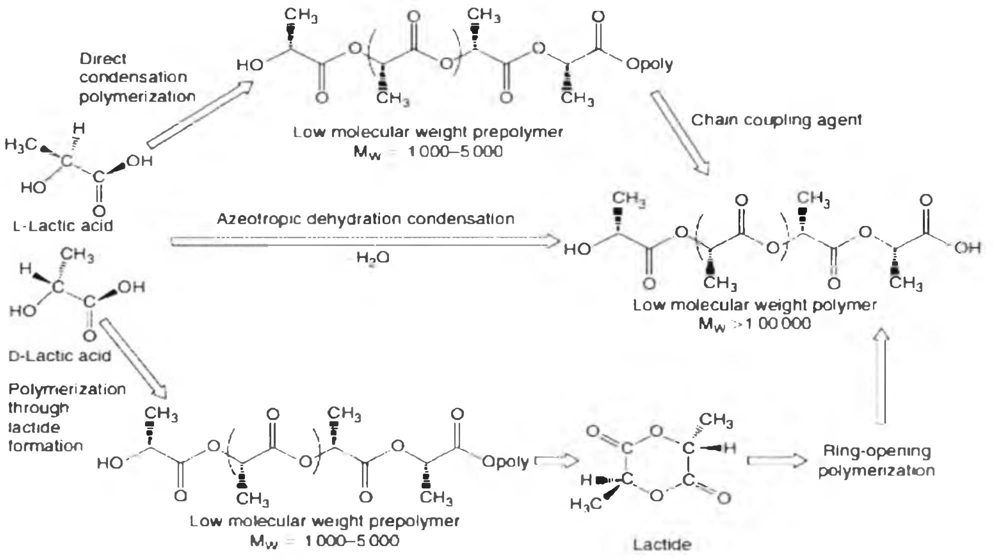


Fig. 2.2 PLA production process.

2.3 Immiscibility problems in Polymer alloys

Miscibility is the same as thermodynamic solubility; that is two polymers are miscible in each other if the free energy of mixing (ΔG_{mix}) is negative. In miscible blends, for which $\Delta H_{mix} = 0$, due to specific interactions, homogeneity is observed at least at the nanometer scale, if not at the molecular level. As it was already mentioned before, the formation of miscible polymer blends requires that the free energy of mixing,

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$$

Where ΔH_{mix} and ΔS_{mix} are the enthalpy and entropy changes,respectively

In general, mixing two polymers results in partially miscible, or completely immiscible system. Many polymers are very difficult to mix or disperse well into another one. These blends have large size domains of dispersed phase and poor adhesion between them. The immiscible blends have coarse phase morphology; the adhesion between phases is poor. As a result, their properties such as mechanical and thermal are irreproducible.

There are many reports about the immiscible blend between PLA and PC. Lee, B.J. *et al.*, (2011) found that the impact strength, tensile strength and flexural strength of the PC/PLA (70/30) blends is lower than that of neat PLA and PC. SEM micrographs revealed that the number-average droplet radius (Rn) of the dispersed PLA in PLA/PC blend is 1.42 μm. These results show that the immiscible between PLA and PC blend.

2.4 Exchange reaction in the melting mixing of PC/PLA blends

In general, PC has hydroxyl and phenyl groups at each side of end groups and PLA has hydroxyl and carboxyl groups at each side of end groups. Therefore, Transesterification reaction will occur via three possible ways during melt processing: ***alcoholysis***, the reaction between the hydroxyl end-groups of PLA with the carbonate groups of PC; ***acidolysis***, the reaction between the carboxyl end-groups of PLA with the carbonate groups of PC; and, ***direct transesterification***, the main process, is the reaction between the ester groups of PLA with the carbonate groups of PC. These possible transesterification can be shown as follows:

Alcoholysis:

- **PC-O-CO-O-PC + HO-PLA ⟶ PC-O-CO-O-PLA + PC-OH**
- **PC-OH + PLA-O-CO-PLA ⟶ PC-O-CO-PLA + PLA-OH**

Acidolysis:

- **PC-O-CO-O-PC + HO-CO-PLA ⟶ PC-O-CO-PLA + PC-OH + CO_2**

Direct transesterification:

- **PC-O-CO-OPC + PLA-O-CO-PLA ⟶ PC-O-CO-PLA + PC-O-CO-PLA**

Paola M. *et al.*,(2002) studied on the molecular structure of PET/PC blends in the presence of transesterification catalyst. This study revealed that the length of block copolymer between PC and PET decreases with increasing mixing time. When length of the PET and PC block decreases to about 15 monomeric units, a single homogeneous amorphous phase is observed. Another author suggested the increasing reaction time, the copolymer changed from block copolymers to random copolymers as follows in fig. 2.3 (Wilkinson, A.N. *et al.*, 1995);

