CHAPTER II
THEORY AND RESEARCH BACKGROUNDS

2.1 Low Density Polyethylene (LDPE) properties

LDPE is polyolefin which contains long chain branching in the order of 1-3 per 1000 carbon atoms as well as 10-30 short chain branching per 1000 carbon atoms which difference structure between LDPE and HDPE are shown in Figure 2.1a and 1.2b consequently. The LLDPE has shorter branch chain than LDPE. LDPE has low tensile strength and modulus, medium impact and tear resistance [6].
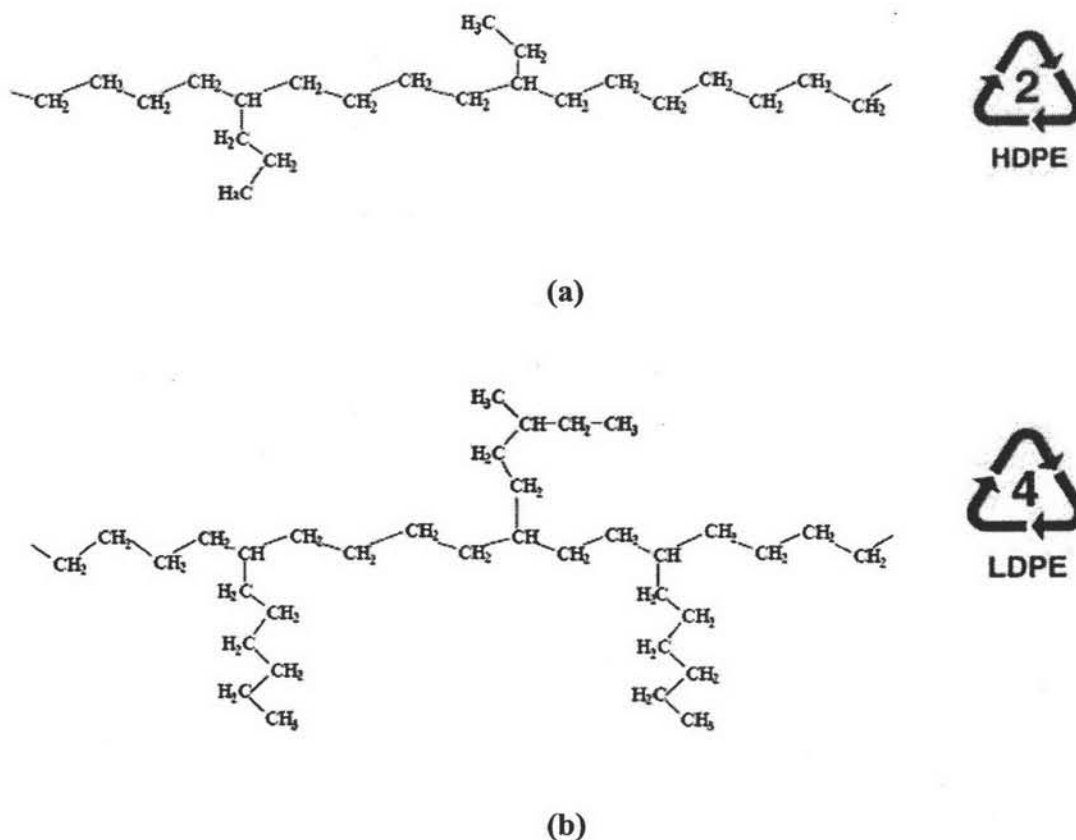

(a)

(b)

Figure 2.1 Model structure of polyethylene: (a) HDPE (b) LDPE

2.2 Poly(Lactic Acid) (PLA) properties

Poly(lactic acid)(PLA) is a linear aliphatic polyester which has chemical structure in Figure 2.2.

