NOVEL POLYOLEFIN ELASTOMER-BASED BLENDS
AND THEIR APPLICATIONS

By

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To my wife, Wei Lu, and my daughters, Aubrey Y. Tang as well as Alicia Tang

with love
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<tr>
<td>AA</td>
<td>acrylic acid</td>
</tr>
<tr>
<td>ABS</td>
<td>acrylonitrile-co-butadiene-co-styrene</td>
</tr>
<tr>
<td>ABS-MA</td>
<td>acrylonitrile-co-butadiene-co-styrene-maleic anhydride</td>
</tr>
<tr>
<td>ABS-g-MA</td>
<td>acrylonitrile-co-butadiene-co-styrene-g-maleic anhydride</td>
</tr>
<tr>
<td>BA</td>
<td>bisphenol A type epoxy resin</td>
</tr>
<tr>
<td>BT</td>
<td>xerographic black toner</td>
</tr>
<tr>
<td>CB</td>
<td>carbon black</td>
</tr>
<tr>
<td>DGEBA</td>
<td>diglycidyl ether of bisphenol A type epoxy resin</td>
</tr>
<tr>
<td>DMAEMA</td>
<td>dimethylaminoethyl methacrylate</td>
</tr>
<tr>
<td>E-GMA</td>
<td>ethylene-glycidyl methacrylate copolymer</td>
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<tr>
<td>E-EA-GMA</td>
<td>ethylene-ethylacrylate-glycidyl methacrylate copolymer</td>
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<tr>
<td>EPDM</td>
<td>poly(ethylene-co-propylene-co-diene)</td>
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<td>e-EPDM</td>
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<td>HEMA</td>
<td>2-hydroxyethyl methacrylate</td>
</tr>
<tr>
<td>HIPS</td>
<td>high impact polystyrene</td>
</tr>
<tr>
<td>HPMA</td>
<td>2-hydroxypropyl methacrylate</td>
</tr>
<tr>
<td>IA</td>
<td>imidized acrylic</td>
</tr>
<tr>
<td>IPO</td>
<td>2-isopropenyl-2-oxazoline</td>
</tr>
<tr>
<td>LCP</td>
<td>liquid crystalline polymer</td>
</tr>
<tr>
<td>LDPE</td>
<td>low density polyethylene</td>
</tr>
<tr>
<td>LDPE-g-DBAE</td>
<td>low density polyethylene-g-dially bisphenol A ether</td>
</tr>
<tr>
<td>LLDPE</td>
<td>linear low density polyethylene</td>
</tr>
<tr>
<td>LPE</td>
<td>linear polyethylene</td>
</tr>
</tbody>
</table>
MA  maleic anhydride
MBS  methyl methacrylate-butadiene-styrene
MBS-GMA  methyl methacrylate-butadiene-styrene-glycidyl methacrylate
NBR  acrylonitrile-cobutadiene-co-acrylic acid rubber
Ox-PP  oxazoline-modified polypropylene
Ox-PS  oxazoline-modified polystyrene
Ox-SAN  oxazoline-modified polystyrene-acrylonitrile copolymer
PA 1010  polyamide 1010
PA 11  polyamide 11
PA 12  polyamide 12
PA 6  polyamide 6
PA 6/6.9  polyamide 6-co-polyamide 6.9
PA 610  polyamide 610
PA 612  polyamide 612
PA 66  polyamide 66
PAA  poly(acrylic acid)
As-PA  alcohol-solube polyamide
PBD  polybutadiene terphthalate
PC  polycarbonate
PCL  poly(ε-caprolactone)
PE  polyethylene
m-PE  meallocene polyethylene
PEA  polyethylene acrylatee
PE-AA  poly(ethylene-co-acrylic acid)
PEEA  poly(ethylene-co-ethyl-co-acrylic)
PEI  polyetheramde
PEIM  polyethyleneimine
PEEK  polyetherether ketone
PE-g-PS  polyethylene-g-polyestyrene
PE-MAA  poly(ethylene-co-methacrylic acid)
PE-ox  oxidized polyethylene
PES  polyethyrsulphone
PET  polyethylene terephthalate
PI  polyisoprene
PMAA  polymethacrylic acid
PMMA  polymethyl methacrylate
PMPI  poly[methylene(phenylene isocyanate)]
PMS  poly(α-methylstyrene)
POE  ethylene-octene copolymer
POE-g-MA  POE-g-maleic anhydride
POE-g-Ox  POE-g-oxazoline
PP  polypropylene
PP-g-PA 6  polypropylene-g-polyamide 6
i-PP  isotactic polypropylene
s-PP  syndiotactic polypropylene
ter-PP  propylene-co-ethylene-co-1-butene copolymer  
Zn-mPP  salt of maleated polypropylene  
PPE  poly(2,6-dimethyl-1,4-phenylene ether)  
PP-g-AA  polypropylene-g-acrylic acid  
PP-g-GMA  polypropylene-g-glycidyl methacrylate  
PP-g-MA  polypropylene-g-maleic anhydride  
PPH  polyphosphonate  
PPO  poly(p-phenylene oxide)  
PS  polystyrene  
PSU  poly(arylethersulfone)  
PU  polyurethane  
PVB  poly(vinyl butyral)  
PVC  poly(vinyl chloride)  
PVDF  poly(vinylidene fluoride)  
PVME  poly(vinyl methyl ether)  
SAG  styrene-crylonitrile-glycidyl methacrylate copolymer  
SAN  styrene-co-acrylonitrile  
SAN-MA  styrene-co-acrylonitrile-co-maleic anhydride terpolymer  
HSBR  hydrogenated poly(styrene-co-butadiene) copolymer  
SB  poly(styrene-b-butadiene) copolymer  
SBS  poly(styrene-co-butadiene-co-styrene)  
SE  poly(styrene-b-ethylene) copolymer  
SES  poly(styrene-b-ethylene-b-styrene) copolymer  
SEBS  styrene-coethylene-butadiene-co-styrene terpolymer  
SEBS-MA  maleated SEBS  
SIS  styrene-isoprene-styrene copolymer  
SGMA  styrene-glycidyl methacrylate copolymer  
SMA  styrene-maleic anhydride copolymer  
SPS  sulfonated polystyrene  
TAC  triallyl cyanurate  
TBAEMA  t-butylaminoethyl methacrylate  
TGDDM  N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenyl methane  
WF  wood flour  
ZnAcAc  zinc acetyl acetonate dihydrate  

xvii
Polyolefin elastomer (POE) is designed to process like a thermoplastic and perform like an elastomer, which bridges the gap between the two, giving us a whole new spectrum of design possibilities. POE can be used as low-cost impact modifier and long-time plasticizer due to its unique feature. As a way of developing polymers to create new materials with greater versatility and flexibility, polymer blending is faster and more economical than developing new polymers. The great majority of blends is immiscible due to positive mixing enthalpy and very small mixing entropy, which leads to a multiphase. In these multiphase polymer blends or alloys, there exist the potential opportunities for combining the attractive features of each material or improving the deficient characteristics of a particular mater.
The mechanical compatibility and thermal miscibility of POE was investigated by physical blending POE with PS, PMMA, GFR-PC, PP and HDPE carried out in a 34-mm twin-screw reactive extruder. Phase separation is observed in all of the blends because of the thermal immiscibility. However, there exists a mechanical compatibility in the blends of PP/POE and HDPE/POE according to the synergistic behavior of the impact resistance. A unique nano-structure of HDPE/POE blend is found by AFM. The crystallinity of PP matrix in the blends of PP/POE transformed from α-form to γ-form during blending. Due to the interfacial modification, the impact properties of PP/POE blends are dramatically enhanced through melt grafting glycidyl methacrylate (GMA) onto POE. In the presence of grafted POE as a compatibilizer, not only the interfacial adhesion between POE and PP matrix is improved but also the agglomeration and the domain size of POE are significantly reduced. In order to simulate the process of interfacial modification and degradation, the rheological behavior of the blends was studied through Brabender internal mixer. Grafted POE has great potential applications for multiphase blending systems because the epoxy functional group of GMA is easily reacted with amine, carboxylic acid, and alcohol groups. In order to investigate the feasibility of functional POE as in-situ compatibilizer, the functional POE was examined in different multiphase blending systems, such as the blends of PP/GFR-PC, PP/PA 6,6 and PS/POE. The mechanical properties of the blends are significantly improved through controlling the morphological behavior with the in-situ grafted POE. The grafted POE was also successfully applied to recycling xerographic toners by reactive extrusion.
CHAPTER 1
GENERAL INTRODUCTION