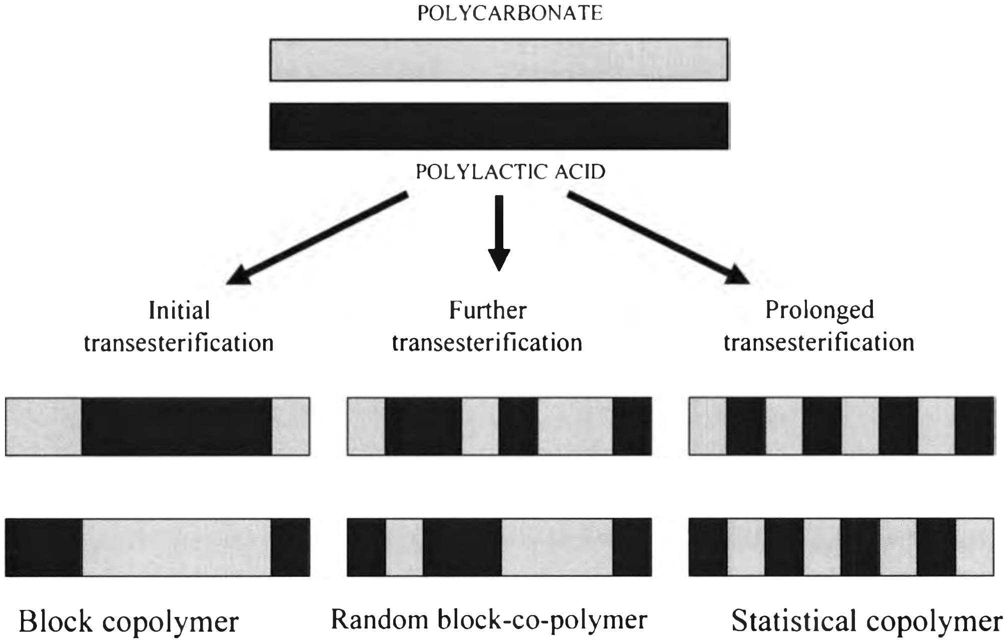


Fig. 2.3 Schematic representation of melt transesterification.

Wilkinson, A.N., (2000) found that a change in the morphology of the blends was observed because of the increasing concentrations of copolymers. In the initial concentration, bicontinuous morphology become to a more finely-dispersed structure and at a high degree of copolymer concentration, a homogeneous, amorphous material was formed.

These copolymers also change the solubility of the blends. Wilkinson, A.N. *et al.*,(1997) reported that the solubility of blends change with increasing in transesterification; at low degrees of reaction of block copolyesters there is reduced solubility, and at higher degrees of reaction, complete solubility of the statistical copolymers.

Some researchers tried to improve the compatibilization of polymer blends by using transesterification catalyst. However, Mendes, L. C., (2011) found that the catalyst caused significant lowering of both moduli (storage and loss) of PET/PC blend due to the lowering of the molar mass and the decrease of the viscosity values.

2.5 Compatibilization Process

To improve properties of immiscible blends, they usually need to be compatibilized. Compatibilization can be carried out either by adding a compatibilizer to a polymer blend, or prepared during the reactive processing.

Compatibilization means a process of improving interfacial properties of an immiscible polymer blend, leading to creation of polymer alloy. A polymer alloy is defined as an immiscible polymer blend which has a modified interface and/or morphology. A somewhat more clearly definition of a polymer alloy would describe a blend of at least two immiscible polymers stabilized either by covalent bond or ionic bond formation between phases, or by attractive intermolecular interaction, e.g. dipole-dipole, ion-dipole, H-bonding, van der waals forces, etc.

There are three goals for the compatibilization process. The first one is to change the interfacial tension, thus producing the desired degree of dispersion. The second is to make the morphology generated during the alloying stage will yield the optimum structure during the forming state, helping the stress transfer and therefore improving performance. There are 2 methods of compatibilization

2.5.1 Non-reactive compatibilization (additional compatibilizer)

Normally, adding block or graft copolymer would help to improve the compatibility of the polymer blend by using copolymer as the interphase in which blended polymer is dissolved and decrease interfacial tension and increase interfacial adhesion such as ethylene-propylene copolymer is a compatibilizer in PE/PP blend, styrene-ethylene/butane-styrene (SEBS) triblock copolymer and poly(ethylene-co-glycidyl methacrylate) (EGMA) in PLA/PC blend.

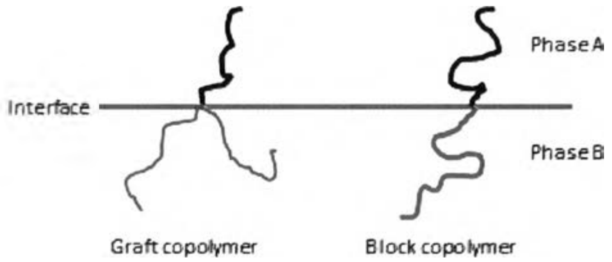


Fig. 2.4 Non-reactive compatibilization.