$$\left[\begin{array}{c} -CH-\overset{\displaystyle O}{\overset{\|}{C}}-O- \\ | \\ CH_3 \end{array} \right]_n$$
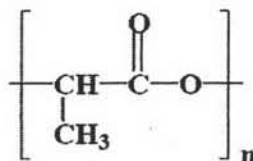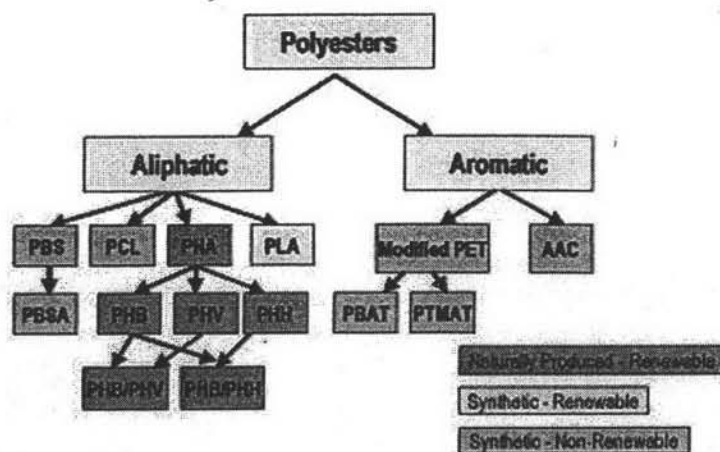
Figure 2.2 Chemical structure of polylactic acid(PLA)

It produced by poly-condensation by naturally produced lactic acid or by the catalytic ring opening of the lactide group. Lactic acid is produced (via starch fermentation) as a co-product of corn wet milling. PLA is one of degradable polyesters family. Lactide is the cyclic dimer of lactic acid that exists as two optical isomers, d and l. The l-lactide is the naturally occurring isomer, and dl-lactide is the synthetic blend of d-lactide and l-lactide. The homopolymer of l-lactide (LPLA) semicrystalline polymer. These types of materials exhibit high tensile strength, low elongation, and consequently high modulus that makes them more suitable for load-bearing applications such as in orthopedic fixation and sutures lactide)(DLPLA) is and amorphous polymer, exhibiting a random distribution of both isomeric forms of lactic acid, and accordingly is unable to arrange into an organized crystalline structure. This material has lower tensile strength, high elongation, and a much more rapid degradation time, making it more attractive as a drug delivery system. Poly(l-lactide) about 37% crystalline, with a melting point of 175-178 °C and a glass-transition temperature of 60-65 °C. The degradation time of LPLA is much slower than that of DLPLA [7]. PLA is fully biodegradable when composted in a large-scale operation with temperatures of 60 °C and above. The first stage of degradation of PLA (two weeks) is via hydrolysis to water soluble compounds and lactic acid. Rapid metabolisation of these products into CO_2, water and biomass by a 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 [7].

Polyester degradable family is showed in Figure 2.3. Characteristic of PLA is contains ester linkages which are sensitive to both chemical hydrolysis and enzymatic chain cleavage.

PHA - polyhydroxyalkanoates   PHB - polyhydroxybutyrate
PHH - polyhydroxyhexanoate   PHV - polyhydroxyvalerate
PLA – poly(lactic acid)   PCL - polycaprolactone
PBS – poly(butylene succinate)   PBSA – poly(butylene succinate adipate)
AAC - Aliphatic-Aromatic copolyesters   PET – poly(ethylene terephthalate)
PBAT – poly(butylene adipate/terephthalate) PTMAT- poly(methylene adipate/terephthalate)

Figure 2.3 Biodegradable polyester family [8]

2.3 Polymer blend

By definition, any physical mixture of two or more different polymer of copolymers 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 of more existing polymers, there is an obvious pecuniary advantage.

A number of technologies have devised to prepare polymer blend. It so happens that most polymers are not compatible. Rather, they separate into discrete phase on being mixed, although an increasing number of completely miscible blends are being developed. Differences between the two types are manifested in appearances, miscible blends are usually clear, immiscible blends are opaque and in such properties as glass transition temperature, miscible blends exhibit a single T_g intermediate between those of the individual components, whereas immiscible bland exhibit separate T_gs characteristic of each component. Miscibility is by no means prerequisite to commercial utility.

Homogeneous polymer blends are more convenient from the standpoint of being able to predict properties of processing characteristics. If additive 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.

In general, the properties of a 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 clearly describe is that of 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 adhesion between the two polymer blends.