In 1993 the Dow Chemical Company commercialized a new class of polyolefin elastomers under the trade name Engage®. Engage® are new polyolefin elastomers (POEs) produced via INSITE™ catalyst and process technology. INSITE™ is a new, homogeneous, single-site catalyst that allows extraordinary control over polymer structure, properties, and rheology. By controlling molecular architecture, INSITE™ makes possible a key advantage: POE delivers an ideal balance of predictable, consistent performance both in processing and in properties without sacrifice. Designed to process like thermoplastics and perform like elastomers, POE bridges the gap between the two, giving us a whole new spectrum of design possibilities. And because the elastomeric properties make it possible to use polyolefin materials where they have never been used before, POE opens up new markets and applications [1-5].

High-impact resistance is required of most polymeric materials designed for engineering applications such as automobile, cable and shoe industries. Super-tough polymeric materials have become a very important subject for engineering investigation in recent years. The super-tough polymeric materials are basically multiphase materials that contain elastomeric impact modifiers and a polymeric matrix. The addition of elastomeric impact modifiers normally increases the overall ductility of the polymer over a wide temperature range and improves impact strength, resistance to notch
sensitivity, surface modification, and so on. Copolymerization and blending are alternative routes for approaching this objective. Blending is a less expensive method than copolymerization. It does not always provide a satisfactory alternative to copolymerization, of course, but polymer blends have been used successfully in an increasing number of applications in recent years. Such successes encourage more attempts to apply this technique to a wider range of problems in polymer-related industries [6-8].

Additives are added to modify properties, assist in processing, and introduce new properties to a material. Many additives have become parts of general formulations developed as much as an art as a science. Plasticizer is a material incorporated in a plastic to increase its workability and flexibility or distensibility. The addition of a plasticizer may lower the melt viscosity, elastic modulus, and glass transition temperature (Tg) of a polymer. The effect of plasticizers may be explained by the lubricity, gel, and free volume theories. The first states that the plasticizer acts as an internal lubricant and permits the polymer chains to slip by each other. The gel theory, which is applicable to amorphous polymers, assumes that a polymer has many intermolecular attractions which are weakened by the presence of a plasticizer. The free volume theory is assumed that the addition of a plasticizer increases the free volume of a polymer and that the free volume is identical for polymers at Tg. Plasticizers in polymers are often not in thermodynamic equilibrium with the polymeric matrix. They try to demix and emigrate. A exudation of low mass plasticizers from the polymer to the surface or the surrounding air occurs if plasticizer and polymer matrix are
thermodynamically immiscible. This exudation can be prevented by polymeric plasticizers with high molecular weights such as POE.

Mixtures of at least two polymers or copolymers are called polymer blends in industry. They are prepared to improve the property of the products as well as to reduce the costs. If a material can be generated at a low cost with properties meeting specifications the manufacturer must use the material to remain competitive [9-11]. There is no doubt that the main reason for blending is economy. In general the following economy-related reasons can be listed:

1. Extending engineering resin performance by diluting the resin with a low-cost polymer.
2. Developing materials with a full set of desired properties.
3. Forming a high-performance blend from synergistically interacting polymers.
4. Adjusting the composition of the blend to customer specifications.
5. Recycling industrial and/or municipal plastics scrap.

The field of polymer blends has been developing rapidly, in terms of both scientific understanding and commercial utility. Polymer blending from existing polymer is the most rapid and economical route to creating new materials with greater versatility and flexibility than the development of new polymers. Most of the blends are immiscible because of positive mixing enthalpy and very small mixing entropy, which leads to phase separation. In these blends, a multiphase mixture is formed. In these multiphase polymer blends or alloys, opportunities exist for combining the attractive features of each material or for improving the deficient characteristics of a particular material. However, the simple blends of immiscible polymers generally exhibit poor
mechanical properties that stem from unfavourable interactions among their molecular segments. This is manifested as a coarse, unstable domain morphology that develops during melt processing and as weak interfaces among the phases in the solid state [7-16].

In order to overcome the problems of incompatible polymer blends, methods for improving compatibilization have grown at an exponential rate during the last two decades. The major role of compatibilization is to reduce the interfacial tension in the melt by causing an emulsifying effect, thus leading to finer domains of the resultant blend. Relative to the uncompatibilized blend, the compatibilized blend tends to widen the thickness of the inter-phase, and therefore improves adhesion at phase boundaries. Compatibilization also can stabilize the dispersed phase against coalescence during thermal annealing. Early studies on compatibilization concentrated on a nonreactive type, where the compatibilizers employed were mainly the block or graft copolymers possessing segments structurally similar or miscible with the blending constituents. However, compatibilization by preformed block or graft copolymers has not been used as extensively as the potential utility might suggest. A primary reason for this is the lack of economically viable and industrially practical routes for synthesis of such additives for systems of interest [9-13].

An attractive alternative, reactive type compatibilization, is to form the block or graft copolymer "in-situ" during preparation via interfacial reaction of added functionalized polymeric components. This approach has already been implemented in a number of commercial products and in many instances appears to be the method of choice for compatibilization. The data clearly show that reactive compatibilization has become the mainstream in compatibilizing incompatible polymer blends during the last
few years. The mechanism of a reactive compatibilization system is relatively more complex than the corresponding nonreactive counterpart. Unlike the nonreactive copolymer compatibilizer, a so-called reactive compatibilizer is itself not considered to be a phase compatibilizer. It serves only as a precursor of the finally formed copolymer; possessing segments structurally identical or chemically miscible with the respective base polymers is the major contributor in compatibilizing the incompatible blend. The final properties of the reactively compatibilized blend depend upon the structure and distribution of the in-situ formed copolymer [17-30].

Reactive extrusion is now being viewed as an efficient means of continuously polymerizing monomers as well as chemically modifying existing polymers in the bulk, combining two traditionally separate operations: the chemical reactions for the polymer synthesis and/or the modification of macromolecules and the processing of the blending extrusion. New polymer blends and alloys of thermoplastics are developing rapidly, and for technical and economical reasons, reactive compounding may provide viable mechanisms for the creation and preservation of the desired blends, with controlled structure and morphology. The hydrocarbon nature of most polymers leads to relatively poor chemical reactivity and dictates the low polarity of the medium, which is not favorable for the chemical activation of the system. For instance, polyolefins, like polyethylene (PE) and polypropylene (PP), are relatively inert versus most of the chemical reactants, like acids and bases, but sensitive to oxidative and or photochemical degradation. It appears that the degradation proceeds through free-radical mechanisms and it is not surprising that the same chemistry has been used in various chemical
modifications of polyolefins for grafting, cross-linking and controlled chain degradation [31-40].

