# CHAPTER II
LITERATURE REVIEW

As we know both PBT and HDPE possess some useful properties, but their uncompatibilized blends do not exhibit many interesting properties. PBT offers strong impact properties, good dimensional stability and excellent electrical resistivity, however, it has a negative swelling during melt extrusion and a relatively high mold shrinkage during compression. Also, its lower melt viscosity result in poorly defined sample shapes during certain processing operations.HDPE,on the other hand, has excellent low temperature flexibility, low mold shrinkage, ease of processing and good resistance to moisture permeation. The combination of the excellent properties of more than one existing polymers is required.

2.1 Poly (butylene terephthalate)

Poly (butylene terephthalate) (PBT) is one member of the terephthalic polyesters, PBT is a general-purpose engineering plastic made through polycondensation of purified terephthalic acid (PTA) with 1,4-butanediol (BDO).Initially, PBT was first used in the textile industry. In the textile sector, PBT is spun into fibers and used in the carpet sector. However, today due to competition with polyamides, PBT is mainly used as a substitute for metals, thermoset resins, and engineering plastics. The most important applications of PBT are for products used in the automotive, electrical, electronics, telecommunication, as well as precision engineering sectors.
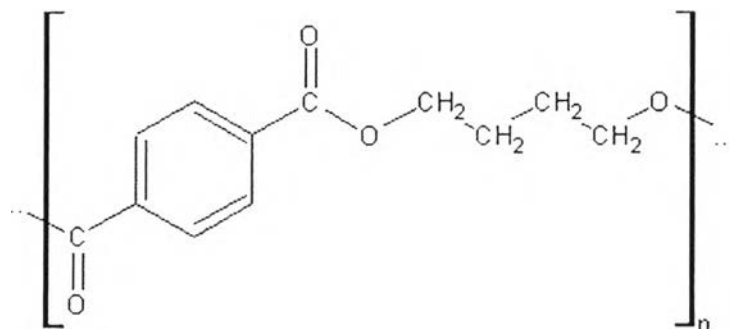
Figure 1: Structure of Poly(butylene terephthalate).

PBT offers a valuable combination of technical properties with its exceptional resistance to heat, creep and chemicals, good processability and good economics for a variety of applications. However, PBT faces inter-material competition from other engineering thermoplastics. In electronics and electrical applications, PBT competes with PET. On the other hand, PBT faces new competition from polytrimethylene terephthalate (PTT), which exhibits performance and processing characteristics similar to high-performance PBT. From their macromolecular structures, we can notice the structural and substantial differences give rise to their different properties.

Structure of Aromatic Polyester Polymers

PET	PTT	PBT
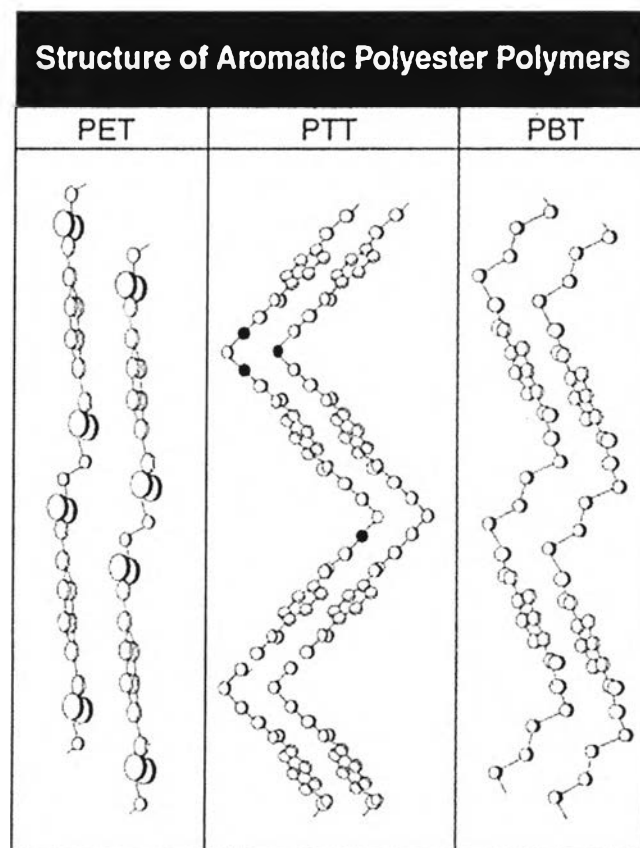
Figure 2: Different structuresof PET, PTT and PBT.