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. Miscible polymer blend has a single phase, in contrast, immiscible blend polymers is a polymer mixture in which polymer-A forms a separate phase from polymer-B. The thermodynamically immiscible blend is associated with the positive value of the Gibb's free energy of mixing i.e. $\Delta G_m = \Delta H_m > 0$.

The compatibility of a polymer-polymer system determines polymer system properties. In general, compatible polymer blends is a homogeneous polymer mixture to the eye with physical properties. Polymer blends that are heterogeneous on a macroscopic level are called incompatible polymer blends [9, 10].

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, giving improve stress transfer. A third effect is to stabilize the dispersed phase against growth during annealing, again by modifying the phase-boundary interface.

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 copolymer represents the most extensively researched approach to compatibilization of blends. Block copolymers have been more frequently investigated, Graft copolymer, and in particular block copolymer containing blocks chemically identical to the blend component polymers. It is perhaps not surprising that block and graft copolymer containing segments chemically identical to blend component are obvious choices as compatibilizers, given that miscibility between the copolymer segments and the corresponding blend component assured, provides the copolymer meets certain structural and molecular weight requirement, and that the copolymer locates preferentially at the blend interfaces.

Many workers have described the addition of functional polymers 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]. Example includes the grafting of maleic anhydride or similar component to polyolefin, the resulting pendent carboxyl group having the ability to form a chemical linkage with polyamides via their terminal amino groups [12].

A comparatively new method of producing compatible thermoplastic blends is via reactive blending, which relies on the *in situ* formation of copolymers or interacting polymers. This differ from other compatibilization routes in that the blend component themselves are either chosen or modified so that reaction occurs during melt blending, with no need for addition of a separate compatibilizer. This route has found commercial application, for example in blends of polyamides with graft-functional polyolefin elastomer. Graft-functionalized elastomer, produced by melt modification, is commercially available for toughening nylons [13].

2.4 Determination of polymer/polymer miscibility

There are several methods that can determine compatibility of polymer blend, each method has a limit of useful range. A variety of experimental techniques have been used to determine the compatibility of polymer blends. Some techniques, such as calorimetry, thermomechanical, dynamic mechanical procedures, are based on the determination of the number and the location of the glass transition temperature; T_g. Other techniques are based on scattering of microscopic techniques.

2.5 Polymer degradation

The durability of polymeric material can be studied under several environmental and artificial conditions, which have been summarized in Figure 2.4.