When a polymer blend is thermodynamically immiscible, it separates into two or more phases, and yields poor practical properties, such as impact strength, tensile strength and modulus of elasticity. It is generally assumed that either the particle size of the dispersed domains is not optimum or the immiscibility of the two phases produces weak interface adhesion between them, which fails too easily under stress. The most popular way of solving these problems is to add a third chemical agent. If this succeeds, the added chemical agent is called a compatibilizer. In most cases, it simply acts as a surfactant to reduce the domain size, or as an adhesive to strengthen the interface bonding between the two immiscible polymer phases. Success is judged by improvement in practical properties, producing practical compatibility [6-15].

Plastics were easy to discard in the good old days: they were put into a landfill like many other old materials. The increasing amount of plastics, the growing demand for more land for landfills and the groundwater contamination by landfills stimulated the search for recycling and other disposal methods. The growth of xerography illustrates a classic example of the successful commercialization of task-specific scientific development. The xerographic toner used in copy machines has been refined and perfected to allow extremely inexpensive methods of image reproduction with very little demand on the user. However, it is estimated that a few million tons of post-consumer and post-industrial waste xerographic toner is collected annually in the world. A waste stream of such magnitude will no doubt contribute to eventual ecological problems, which will only be augmented with increased demand and use. The design of successful
recycling techniques could provide an alternative method of disposal that is potentially beneficial economically as well as ecologically. It is well proven that xerographic toner needs to be very brittle to allow itself to fit in toner size (c.a. 10 μm) particles. The pursuit of polymeric materials exhibiting specific properties has led to an increasingly expanding field of research on the blending of different polymers. Blending provides an easy and economical process in comparison to many other methods relying on complete synthesis of a new material [41-44].

Several articles discuss blends of polyolefin elastomer (POE) [45-54]. The objectives of this dissertation are illustrated in Figure 1.1. The general objectives in this research are the study of feasibility for using POE as low-cost impact modifier as well as long-time plasticizer. The whole project is divided into three phases. In phase I, we fundamentally studied the physical properties of POEs. In order to investigate the thermodynamical miscibility and mechanical compatibility of POE with other polymer pairs, the physical blends of POEs were studied. Also a promising binary blending system, such as polypropylene (PP)/POE, was selected for further study. In phase II, we fundamentally explored the functional POE as well as the relationships among processing-structure-property for functional POE employed as a compatibilizer in the binary blending system of PP/POE. In phase III, in order to investigate the feasibility of functional POE used in multiphase blending as a in-situ compatibilizer, different multiphase blending systems were initially examined. Functional POE was also employed for recycling xerographic black toner (BT).
General Objectives
a) Low-cost impact modifier;
b) Long-time plasticizer.

Phase I: a) Fundamental study for the physical properties POEs as well as their thermodynamical miscibility and mechanical compatibility with other polymers;
b) Selecting a promising binary blending system.

Phase II: Fundamental study on functional POE as well as the relationships among Processing - Structure - Properties for functional POE employed as a compatibilizer in the binary blending system (PP/POE).

Phase III: Initial study for the functional POE used as a compatibilizer for different multiphase systems, such as the development of morphology during mixing, mechanical behaviors, etc.

Conclusions and Further Recommendation

Figure 1.1 Flow diagram of objectives of this dissertation
CHAPTER 2
BACKGROUND/LITERATURE REVIEW

2.1 Metallocene-catalysted Polyolefin Elastomers

2.1.1 Metallocene Catalysts

Homogeneous catalysts capable of producing polyethylene and isotactic polypropylene employ metallocenes. These are organometallic coordination compounds comprising two cyclopentadienyl rings bonded to a metal atom, as in Figure 2.1.

![Figure 2.1 Scheme of single-site metallocene catalyst](image-url)
The catalysts vary in the number of rings, the nature of their substituents (R), the transition metal (M), and its substituents (Y) as well as the type of bridge (B). Their essential feature is that the transition metal is constrained between two rings, providing a sterically hindered catalytic site. They differ from the heterogeneous Ziegler-Natta catalysts because they are homogeneous, i.e. soluble in hydrocarbons, and most notably, they produce polyolefins with different characteristics. This is because the metallocene catalysts are single-site systems. They yield more uniform ethylene α-olefin copolymers than can be obtained through Ziegler-Natta catalysis. In conventional linear low density polyethylene (LLDPE), the lower molecular weight species are richest in the olefin comonomer, resulting in a fraction of a few weight percent that is highly branched and not crystallizable. Metallocene-based catalytic systems permit incorporation of the higher olefin comonomer uniformly or preferentially in the higher molecular weight species of the copolymer, thus reducing the extractable content [1-3].

2.1.2 Engage® Polyolefin Elastomers

Engage® polyolefin elastomers (POEs) are ethylene-octene copolymers produced by a new single-site metallocene catalyst. POE is produced using INSITE™, a catalyst and process technology that allows extraordinary control over polymer structure, properties, and rheology [4]. Classification of homogeneous ethylene-octene copolymers based on comonomer content studied by Bensason et al. indicated that ethylene-octene copolymers prepared by Dow’s INSITE™ constrained geometry catalyst technology (CGCT) presented a broad range of solid-state structures from highly crystalline, lamellar morphologies to the granular morphology of low
crystallinity copolymers. As the comonomer content increases, the accompanying tensile behavior changes from necking and cold drawing, typical of semicrystalline thermoplastics, to uniform drawing and high recovery, characteristic of an elastomer. Although changes in morphological features and tensile properties occur gradually with increasing comonomer content, the combined body of observations from melting behavior, morphology, dynamic mechanical responses, yielding, and large scale deformation suggests a classification scheme with four distinct categories. Materials with densities higher than 0.93 g/cm$^3$, type IV, exhibit a lamellar morphology with well-developed spherulitic superstructure. Type III polymers with density between 0.93 and 0.91 g/cm$^3$ have thinner lamellae and smaller spherulites. Type II materials with densities between 0.91 and 0.89 g/cm$^3$ have a mixed morphology of small lamellae and bundled crystals. These materials can form very small spherulites. Type I copolymers with densities less than 0.89 g/cm$^3$ have no lamellae or spherulites. Fringed micellar or bundled crystals are inferred from the low degree of crystallinity, the low melting temperature, and the granular, nonlamellar morphology [5, 55].

Kale et al. showed that the structure-property relationships of homogeneous ethylene-1-butene copolymers made by INSITE™ technology, are explored and compared with DOW’s current Affinity polyolefin plastomer and ethylene-octene copolymers. The performance of ethylene-butene copolymers and ethylene-octene copolymers with densities of 0.910 and 0.920 g/cm$^3$ is used. Ethylene-octene copolymer has better tear, impact and tensile properties than the ethylene-butene copolymers. This study confirms the general observation that the performance of polyethylenes increases with $\alpha$–olefin branch length. The longer branches of the octene
comonomer are believed to result in a larger fraction of tie-molecules in the interlamellar region [56].

Comparison of the solid-state properties of ethylene-octene copolymer with ethylene-propylene-diene rubbers (EPDM) examined by Turek et al. indicated that ethylene-octene copolymers developed from single-site INSITE™ metallocene catalyst technology had comparable solid-state properties in the uncured state to those of various commercial EPDMs. The tensile properties of similar crystalline ethylene-octene copolymers equal that of EPDM at slightly lower molecular weight. Depending on composition they share similar glass transition temperatures, broad melting behavior, softening characteristics and tensile properties. Unlike propylene-containing elastomers, octene comonomer is excluded from the ethylene crystal lattice resulting in improved mechanical performance and slightly elevated melting temperatures. In addition, ethylene-octene copolymers can be further differentiated from EPDM by better UV stability and peroxide cure efficiency [57].