B. Lee et al. (2011) reported that the impact strength of the PC/PLA (70/30) blend is highest when adding SAN-g-MAH in the amount of 5 phr. For EOR-MAH and EGMA, when the compatibilizers content is at 1 phr, the impact strength of the PC/PLA (70/30) blends increases, then the impact strength would decreases as the increasing compatibilizers content.

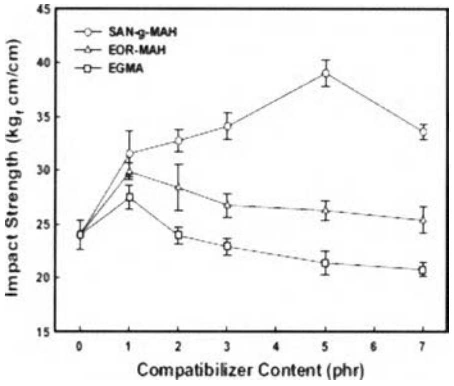


Fig. 2.5 Impact strength of PC/PLA (70/30) blend with the type of compatibilizer; (○) SAN-g-MAH ;(□) EGMA ;(Δ) EOR-MAH.

Mechanical properties of polymer blends are related to the particle size of the dispersed phase and interfacial tension between the two phases. Dispersed phase of PC/PLA (70/30) blends with SAN-g-MAH in the amount of 5 phr decreases most significantly. Thus, the results of mechanical properties of the PC/PLA (70/30) blend in presence of SAN-g- MAH at 5 phr show the maximum mechanical strength.

Therefore, the decrease in particle size of the blends suggests the increase of the compatibility between the PC and PLA components.

2.5.2 Reactive compatibilization

2.5.2.1 Reactive + Reactive: Both of polymer A and B have reactive group and reactive each together become copolymer at interphase such as PA6, 6 (there are terminal amine and carboxylic group.).

Harada M. *et al.*,(2008) reported that lysine triisocyanate (LTI) is the most appropriate reactive compatibilizer comparing with others which are 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione;epoxide-trimethylolpropane triglycidyl ether and 1,3,5-tris(6-isocyanatohexyl)biuret in PLA/PCL blend. PLA/PCL blended in the presence of LTI had the highest torque in a mixer test. Moreover, The MFR values of PLA/PCL blends decreased with increasing amount of LTI. LSCM showed that the diameters of PCL in PLA/PCL (80/20) were dispersed about 0.4 μm in the presence of 0.5 phr LTI. VEAFM showed that the spherical diameter of PCL islands was about 50 nm, much smaller than that for the physical blend. These results indicate that isocyanate groups of LTI react with both terminal hydroxyl or carboxyl groups of PLA and PCL, and the compatibility of PLA/PCL blends was improved by LTI.

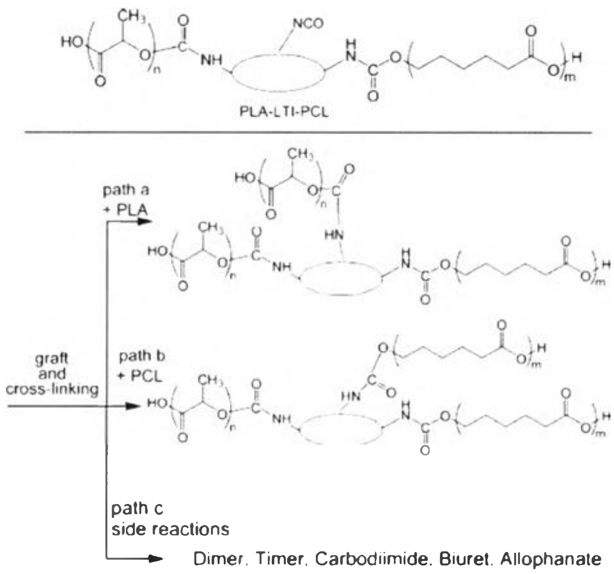


Fig. 2.6 Predicted reaction pathway of PLA-LTI-PCL, PLA, and PCL.

Chianc C.H. *et al.*,(1996) found that The epoxy functional groups in Styrene Glycidyl methacrylate copolymers can react with the PA6 amine and carbonyl endgroups at interface of Polyamide-6 (PA6) to form various SG-g-PA6 copolymers. The styrene and the SG segments of the Styrene Glycidyl methacrylate copolymers are miscible with PPO due to the identical structure. The schematic diagram illustrate the distribution and structure of the Styrene Glycidyl methacrylate copolymers where the SG-g-PPO and SG-g-PA6 are grafted.