Biodegradation [15] is an event which takes place through the action of enzymes and /or chemical decomposition associated with living organisms (bacteria, fungi, etc.) or their secretion products. Microbiological deterioration can be achieved by exo- and endo-enzymes or by products secreted biochemically or chemically from these. Macroorganisms can also eat and, sometimes, digest polymers and give a mechanical, chemical or enzymatic ageing. There are many different degradation modes that in nature combine synergistically to degrade polymers. Biodegradation might be better used as term only when it is essential to distinguish clearly between the action of living organisms an other degradation modes (e.g. photolysis, oxidation, hydrolysis).
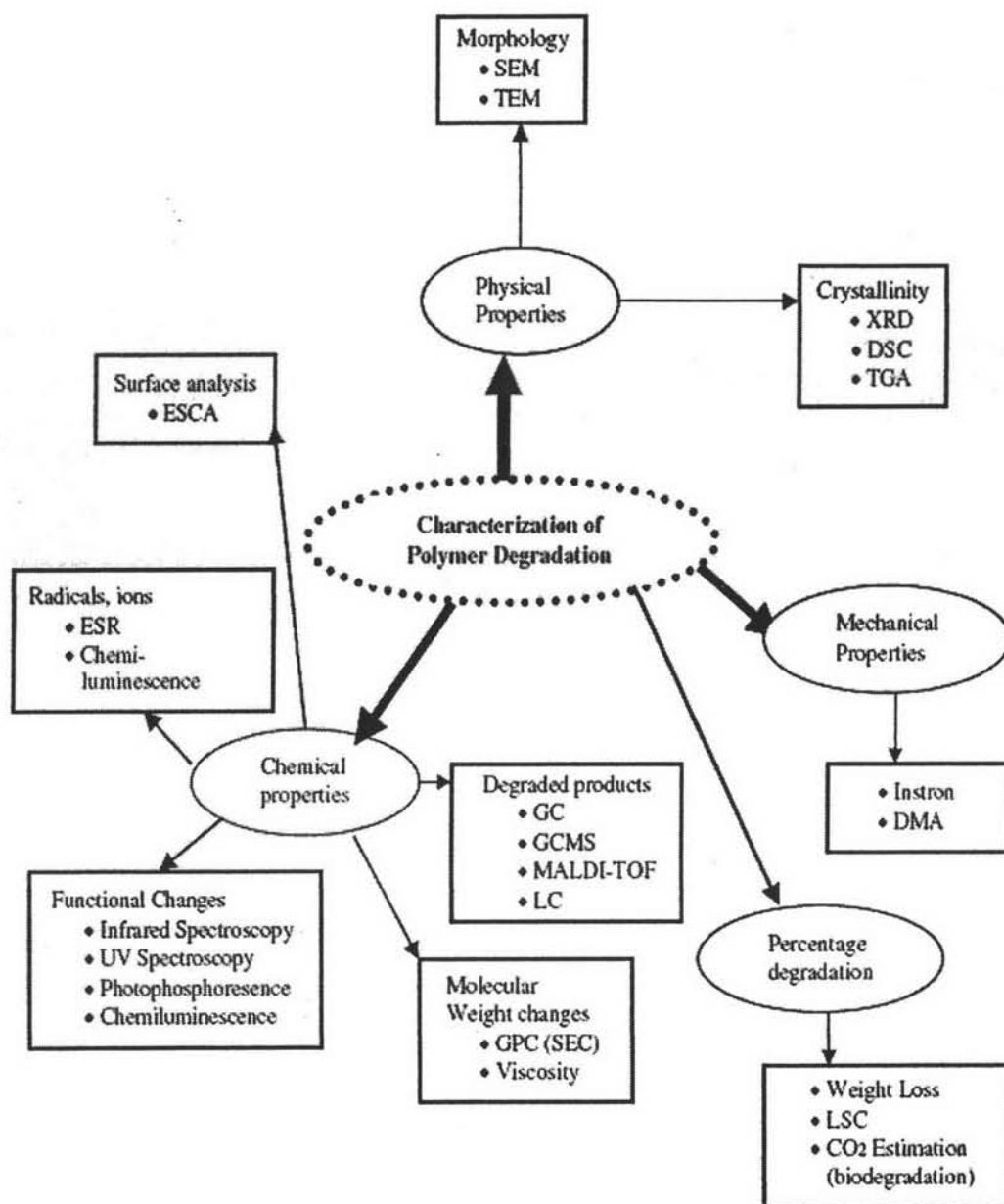
Figure 2.4 Different analytical techniques to analyze the polymer durability [14]

Table 2.1 Reaction catalyzed and reactive bonds of different classes of enzyme [16]

Enzyme class	Reaction catalyzed	Reactive bonds
1. Oxidoreductase	Redox reactions	• $C=O$ • $C-NH_2$
2. Transferase	Transfer of functional group	• One C-groups • Acetyl groups • Peptides
3. Hydrolase	Hydrolysis	• Esters • Peptides
4. Lyase	Addition to double bonds	• $HC=CH$ • $C=O$
5. Isomerase	Isomerisation	• Racemases
6. Ligase	Formation of new bonds using ATP	• C-O • C-S • C-N