The melting and crystallization behavior of metallocene-catalyzed commercial ethylene-octene copolymers investigated by R. Androsch showed that the thermal behavior of the ethylene-octene copolymer was characterized by a very broad melting and crystallization range. The melting and the crystallization are complex transitions of at least two processes with different kinetics. On decreasing the temperature, crystallization started with the formation of a separate crystalline phase and continued gradually with development of an amorphous-crystalline mesophase until the glass transition was reached. In temperature-modulated differential scanning calorimetry (TMd.s.c.), the formation of the crystalline phase was observed as an irreversible
process, whereas the glass transition gave a reversing heat flow signal. Similarly, on heating, the melting process was initiated after traversing the glass transition as a largely reversing process, followed by melting of the crystalline phase with nonreversing character in a narrower temperature range [58].

Bensason et al. also indicated that ethylene-octene copolymers with narrow molecular weight distribution, homogeneous comonomer distribution and homogenous long-chain branching structure could be prepared by Dow’s INSITE™ constrained geometry catalyst and process technology. A POE with higher comonomer content than the target was blended by the appropriate amount of a lower comonomer-content copolymer to obtain the target level of crystallinity. Thermal analysis showed that the components crystallized separately in all the blends. The stress-stain behavior of the ethylene-octene copolymers and their blends was evaluated as a function of temperature. At ambient temperature, the total amount of crystallinity primarily determined the stress-strain relationship regardless of whether the material was a single ethylene-octene copolymer or an ethylene-octene copolymer blend. The effects of phase morphology were subtle at ambient temperature. At higher temperatures, where the network junctions started to melt, miscibility of the noncrystalline regions produced a synergistic effect on the tensile strength. However, if the branch concentration of the blended ethylene-octene copolymer was too different, the noncrystalline regions were immiscible, and the ethylene-octene copolymer blend had a lower tensile strength than the target at higher temperatures [48, 59].

The thermal and mechanical properties for binary blends, high-density polyethylene (HDPE)/metallocene polyethylene (m-PE), polypropylene (PP)/m-PE,
poly(propylene-co-ethylene) (coPP)/m-PE, and poly(propylene-co-ethylene-co-1-butene) (terPP)/m-PE investigated by Rana et al. showed all the blend systems that were thermodynamically immiscible but mechanically compatible which had been understood by their thermal and mechanical behavior. A lower content of m-PE (up to 50%) in PP/m-PE, coPP/m-PE, and terPP/m-PE blends illustrated discernibly two \(\beta\) transitions, whereas \(\beta\) relaxation was shifted to a lower temperature with the m-PE content in the HDPE/m-PE system. It was concluded that the degree of compatibility in the HDPE/m-PE blend was the largest among the blend systems [60].

The blends of linear low-density polyethylene (ethylene-octene copolymer) and ethylene-propylene-butene terpolymer (ter-PP) studied by Cho et al. showed that melting and crystallization behaviors of the blends by DSC and the \(\alpha\), \(\beta\), and \(\gamma\) dynamic mechanical relaxations proposed that the blend was immiscible in the amorphous and crystalline phases by observing the characteristic peaks that arose solely from those of the constituents. The lack of interfacial interaction among the components was suggested by the SEM study. A strong negative deviation of melt viscosity confirmed the immiscibility in melt-state. Incorporation of ter-PP induced a reduction in melt viscosity, shear stress, and final load. Flexural modulus and yield stress were linearly increased with ter-PP content, while the tensile strength and elongation at break were more or less changed. Although this blend system was immiscible in the solid and melt states, addition of less than 20 wt\% ter-PP in the blend is viable for engineering applications with the advantages of improved processibility and mechanical properties [61].
The ethylene-octene copolymers prepared by a metallocene catalyst studied by Simanke et al. showed that through dynamic mechanical spectroscopy (DMS), differential scanning calorimetry (DSC), Raman spectroscopy and gel permeation chromatography (GPC), the influence of comonomer content on the ethylene-octene properties, especially those related to the dynamic-mechanical behavior, were investigated. It was observed that the intensity of the β–transition increases as the comonomer content increases and crystallinity decreases [62].

The crystallization of ethylene-octene copolymers investigated by Minick et al. illustrated that crystal distribution in homogeneous ethylene-octene copolymers could be analyzed by DSC. To minimize ambiguities from thermal history effects, copolymers were isothermally annealed at temperatures within the melting range. The cumulative crystallinity was related to the crystal distribution by the Gibbs-Thomson equation. The results provided a clear distinction between Type I copolymers (density less than 0.89 g/ cm³) and Type II copolymers (densities between 0.89 and 0.91 g/ cm³). The former had a single crystal population that was identified with the bundled crystals illustrated in transmission electron micrographs (TEM). In comparison, the latter had two crystal populations that correlated with lamellar crystals and bundled crystals [63].

Alamo et al. showed that the phase structure of a series of random ethylene copolymers with 1-butene, 1-hexene, or 1-octene as comonomers which had narrow molecular weight and composition distributions had been studied by treating both the co-unit content and molecular weight as independent variables. Essentially no difference in behavior was found among the three types of branches in most of the properties analyzed. However, the interphase was shown to be a relatively important
component of the copolymeric lamellae, with thicknesses varying from 10 to 45 Å. The melting temperatures and the levels of crystallinity of these copolymers adhere to the reference curves established for the model hydrogenated polybutadienes and random copolymers. It was found to be very important to separate and distinguish the influence of molecular weight and copolymer composition on the phase structure [64].

The liquid-liquid phase separation in ternary blends of linear polyethylene with two ethylene-butene copolymers was studied by Morgan et al. [65]. Thomas et al. showed that blends of linear polyethylene with two ethylene-octene copolymers of 2 and 8 mol% octene content had been prepared and their melt-phase behavior determined by examination of quenched samples by DSC and TEM using surface replicas. The ternary phase diagram for the system had been found. Three distinct regions of liquid-liquid phase separation were shown [66]. To the liquid-liquid phase segregation in blends of linear polyethylene (LPE) with a series of octene copolymers of differing branch content, the coarsening occurring through the process of Ostwald ripening in ethylene-octene copolymers with different comonomers, the minimum branch content for detection of liquid-liquid phase separation in blends of polyethylene with ethylene-octene and ethylene-butene copolymers and the morphology maps of binary blends of commercial polyethylene copolymer produced using the metallocene catalyst process were intensively studied by Hill et al. [49, 67-70].

Wagner et al. showed that the crystallization behavior of a series of ethylene-octene copolymers synthesized using metallocene catalysts was studied using the Ding-Spruiell method of rapid cooling. In conventional crystallization experiments, it was found that the spherulite growth rates varied with octene and molecular weight. When
studied at rapid cooling rates, the polymers generated their own pseudo-isothermal crystallization temperatures. It is in agreement with Ding-Spruiell’s studies on other systems. However, at lower temperatures of crystallization, the spherulite growth rates of all of the copolymers studied merged and were virtually indistinguishable. Results indicated that there was a major change of crystallization mechanism under these conditions under considerable relevance to polymer-processing operations [71].

Ruiten et al. pointed out that very-low-density polyethylene (VLDPE) was a heterogeneous blend of molecules with widely different comonomer contents. There existed distinct regions of highly different crystallinity. This highly crystallinity dispersed phase occurred in smooth, spherical semicrystalline domains due to demixing in the melt. The study of the mixing and demixing of a heterogeneous ethylene-octene copolymer as a function of time and temperature and the influence of crystallization on this behavior showed that the mixing occurred at higher temperatures, and demixing occurred in the melt under certain conditions. This demixing was binodal in character [72].