In the year 2000, Yeong-TarngShien *et al.,* studied the mixture of PP–MA and an epoxy resin was demonstrated to be an efficient dual reactive compatibilizer for immiscible and incompatible PP/PBT blends. The PP–MA with a low MA content is miscible with PP to make it quasi-functionalized, while the multifunctional

content is miscible with PP to make it quasi-functionalized, while the multifunctional epoxy has the chance to react with PBT and PP–MA at the interface simultaneously. Thus, the *in situ*-formed PP–MA-*co*-epoxy-*co*-PBT copolymers are able to anchoralong the interface and serve as efficient compatibilizers. The mechanical properties of the PBT–richblends are improved by increasing the epoxycontent to 0.3 phr. An epoxy content of 0.5phr can lead to a light crosslinking in the PBT phase of the PBT-rich blends and result in a lack of a compatibilization effect. Epoxy does not demonstrate compatibilization effects for the PP/PBTblends without the presence of PP–MA in theblends.

Sadhan C. Jana (*et al.,* 2001) studied low molecular weight epoxy molecules in compatibilization of PBT-PPE blends. The blend morphology and stability of morphology against annealing depended on epoxy content and the type of epoxy. It was found that a minimum of 2phr of EPON[®]832, 5phr of EPON[®]828, or 10phr of EPON[®] SU-8 were required to effectively compatibilize the PBT-rich blends. The effects of compatibilization by epoxy were also reflected in tensile and impact strengths. The best improvements were obtained in blends containing EPON[®]832, probably due to better chain flexibility of the molecules, a three-fold increase of tensile strength and a four-fold increase of impact strength over uncompatibilized blend were observed.

S.H. Jafari (*etal.,*2005) studied the morphology and thermal characteristics of poly(trimethyleneterephthalate) (PTT)/metallocene linear low-density polyethylene (m-LLDPE) blends with different amounts of a terpolymer based on glycidyl methacrylate (GMA), employed as a possible compatibilizer, were systematically examined. DMTA results showed two distinct peaks in all the blends associated with each component. DSC thermograms of the blends also revealed two separate melt crystallization peaks and two distinct melting peaks showing that two polymers crystallize separately to form their own crystallites.It was verified that the presence of PTT retards the crystallization ability of m-LLDPE owing to the influence of the compatibilizer in changing the state of dispersion of minor component. The addition of the terpolymer to the system efficiently reduced the droplet size of the dispersed phase associated with the role of interfacial products in suppressing the coalescence. However, the effectiveness of the terpolymer as a

compatibilizer beyond 5 wt% decreases which can be assigned to the formation of micelles in the bulk phases.

JoungSook Hong (*et al.,* 2006) When two immiscible polymers, PBT and PE, are mixed, specifically when PBT phase is matrix, a size reductionis obtained by the addition of organoclay having a specific preference for one of the blend components, and the resultingblend shows a stable morphology with a homogeneous domainsize. The effect of the organoclay on the reduction in thedroplet size is governed by the location of the organoclay, which is determined by the difference in the affinity of the organoclay with each component and the clay content. The presence of organoclay at the interface hydrodynamically stabilizes the blend morphology by suppressingthe coalescence of the droplets and also makes themorphology thermally stable.