Chemical structure of the substrate is critically important for any enzymatic attack and the creation of a new kind of enzyme which are summarized in Table 2.1. Enzymes are biological catalysts, with the same action as chemical catalysts, i.e. by lowering the activation energy they can induce or increase in reaction rates in an environment otherwise unfavorable for chemical reaction. A purely enzymatic degradation of a long straight olefin chain dependent on the enzymatic cleavage of the C-C bond should not be expected, since such an endoenzyme does not occur in nature. Oxidation is instead the critical initial step in the degradation of many rather inert organic molecules. Esters bond in PLA could be hydrolyzed by enzyme class of hydrolase and the hydrolysis reaction of PLA shows in Figure 2.5.
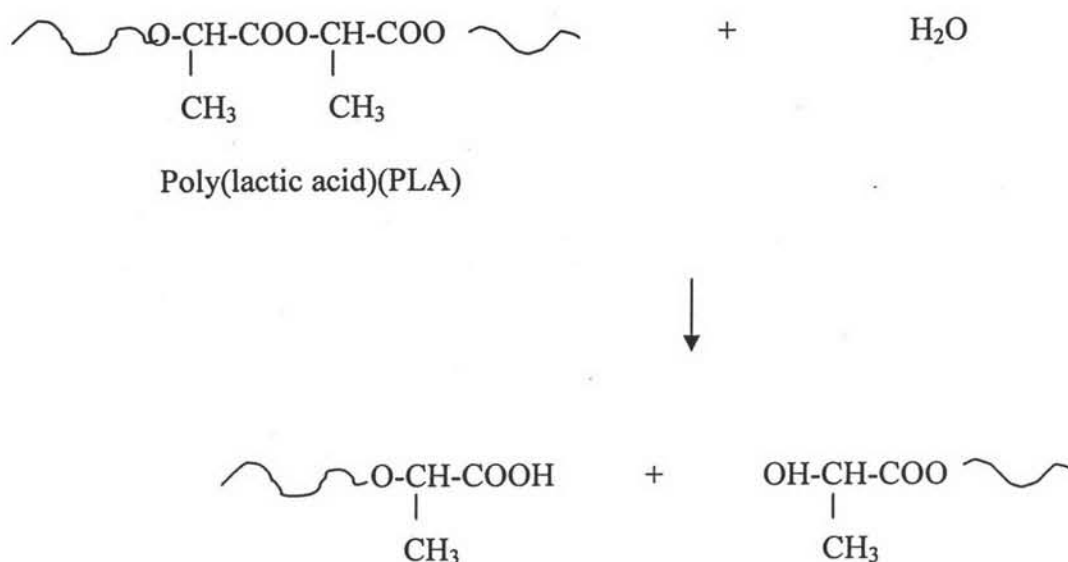
~~O-CH-COO-CH-COO~~   + H_2O

| | |
| CH_3 | CH_3 |

Poly(lactic acid)(PLA)

↓

~~O-CH-COOH~~   +   OH-CH-COO~~

| | |
| CH_3 | CH_3 |

Figure 2.5 Hydrolysis reaction of PLA [17]

2.6 Literature review

Chen et al [18] studied preparation and characterization of biodegradable PLA polymeric blends. PLLA and PDLLA blends were prepared by mixing different percentages with solution blending. The result has shown that pure PLLA is hard and brittle, and that adding PDLLA or PCL can change its original properties. Solution-blending is an effective and easy way to achieve the purposes mentioned above. PLLA/PDLLA has poor miscibility which can be significantly improved by addition of a copolymer of ethylene oxide and propylene oxide surfactant, and PLLA/PDLLA is hard and tough after adding the surfactant. The DMA data show that 40/60 PLLA/PDLLA has harder and tougher mechanical properties than PLLA, and that adding 2% surfactant to the blends can increase their miscibility, especially for the 50/50 PLLA/PDLLA blend. In comparison with PLLA/PDLLA blends, the PLLA/PCL blends have higher elongation and weaker mechanical properties.

Shinoda et al. [19] studied the amphiphilic biodegradable copolymer, poly(aspartic acid)-*co*-lactide by acceleration of degradation rate and improvement of thermal stability for poly(lactic acid) and other biodegradable polymer. Poly(L-lactic acid) (PLA) was melt-blended with a small amount of poly[(aspartic acid)-*co*-lactide] (PAL) or poly((sodium aspirate)-*co*-lactide) (PALNa) and processed into homogeneous press films. The mechanical properties and transparency of such blends are comparable to that of the non-blended PLA film. The degradation behavior of the blend film in phosphate buffered solution, in compost and soil was investigated in terms of the polymers mechanical properties, molecular weight, morphology and crystallinity. The results suggested that PAL and PALNa are effective additives for acceleration of the hydrolysis of PLA. The non-enzymatic hydrolysis rates of poly(butylene succinate) (PBS) and polycaprolactone (PCL) were also enhanced by the presence of PAL in the blend. The melting test of PAL/PLA blend film revealed that the PAL can improve the thermal stability of PLA as well