Unification of ductile failure and slow crack growth in an ethylene-octene copolymer and the dependence of slow crack growth in a polyethylene copolymer on test temperature and morphology were examined by Lu et al. [73-74]. The mechanism of slow crack growth in polyethylene by an environmental stress cracking agent was studied by Ward et al. [75]. Starck et al. illustrated that a new fractionation technique for segregation fractionation by DSC was applied to commercial metallocene copolymers with a variety of comonomers. The new method represented an alternative tool for the relative qualitative analysis of chemical composition distribution (CCD)
and the technique was found useful for characterization of comonomer unit distribution [76].

The homogeneous ethylene-octene copolymers synthesized by a V-based Ziegler-Natta catalyst as a function of the short chain branching content (SCBC) and the molar mass studied by Peeters et al. showed that for linear polyethylenes (LPE) samples, an increase in molar mass resulted in an increase of the long period and the crystalline lamella thickness, a decreased cooling rate resulting in an increased melting temperature, and an evolution from spherulitic structures to perfectly stacked lamella. For the branched samples, increasing the SCBC resulted in a decrease of the melting and the crystallization temperature, crystallinity, spherulite radius, the long period, the crystalline lamella thickness and a limiting value on reaching a SCBC of 20 CH₃/1000C. On the other hand, increasing the cooling rate just affected the crystallinity of the least branched samples. Furthermore decreasing the cooling rate resulting in smaller spherulites had a minor influence on the lamellar parameters and reduced the dimensions of the basal plane of the unit cell. Increasing the molar mass of the branched samples resulted in a drop of the crystallinity, a deterioration of the superstructure, enlarging the amorphous layer thickness and the different crystallization regimes when different molar masses, SCBC and cooling rates were used [77].

2.2 General Aspects of Polymer Blends

Adding a polymeric material to a different polymer is a simple method for combining the attractive features of each material into a desired material or for improving the deficient characteristics of a particular material. This is called polymer
blending. Examples of the improved properties that can be achieved by using the technique are enhancements in the impact strength, processibility, tensile strength, chemical resistance, barrier properties and so forth. More recently, polymer blending also has enabled the reuse of recycling industrial and municipal plastic scraps. Finally, the production of new materials designed through blending implies lower costs together with a shorter time scale with respect to the search for new monomers and new copolymer synthesis. The mentioned technological, economical, and ecological advantages resulting from polymer-mixing processes led over the last decade to a 9% annual increase in the production of polymer blends, which recently has reached about 30% of the overall plastics production [6-8, 78].

2.2.1 Miscibility of Polymer

Polymer blends are mixers of at least two macromolecular species, polymers and copolymers. For practical reasons, the name blend is given to a system only when the minor component content exceeds 2wt%. Depending on the sign of free energy of mixing, blends are either miscible or immiscible. It is well known that, because of the thermodynamic limitations, only a few polymers form truly miscible blends [i.e. polystyrene (PS)/ polyphenylene oxide (PPO), PS/ poly(2,6-dimethyl-1,4-phenylene ether) (PPE) and poly(vinyl chloride) (PVC)/ poly(butylene terephthalate) (PBT). Most polymers are immiscible because of their small combinatorial entropy of mixing and their positive enthalpy of mixing when specific interactions between components are absent [9-10].

In general, blends formed by immiscible polymers have poor mechanical properties relative to their components, and their phase morphology depends strongly
on details of the processing history. Because polymers are usually blended in the melten state, shear and elongational flow imposes a diminution of phase morphology in melt processing. Most of polymer blends is immiscible; separate phases are formed when mixed. In a blend of only two polymers, droplets may form in the final product. As the relative volume of each polymer increases, a co-continuous morphology is a three-dimensional network of one polymer submerged in another polymer. The domain size of the dispersed phase is mainly dependent on the interfacial tension. It usually decreases with a reduction in interfacial tension in the melt. This phenomenon along with the high viscosity of polymer contributes to the inherent difficulty in dispersing the components to a proper extent during mixing and leads to a lack of stability with phase rearrangements during low stress or quiescent conditions. In addition, it leads to poor interfacial adhesion in the solid state, causing premature mechanical failure via weak adhesion between phases [9, 11-12].

2.2.2 Compatibility of Polymer

The term compatibility usually means the miscibility of polymers with other polymers, plasticizers, or diluents. A typical criterion for compatibility requires the formation of transparent films even when the refractive indices of the components differ. This indicates that the polymer molecules must be dispersed so well that the dimensions of any segregated regions are smaller than the wavelength of light. Such a fine scale of segregation can be achieved most readily if the components are miscible. However, some mixtures that are compatible may appear not to be miscible, by this standard, if it is difficult to produce an intimate mixture. In some cases, this may happen when two high-molecular-weight polymers are blended or when a small
quantity of a very viscous liquid is being dispersed in a more-fluid medium. Another common criterion is based on the observation that miscible polymer mixtures exhibit a single glass transition temperature. When a polymer is mixed with compatible diluents, the glass-rubber transition range is broader and the glass transition temperature is shifted to lower temperatures. A homogeneous blend exhibits one Tg intermediate among the components. Heterogeneous blends with very fine scales of segregation may have very broad glass transition regions and good optical clarity [8-13].

The presence of a third component is usually required to overcome the phase-separated problems and to obtain a tailored phase structure modifying the polymer interfaces of an immiscible blend. It has been found that the addition of small amounts of a third ingredient to a binary blend stabilizes the phase morphology. These additives are often called compatibilizers, and they act as interfacial agents. By concentrating at the interface as surfactants and reducing the interfacial tension, compatibilizers are able to combine the integrity of the immiscible systems and the proper diversity of an alloy.Compatibilizing agents basically are block or graft copolymers. Usually block or graft copolymers have different polymer segments that are individually capable of specific interactions or chemical reactions with one of the phases in the blend, or both. And they reside preferentially at the polymer interface. The influence of the copolymers on the final blend properties differs, therefore, from their ability (a) to increase the degree of dispersion of one phase in another; (b) to improve the adhesion at the phase boundaries, thus providing enhanced stress transfer; and (c) to stabilize the dispersed phase against coalescence. Nevertheless, preformed block or graft copolymers (nonreactive compatibilizers) have not always been used as extensively as their potential utility
might suggest because of the excessive cost for their industrial-scale synthesis. An attractive alternative route is the formation of graft copolymers in situ during blend preparation through an interfacial reaction of added functionalized polymeric components (reactive blending). If two co-reactive polymers are incorporated into a blend, the appropriate bridging copolymers at the interface of the blend can be formed [8-13, 79-81].

2.2.3 Classification of Polymer Blends

2.2.3.1 The physical blends of polypropylene (PP)

Morphologies and mechanical properties of syndiotactic polypropylene (sPP)/polyethylene (PE) blends studied by Loos et al. showed that in order to understand the unexpected decrease in ductility, the crystallization behavior of these blends was characterized by TEM and in-situ Raman spectroscopy. In the blends, demixing occurred and low HDPE concentrations in an island-like morphology of HDPE domains embedded in a continuous sPP matrix. And the start temperature of the sPP crystallization significantly increased with increasing HDPE content [82].