2.2 High Density Polyethylene (HDPE)

High-density polyethylene (HDPE) is one type of polyethylene (PE) family which has many types being different density such as low density polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE) , also high density polyethylene (HDPE) and Ultra High Molecular Weight Polyethylene (UHMW-PE).Although the density of HDPE is only marginally higher than that of low-density polyethylene, HDPE has little branching, giving it stronger intermolecular forces and tensile strength than LDPE. The lack of branching is ensured by an appropriate choice of catalyst (e.g., Ziegler-Natta catalysts) and reaction conditions.The difference in strength exceeds the difference in density, giving HDPE a higher specific strength. It is also harder and more opaque and can withstand somewhat higher temperatures (120°C/248°F for short periods, 110 °C /230 °F continuously).

There is both homogeneous and heterogeneous polymer blending. For homogeneous blend, each blend component loses their unique properties and the blend properties are about the average of both blend components. For heterogeneous blends, the properties of each blend component still present. The poor properties of one component can be improved by the strength of the other blend component. There

are several of morphologies of heterogeneous blends. The most frequently founded are i) a dispersion of one polymer in the matrix of another polymer, ii) a co-continuous two-phase morphology. The type morphology that will be obtained depends on the characteristic of the blend component.

T.L. Dimitrova (*et al.,* 2000) studied on the compatibilization of PET/HDPE blends, their morphology, rheological and mechanical properties have been compared with those of the same blends compatibilized with a class of EVA and EVOH based copolyesters. The incompatibility of these two classes of polymers, polyesters and polyolefins, gives rise to gross phase separation, lack of adhesion between the phase and then to poor mechanical and barrier properties. On the basis of its structure, PET is capable both of chemical reactions with polar polymers and of specific polar interactions, like H-bonding. A significant improvement of the morphology and of the mechanical properties, and in particular of the elongation at break, can be achieved by using a third component acting as compatibilizing agent. The compatibilizing capability of the functionalizedelastomer and of the copolyester used in this workis confirmed both by the viscosity curves and by the SEM micrographs. The compatibilizing action of the functionalized elastomer employed in this work can be attributed to the formation of H-bonding with the polar component.

Kilwon Cho(*et al.,* 1993) It was found that each HDPE/ionomer blend had two well-separated melting peaks and two crystallization peaks, which indicates that the components of such a blend are immiscible with each other. The tensile behavior of the ionomer showed severe strain hardening just above the yield point, which leads to a lower elongation at break and a higher tensile strength than HDPE, possibly due to a network-like structure formation of ionic aggregates. The tensile properties of HDPE/ionomer blends were generally inferior to those of the pure components. Furthermore, the tensile properties exhibited severe negative deviation from linear additivity of properties, which is characteristic of incompatible blends. The negative deviation was also observed for tear strength of HDPE/ionomer blends. Observation of tear fracture surfaces of the blends showed fibrillar structure when ionomer content was relatively low. However, for the blends of higher ionomer composition much less fibrillation on the fracture surface was observed, which yields