Guimaraes et al. [20] studied the effect of molecular weight and long chain branching of metallocene elastomer on the properties of high density polyethylene blends. The rheological properties and morphological characteristics of blends based on high density polyethylene (HDPE) and two different grades of poly(ethylene-co-octene) metallocene elastomer (EOC) were studied. These elastomers were commercial samples differing in molecular weight, and rheology index (DRI). Blends were processed in a single screw extruder (L/D = 32), at 230 °C and 50 rpm, using a mass fraction weight percent of EOC in the range from 5-80%. The rheological properties were evaluated in dynamic experiments at 190 °C and frequency range from 10^{-1} s^{-1} - 10^{-2} s^{-1}. The blends exhibited pseudoplasticity and complex rheological behavior. The complex behavior was intensified by increasing molecular weight and long chain branching proportion (DRI) of EOC elastomer. The morphological characterization was carried out using scanning microscopy (SEM). The blends exhibited dispersed morphologies with EOC domains distributed homogeneously and with particle size inferior to 2 μm.

Anderson and Hillmyer [21] studied the influence of block copolymer microstructure on the toughness of compatibilized polylactide/polyethylene blends Poly(L-lactide) (PLLA) was melt blended with a set of polyethylene (PE) in an effort to increase the impact strength of the PLLA. As compatibilizers, they prepared a series of molecularly distinct polylactide–polyethylene block copolymers. The

influence of the copolymer structure on the matrix/dispersed phase interfacial adhesion was correlated with the mechanical properties of the PLLA composites. For the lowest modulus PE dispersed phase, the block copolymer that gave the strongest interfacial adhesion was necessary to achieve the most significant improvement in toughening. Whereas with the stiffest PE, the block copolymer that gave the weakest interfacial adhesion resulted in the greatest improvement in impact strength. For the intermediate stiffness PE, an intermediate degree of adhesion was necessary to obtain the largest increase in the impact properties. The impact properties of the composites were also found to be highly dependent on the dispersed phase properties

Biresaw and Carriere [22] studied compatibility and mechanical properties of blends of polystyrene with biodegradable polyesters. The tensile properties of binary blends of polystyrene(PS) with the biodegradable polyesters,polycaprolactone (PCL), D,L-poly(lactic acid) (PLA), and Eastar Bio Ultra (EBU) were investigated Blend composition ranging from pure PS to pure biodegradable polyester, in 25% increments, were compounded, injection molded, and used in tensile tests, from which the following tensile properties were calculated: yield stress, yield strain, and modulus. In general, the tensile properties of the PS/biodegradable polyester blends were found to be between the values of the corresponding pure components. PLA/PS>PCL/PS>EBU/PS, which is the exact opposite of the reported trend in the interfacial tensions of these blends. This implies a correlation between tensile and interfacial properties that is consistent with expectations. However, the data also showed the yield strain and modulus of the pure biodegradable polyesters decreasing in the order: PLA>PCL>EBU, which is identical to the observation on the blends with 25%PS. Thus, the observed trend in the tensile properties could also be due to a contribution from the bulk properties of the biodegradable polyesters.

Galloway et al [23] studied the effect of block copolymers on the cocontinuous morphology of 50/50 (w/w) polystyrene (PS)/high density polyethylene (HDPE) blends investigated using symmetric polystyrene–polyethylene block copolymers (PS–PE) with molecular weights varying from 6 to 200 kg/mol. The coarsening rate during annealing was compared to the Doi–Ohta theory. An intermediate molecular weight PS–PE, 40 kg/mol, showed remarkable results in reducing the phase size and stabilizing the blend morphology during annealing. Mixing small amounts of 6, 100 or 200 kg/mol PS–PE in the blend did not reduce the phase size significantly, but did decrease the coarsening rate during annealing. In stabilizing the morphology,

6 kg/mol PS–PE was inferior to 100 and 200 kg/mol. The existence of an optimal molecular weight block copolymer is due to a balance between the ability of the block copolymer to reach the interface and its relative stabilization effect at the interface.