The low-temperature mechanical behavior of isotactic polypropylene(iPP) blended with both Zeigler-Natta polyethylene(PE) and metallocene PE (mPE) investigated by Chaffin et al. pointed out that the predominate failure mode in the Zeigler-Natta blend was interfacial, while that in the metallocene blend was failure of the iPP matrix. The observed change in failure mode was accompanied by a 40% increase in both tensile toughness and elongation at $-10^\circ$C. They argued that crystallite anchoring of interfacially entangled chains is responsible for this dramatic property improvement in the metallocene blend. The interfacial width between PE and iPP melts
was approximately 40Å, allowing significant interfacial entanglement in both blends. The segregation of low molecular weight amorphous material in the Zeigler-Natta blend reduced the number and quality of crystallite anchors as compared with the metallocene blend. It was demonstrated that anchored interfacial entanglements were a critical factor in designing semicrystalline blends with improved low-temperature properties [83].

Polypropylene (PP) matrix combined with talc, and modified by ethylene-propylene rubber (EPR) and/or ethylene-butene rubber (EBR) with different molecular weights was investigated by Yokoyama et al. It was found that: (a) EBR had a higher toughening efficiency than EPR; (b) the fracture toughness increased by increasing the molecular weight. It was indicated that the presence of EBR in the blends reduces cavitation and crazing, and induces a large amount of shear yielding. And dynamic thermomechanical analysis (DMA) indicated that EBR had a stronger interaction than EPR with the PP matrix [84].

Physical characterization of the blend of isotactic polypropylene (iPP)/ethylene-propylenediene rubber (EPDM) and morphology and elastomeric properties of iPP/hydrogenated poly(styrene-co-butadiene) blends were studied by Yang et al. [85-86]. The effects of the copolymer microstructure and content on rheology, morphology and mechanical properties of the blends of iPP/EPR (60/40) were examined by Orazio et al. [87]. It was found that both the melts were to be classified 'negative deviation blends' and that for such a composition the copolymer represented the dispersed phase. SEM investigations showed in fact that the EPR phase segregate into irregular shaped domains localized in the core of the bars, the dispersion coarseness increasing with an
increase in the ratio between the EPR viscosity and iPP viscosity. At low temperatures, the iPP impact strength was improved with comparatively better properties being shown by the blends containing the EPR\textsubscript{v} copolymer synthesized by using a traditional vanadium based catalyst. The different behavior of EPR\textsubscript{t1} synthesized by means of a titanium based catalyst with very high stero-specific activity and EPR\textsubscript{v} phases as impact modifiers was ascribed to their both different dispersion degree and microstructure.

Early work of the blends of EPR with PP and blends of EPDM and PP summarized by E.N. Kresge illustrated that polyolefins were based on coordination catalysts that did not easily lend themselves to block or multisegmented copolymer synthesis. However, since polyolefins had many important attributes favorable to useful elastomeric systems, there was considerable incentive to produce thermoplastic elastomers based on simple \( \alpha \)-olefins by some means. The low density, chemical stability, weather resistance, and ability to accept compounding ingredients without compromising physical properties are highly desirable. These considerations led to the development of polyolefin thermoplastic elastomer blends. Two types were widely used: blends of ethylene-propylene rubber (EPM) with polypropylene (PP) and blends of EPDM with PP in which the rubber phase is highly crosslinked. Both physical and rheological properties were very dependent on the morphology and crosslink density of the blend system. Moreover, the usefulness of practical systems depended extensively on compounding technology based on added plasticizers and fillers [88].

The characterization of immiscible elastomer blends summarized by Hess et al. indicated that the last 30 years had seen a remarkable increase in both the usage of
polymer blends as well as the development of many new types of blends which included elastomeric alloys (EA) and interpenetrating polymer networks (IPN). Most elastomer blending continues to be based on mechanical mixing procedures. The use of blends remains at a high level throughout the plastic and rubber industry. The major reasons cited for utilizing blends rather than individual elastomers pertained to reduced compound cost, simplification or improvement and enhanced final product performance [89]. The influence of interparticle distance and temperature on the fracture toughness of PER diluted with propylene-ethylene random copolymer to get materials with constant EPR/PE particle size but various interparticle distance studied by Starke et al. showed that according to the results of impact tests, brittle-to-tough transitions were found at -21°C, -10°C, 0°C, +10°C and room temperature. The critical interparticle distance shifted linearly over the range of measurements of conventional notched Charpy impact strength at room temperature [90]. Shear viscosity of PP-EPDM dynamically vulcanized thermoplastic elastomers and ABS resins investigated by Araki et al. [91].

Polypropylene/EPDM rubber blends were studied intensively by Wal et al. In the blends, the rubber content ranged from 0 to 40 vol.%. It was found the tensile modulus and the yield stress decreased linearly with increasing rubber content and the crystallinity of the PP phase did not change with rubber content. The brittle-ductile transition temperature ($T_{bd}$) decreased with increasing rubber content from 85°C for pure polypropylene to -50°C for a 40 vol.% blend. The brittle-ductile transition at the low test speed was gradual, while at high test speeds the transition was abrupt and discontinuous [92]. The yield strength increased with the strain rate. At high rates, this
increase was stronger. At low test speeds, the fracture energy decreased rapidly with test speed. At intermediate test speeds, however, the fracture energy increased with increasing test speed. On the micrographs of the high speed deformed samples, the formation of a melt zone was observed [93]. The effect of the rubber particle size and rubber content on the fracture behavior of polypropylene-EPR blends was studied at low and high test speeds. The particle size of EPR ranged from about 0.5 to around 4.0μm. The fracture behavior was determined as a function of temperature by the notched Izod impact test (high test speed) and by a tensile test on notched Izod bars at 1 mm/s (low test speed). At high-test speed, the brittle-ductile transition temperature (Tbd) increased with increasing particle size. At low-test speed, the Tbd decreased slightly with increasing particle size. The weight average particle size gave a better correlation with the notched Izod results than the number average particle size. It was believed that the large particles initiate the fracture more easily [94]. The deformation mechanism of polypropylene-EPDM rubber blends during fracture was also studied. Brittle fracture merely gave rise to voids, which were caused by voiding of the rubber particles. In the case of ductile fracture, voiding of rubber particles and strong shear yielding of the matrix took place. In this yielding process, these voids became elongated. As the fracture surface was approached the voids were more deformed. At high-test speed, in ductile fracture, along the fracture surface a layer, which thickness was 10-100μm, was formed without deformation. This layer without deformation indicated that during deformation relaxation of the matrix material in this layer had taken place. With the formation of the relaxation layer, the impact energy increased. The polypropylene
matrix was found to deform by a shear yielding mechanism and multiple crazing was not observed [95].

Depth profiling in PP/EPR blends measured with photoacoustic Fourier Transform infrared (PAFTIR) was studied by Pennington et al. [96]. The fracture toughness of PP/PE blends at room temperature using the “essential work of fracture” (EWF) method studied by Marchal et al. showed that the EWF method proves to be a sensitive technique to monitor the effect of composition and morphology of the blend on fracture toughness. Moreover, the application of the EWF method allowed monitoring how the fracture toughness of a material depended on its ability to deform extensively before fracturing and its capacity to bear some load [97]. The mechanism of deformation of iPP/ethylen-1-hexene rubbery (EHR) investigated by Yamaguchi et al. pointed out that the compatible blends hardly showed stress-whitening below 333 K. Furthermore, microscopy defects, such as micro-voids and crystalline defects, were found to be precursors for crazing which were origin of the stress-whitening [98]. Montes et al. were found that phase ripening took place progressively with time as iPP/HDPE blends were held in the melt with TEM. This ripening could be used to detect phase separation where the driving force was low (i.e. near to phase boundaries). The composition range where phase separation was observed decreased gradually with temperature between 170 and 200°C [99].