a higher value of tear energy. This is attributed to a network-like structure of the ionomer continuous phase of the blends.
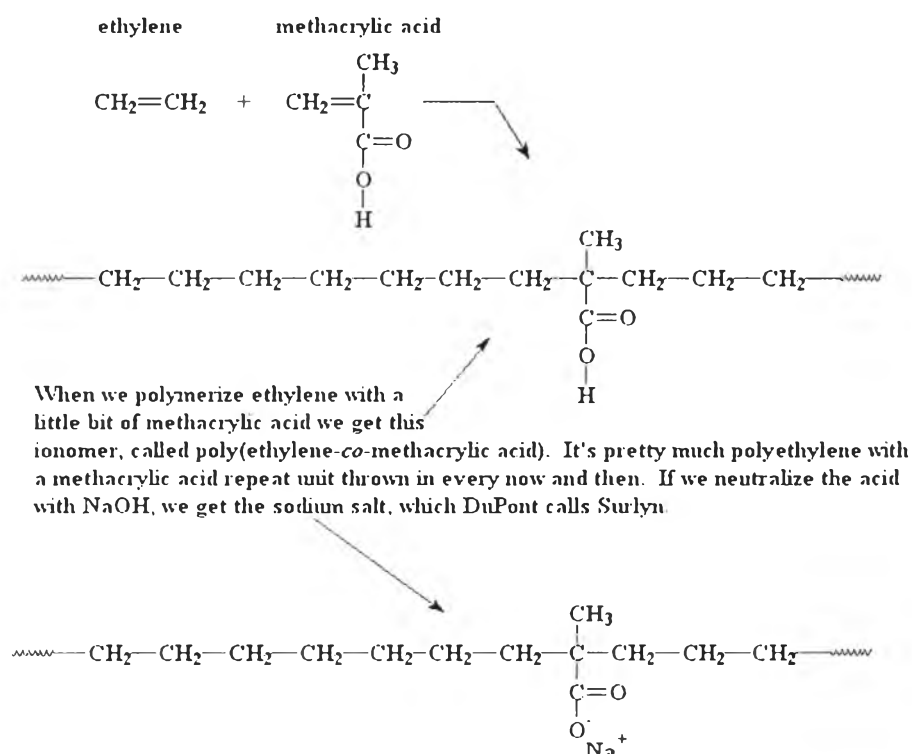
2.3 Na-EMAA ionomer

Polymers with small mole fractions (<15 mol%) of ionic groups covalently bonded to the polymer backbone are called ionomers. Usually, the ionic groups result from neutralization of sulphonic acid or carboxylic acid groups. Either monovalent (e.g. Na^+, K^+) or divalent (e.g. Zn^{2+}) metal cations are used as counterions. Sulphonic acid or carboxylic acid groupsareintroduced into the polymerchains by copolymerization or chemical modification of existing polymers. Whatever the cation, the ionic groups tend to associate into multiplets, which at sufficiently high concentrations can associate into clusters. Multiplets and clusters act as physical crosslinks between polymer chains. At elevated temperatures, these ionic crosslinks become reversible.

HEAT

When heated, ionic groups lose their attractions and the chains move around freely.
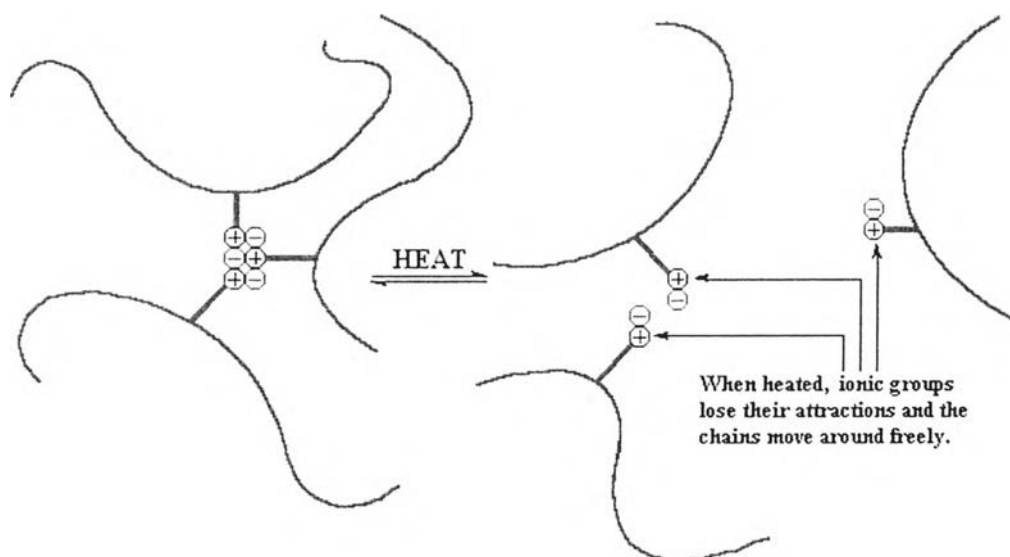
Figure 3: illustration of thermoreversible crosslink of ionomer.