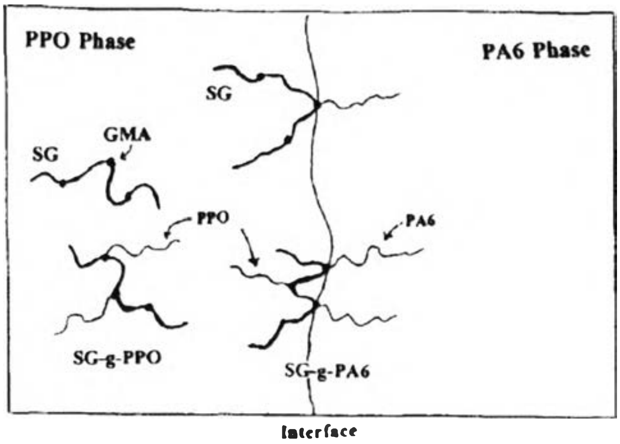
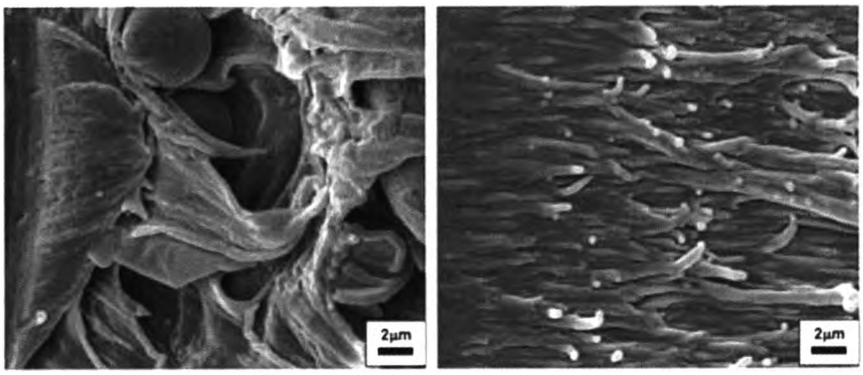


Fig. 2.7 Schematic diagrams illustrate the distribution and structure of the Styrene Glycidyl methacrylate copolymers around interface.

The presence of Styrene Glycidyl methacrylate compatibilizer in the PA6/PPO blends is able to reduce domain size, enhances the interfacial adhesion, and improves the resultant mechanical properties. Styrene Glycidyl methacrylate copolymer has been demonstrated as an effective reactive compatibilizer for the PA6/ PPO blends.

Vilay, V. *et al.*,(2010) found that LTI addition significant improves the compatibility between PLLA and poly(butylene succinate-*co*-e-caprolactone) (PBSC). FE-SEM micrographs show that PLLA/PBSC blends with LTI, apparent spherulitic structures of PBSC could not be observed on the surfaces.



(a) (b)

Fig. 2.8 FE-SEM micrographs of fractured surfaces (a) PLA/PBSC
(b) PLA/PBSC/LTI.

The FE-SEM micrographs of fractured surfaces (Fig.5a) show that the PLA/PBSC specimen exhibits two-phase morphology proved by the presence of many voids which were created because of debonding at the interfaces between the PBSC and PLLA spherulites. On the other hand, for PLLA/PBSC/LTI blends (Fig.5b), void formation was disappeared because of increase of entanglement of PLLA and PBSC molecules caused by chemical reaction. This corresponded to the improvement of immiscibility between PLLA and PBSC in the presence of LTI.

2.5.2.2 *Reactive + Unreactive:* Polymer A has reactive group and polymer B has inert chemicals. The concept of this compatibilization is chemical reaction between polymer A and one side of reactive compatibilizers. Another side of them can dissolve with polymer A such as PE and PC in presence of Ethylene acrylic acid copolymers (EAA). Ethylene in EAA can completely dissolve in PE and acrylic acid can occur ester and acid reaction with PC.

Yin B. *et al.*,(2006) focus on PC/HDPE blend by using a grafted copolymer PC-graft-ethylene-co-acrylic acid (PC-graft-EAA) as a compatibilizer in situ during processing operation by ester and acid reaction between PC and ethylene-acrylic acid (EAA) in the presence of the catalyst dibutyl tin oxide (DBTO). The EAA segment of this copolymer is miscible with PE phase and the PC graft would be soluble with the PC phase. From morphological studies, the particle size and its distribution of EAA dispersed phase in PC/PE blend in the presence of DBTO has an obvious improvement comparing with the absence of DBTO, which indicates that a PC-graft-EAA copolymer formed during mixing acts as an interfacial agent in improving the compatibilization of an EAA/PC blend. However, DSC analysis show a decrease in the degree of the crystallinity of the EAA and PE phase in ternary PC/PE/EAA blends in the presence of DBTO.