2.2.3.2 Functionalized PP by free radical melt grafting

Glycidyl methacrylate (GMA), 2-hydroxyethyl methacrylate (HEMA), 2-hydroxypropyl methacrylate (HPMA), t-butylaminoethyl methacrylate (TBAEMA), dimethylaminoethyl methacrylate (DMAEMA), and 2-isopropenyl-2-oxazoline (IPO)
grafted onto a polypropylene (PP) homopolymer was studied by Liu et al. It was found that IPO and GMA are effective in compatibilizing the PP/NBR blends, with a nine-fold improvement in impact energy over pure PP and an uncompatibilizing PP/NBR blend. The other functional groups are much less effective for the blend system where carboxylic acid is the co-reactive group [17]. Moderate levels of interfacial chemical bonding are required for a transition from a brittle to ductile failure to be observed in PP/NBR blends. Blends without any interfacial chemical bonding showed no improvement in impact energy whereas up to a 13.5-fold improvement in impact energy was observed for reactive blends above the brittle-tough transitions [18].

A novel method to obtain a high grafting degree of gycidyle methacrylate (GMA) with little degradation of PP using acrylamide (AM) as the initiating agent was developed by Huang et al. [19]. The grafting process occurred before or during the melting of PP, at which temperature cross-linking is preferred over chain scission. Primary free radicals generated from the rapid decomposition of AM have a higher tendency to attack GMA molecules than PP chains. At the same estimated amount of primary radicals, both grafting degree and grafting efficiency increase with decreasing decomposition temperature of the initiator in the order of AM>benzoyl peroxide (BPO)>2,5-di(t-butylperoxy)-2,5-dimethyl-3-hexyne (LPO). Functionalized PP with the desired grafting degree and little degradation of PP could be obtained by the use of mixed initiators.

Free radical grafting of glycidyl methacrylate (GMA) onto molten polypropylene (PP) was examined by Sun et al. [20]. It was found that the presence of styrene as a second monomer increased the GMA grafting yield greatly with reduced
PP chain degradation. The ultimate GMA grafting yield increased with increasing concentration of 1,3-bis(tert-butylperoxyisopropyl) benzene. There exists a similarity between the batch mixer and the extruder, that is the concentration of the peroxide and its half lifetime that determine the grafting rate and the ultimate grafting yield. The GMA grafting yield decreased with increasing screw speed or feed rate. In other words, the GMA grafting yield is affected primarily by the residence time in the zone in which free radicals are not depleted. The effects of screw speed, feed rate, and specific throughput manifest mainly through this local distribution of residence time.

Chen et al. showed that the extent of GMA grafting and the molecular weight of the functionalized PP copolymers could be controlled by carefully manipulating various reaction factors, such as monomer concentration, initiator concentration, reaction temperature and molecular weight of PP homopolymer. The use of a second monomer, styrene, in the grafting process helped to increase GMA grafting further and reduce chain scission. Up to an eight-fold increase in the impact energy of the PP/NBR blend was obtained. The characteristics of the extent of functionalization and the molecular weight were found to have significant influences on the compatibilizing capacity, in terms of impact energy improvement of the PP/ acrylonitrile-co-butadiene-co-acrylic acid rubber (NBR) blend. A large amount of moderately functionalized copolymer offers better compatibilization than a small amount of highly functionalized copolymer. Up to an eight-fold increase in the impact energy of the PP/NBR blend was obtained. A significant drop in impact energy was observed with declining molecular weight of the copolymer [21].
The effect of initiator and comonomer concentrations of grafting of glycidy methacrylate (GMA) onto polypropylene PP by reactive extrusion was investigated by Roux et al. Results indicated that the styrene comonomer increases the grafting level and reduces the polypropylene chain scission. The grafting increases with peroxide concentration and that longer half-life peroxides were more effective for grafting purposes but detrimental for PP chain scission [22]. The correlation between FTIR and $^1$H-NMR analysis on the grafting yield in glycidyl methacrylate-grafted ethylene /propylene/diene rubber (EPDM-g-GMA) was studied by Papke et al. [23]. The effect of the poly(acrylic acid) homopolymer [PAA] existing in poly(propylene-graft-acrylic) [pp-g-AA] on the morphology and rheological properties of a PP-g-AA and polystyrene [PS] blend with varying amounts of poly(styrene-ran-glycidyl-methacrylate) [PS-GMA] was investigated by Kim et al. [24]. Variable quantities of functionalized peroxides bearing carboxylic acid groups reacted with polypropylene (PP) in a twin-screw extruder were studied by Assoun et al. [25].

A factorial design applied to polypropylene (PP) functionalized with maleic anhydride (MA) was examined by Nachtigall et al. Two levels of maleic anhydride (MA) concentration, dicumy peroxide (DCP) concentration, reaction time, and temperature were employed. The reaction time showed no appreciable effect within the studied range. However, the other three factors showed significant main effects. MA and temperature presented an important interaction effect on the degree of functionalization and molecular weights. The highest degrees of functionalization were related to the smallest molecular weights. The maleic anhydride (MA) grafting of polypropylene (PP) with organic peroxides studied by Caliais et al. showed that the
grafting of maleic anhydride onto polyolefins was of particular interest to improve the adhesion properties. However, side reactions, such as cross-linking in polyethylene and chain scission in polypropylene, are difficult to overcome [26]. The grafting of MA on polypropylene was studied by Khunova et al. under a variety of conditions by free radical, ionic, mechanochemical, and free-radical initiators, or radiation-initiation techniques in both the solution and the melt phases [27].

The reactive compatibilization of polypropylene/polyethylene terphthalate (PP/PET) blends through addition of glycidyl methacrylate grafted PP (PP-g-GMA) was studied by Champagne et al. [28]. The use of the copolymers changed the tensile mechanical behavior of the blends from fragile to ductile. The tensile strength was improved by 10% and elongation at break shown 10 to 20-fold increases while stiffness remained constant. The PP average domain size in injection molded specimens decreased to the micron/sub-micron size upon addition of the GMA modified resins, while the unmodified blends exhibited heterogenous morphology comprising large lamellae 10-20 μm wide. The PP with low GMA graft content seemed slightly more efficient than the PP with high GMA content in emulsifying PP/PET blends. The mechanical behavior in the range of GMA graft density was provided by the two modified resins investigated. Cartier et al. showed that when a monomer is to be grafted onto a polymer backbone by a free radical mechanism in a twin screw extruder, the grafting process occurred mainly, if not exclusively, in the plastification (melting) zone. The free radical grafting of glycidyl methacrylate (GMA) onto polypropylene (PP) and polyethylene (PE) was chosen as model systems. It was found that any relevant analysis or model of a free radical grafting process carried out in a screw
extruder must be based on detailed information generated at the die exit and in the plastification zone [29].

2.2.3.3 The blends of polycarbonate (PC)

The effects of the compatibilizer polypropylene grafted with glycidyl methacrylate (PP-g-GMA) on the morphological, thermal, rheological and mechanical properties of polypropylene and polycarbonate blends (PP/PC) were studied by Yin et al. [30]. It was found that the addition of PP-g-GMA significantly changed their morphology. The mean size of domains reduced from 20μm to less than 5μm. The dispersed domain size is also strongly dependent upon the content of PP-g-GMA. The interfacial tension of PP/PC/PP-g-GMA (50/30/20) is only about one-tenth of PP/PC (70/30). The crystallization temperature of PP in PP/PC/PP-g-GMA is 5-8°C higher than that of PP in PP/PC blends.