Na-EMAA is a family of ethylene methacrylic acid (E-MAA) copolymer, in which part of the methacrylic acid is neutralized with sodium metal ions. Themorphology of ionomers based on poly(ethylene-co-methacrylic acid) (EMAA) consists of three regions: amorphous phases, crystallinephases, and ionic clusters.

The ionic clusters act as thermoreversible crosslinks and improve the toughness, meltviscosity, clarity, and adhesion properties of the copolymer.

Figure 4: illustration of EMAA ionomer.

The two most common neutralizing cations are zinc (Zn^{2+}) or sodium (Na^{+}). The properties of zinc-neutralized and sodium neutralized carboxylate ionomers are very different; for example sodium ionomers absorb significantly more water and tend to have higher fractional crystallinities than zinc ionomers due to the effect of structure. As monovalent Na^{+} neutralized ionomer is easier to form an ion-dipole interaction while divalent Zn^{2+} neutralized ionomer is more sterically hinderance.
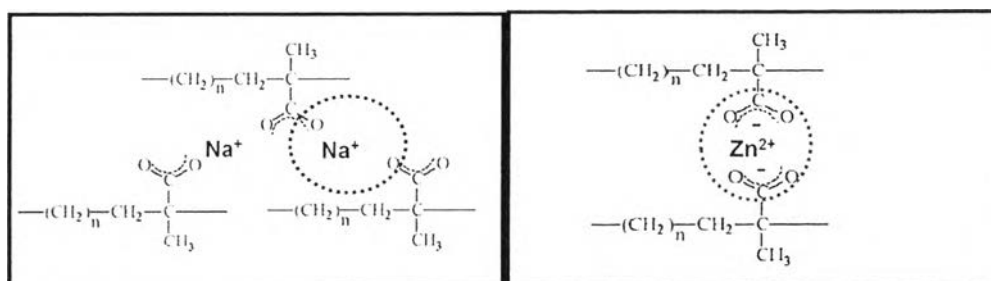
Figure 5: illustration of sodium-neutralized and zinc-neutralized ionomer.

In blends of PBT/HDPE, PBT has polarity while HDPE has non-polarity, then the addition of a PE based ionomer should be sufficient for obtaining a compatible blend since the interactions between the ionic groups of PE and the polar functional groups of PBT are strong enough to generate a kind of a grafted copolymer at the interface.

Atchara Lahor.(*et al.,* 2004) In the research of 'Blends of low-density polyethylene with nylon compatibilized with a sodium-neutralized carboxylate ionomer, an ethylene-methacrylic acid copolymer partially neutralized with sodium (Na-EMAA) was successfully used to compatibilize Nylon 6 and low-density polyethylene(LDPE) blends. The addition of small amounts (0.5phr) of Na-EMAA improved the compatibility of Ny6/LDPE blends as evidenced by a significant reduction in dispersed phase sizes. Additionof small amounts of Na-EMAA reduces the dispersedphase size by approximately a factor of 5, andas little as 0.5phr of Na-EMAA was sufficient to producea maximum reduction of dispersed phase size.

The presence of Na-EMAA decreased the crystallization temperature and melting temperature of Ny6 in binaryblends, indicating that Na-EMAA retards nylon crystallization.However, the effects of this retardation are not seen in the ternary blends, nor in the LDPE/Na-EMAA blends. Zinc-neutralized ionomers have been studied as blend compatibilizer for the nylon-PE system extensively. The addition of compatibilizer has been shown repeatedly to increase compatibility between the two components, including improvements in mechanical properties, injection molding properties, barrier properties, as well as smaller dispersed domain sizes.Although not from the same base resinnor the same neutralization level, the Na^+ carboxylate ionomers were more effective compatibilizers than the Zn^{2+} carboxylate ionomers due to the lower dispersed phase size and higher thermal stability of the resulting blends.