HDPE / PC Blends compatibilized with low density polyethylene grafted diallyl bisphenol A ether (LDPE-g-DBAE) was studied by Yang et al. [100]. The blends without compatibilizer exhibited a phase growth and no adhesive between the HDPE matrix and the dispersed PC phase. In the presence of 10% by weight of LDPE-g-DBAE as a compatibilizer, more fine particles and a dim phase interface were observed, and the blends showed a remarkable increase in heat distortion temperature and mechanical properties. The compatibilized blends possessed a high apparent viscosity as compared with the noncompatibilized ones. However, the apparent viscosity of the blends, with or without the compatibilizer, was lower than that of the neat HDPE and PC. The melting point and the crystallinity of HDPE in the blends with the compatibilizer decreased. It could be interpreted that the efficient compatible effect of
the LDPE-g-DBAE resulted from the interaction between the diallyl bisphenol A ether unit of LDPE-g-DBAE in PC, and the miscibility of the LDPE unit in HDPE.

Ignatov et al. showed that one-step extrusion was proved to be an innovative technique for the production of poly(ethylene terephthalate)/bisphenol A polycarbonate (PET/PC) compatible blends and copolymers by transesterification in the presence of a small amount of samarium acetyl acetonate that was mechanically dispersed on the polymers before their extrusion. The reactive blending of poly(ethylene terephthalate) (PET) with bisphenol A polycarbonate (PC) (50/50) using samarium acetyl acetonate as a catalyst was performed by this method for about 1 min at 275°C. The product appeared to be a transparent amorphous plastic with a single glass transition temperature. This approach provides a possibility to produce PET/PC block copolymers directly by extrusion of homopolymers or to create their compatible blends during one-step extrusion by varying the type and concentration of the catalyst [101-102].

The effects of processing conditions on the phase morphology of the physical blends of PC/ acrylonitrile-butadiene-styrene terpolymer (ABS) were studied by Chaudhry et al. [103]. Balakrishnan et al. showed that blends of PC/ABS and PC/maleic anhydride grafted ABS (PC/MABS) were prepared over the whole range of compositions using a single-screw extruder. Mechanical properties of PC/MABS blends are nearly equal to or higher than those predicted by the rule of mixtures, while those of PC/ABS blends show nearly equal to or negative deviation. The notched impact strength of PC/MABS blends shows a positive blending effect and proportionate increases from 25wt% PC to 75wt% PC [104].
The effect of reactive compatibilization and matrix phase viscosity on coalescence in PC/styrene-acrylonitrile (SAN) blends was examined by Wildes et al. [105]. The behavior of ionomer sulphonated poly(butylene terphthalate) (SPBT) and the blends of SPBT/PC was investigated by Nicholson et al. [106]. It was found that the samples with a degree of sulphonation above 7 mol. % had the partial miscibility as well as improved optical clarity with respect to blends of non-sulphonated PBT/PC. Kim et al. indicated that for polycarbonate (PC)/Nylon6-co-12 (50/50) blend, modulated structure was observed. And coarsening behavior was similar to that of spinodal decomposition. However, for PC/Nylon6-co-12 (50/50) blend with styrene-acrylonitrle-maleic anhydride terpolymer (SAN-MA), sea-island structure was developed and the size of domain did not increase although the sample was annealed for 90 min, at above Tm. It was confirmed that SAN-MAH retards coarsening of morphology [107]. The studies on miscibility in PC/SAN blends through the interfacial thickness measured by ellipsometry were explored by Li et al. [108].

2.2.3.4 The blends of polyamides (PA)

Super-tough nylon 6 prepared by using polyethylene-octene elastomer (POE) grafted with maleic anhydride as a toughener was studied by Yu et al. [51]. The results indicated that the unmodified POE has hardly any contribution to toughness of nylon 6. The maleic anhydride-grafted POE (POE-g-MA) significantly improves the compatibility of POE with nylon 6 and sharply reduces its size in the nylon 6 matrix due to the in situ formation of a graft copolymer between POE-g-MA and nylon 6 during melt processing. With the POE-g-MA, a brittle-ductile transition occurs. And the brittle-ductile transition curve was shifted to a lower POE-g-MA content with the
use of a compatibilizer in nylon 6/POE-g-MA system. Super-tough nylon 6 prepared by using maleic anhydride grafted polyethylene-octene rubber / semicrystalline polyolefin blend (TPEg) as an impact modifier was also studied. The TPEg with a semicrystalline polyolefin core and a polyethylene-octane rubber shell possesses not only a better process-ability of extruding and pelletizing with a lower cost but also an improved toughening effect in comparison with the maleated pure polyethylene-octene rubber. The effects of nylon 6 matrix viscosity and a multifunctional epoxy interfacial modified on the notched impact strength of the blends of nylon 6 with a maleic anhydride modified polyethylene-octene elastomer/semi-crystalline polyolefin blend (TPEg) were also studied. The shear yielding is the main mechanism of the impact energy dissipation. In addition, the influence of melt viscosity of nylon 6 on toughening effectiveness was also investigated. High melt viscosity of matrix is advantageous to the improvement of notched Izod impact strength. Because the viscosity of the TPEg is much higher than that of nylon 6, an increase in the viscosity of nylon 6 reduces the viscosity mismatch between the dispersed phase and the matrix, and increases notched impact strength of the blends. Moreover, addition of 0.3 to 0.9 phr of the interfacial modifier leads to a finer dispersion of the TPEg and greatly improves the notched impact strength of the nylon 6/TPEg blends. This is because the multi-epoxy interfacial modifier can react with nylon 6 and the maleated TPEg. The reaction with nylon 6 increase the viscosity of the matrix while the coupling reaction at the interfacial between nylon 6 and the maleated TPEg leads to better compatibilization [50].

The blends of PP/PA 6 compatibilized by PP-g-MA were examined by Cartier et al. [110]. It was found that the morphology of in situ compatibilized blends develops
much faster than that of mechanical ones. The size of the dispersed phase (PA 6) undergoes a $10^4$ fold reduction from a few millimeters to sub-micron during its phase transition from solid pellets to a viscoelastic fluid. The final morphology is reached as soon as the phase transition is completed. Screw profiles and processing conditions (screw speed, throughput and barrel temperature) control the PA 6’s melting location and/or rate, but do not have significant impact on the ultimate morphological and mechanical properties of in situ compatibilized blends. The effect of PP-g-PA 6 as compatibilizer on PP/PA 6 blends was studied by Li et al. [111]. It was observed that the presence of PP-g-PA 6 in a PP/PA 6 blend accelerated the rate of melting of the PA 6 only when the compatibilizer itself was melted and migrated to the interfacial layer between the PA6 and PP phases. It is believed that the presence of the compatibilizer increased the chain entanglements at the PP and PA6 interface and consequently reduced the thermal resistance of the interfacial layer. Li et al. found that when PA-6 was in the dispersed phase, it could deform and fibrillate in the PP matrix in the shear force field generated by the rotating screw. With the addition of PP-g-MA as a compatibilizer, the number of fibrils decreased and the dimension of the strong effect on the in-situ fibrillation [112].

Addition of rigid poly(styrene-co-maleic anhydride) (SMA) to a polyamide-6 (PA 6) matrix leading to a system with increased stiffness and unchanged toughness as a consequence of absorption of deformational energy by the plastic deformation of brittle inclusions together with the matrix was investigated by Kelnar et al. [113]. Reactive compatibilization of blends of nylon 6 with various ABS materials including its styrene-acrylonitrile (SAN) was examined by Triacca et al. [114]. Bisphenol-A type solid epoxy resin using as a efficient compatibilizer for the immiscible and
incompatible blends of polyamide 6,6 (PA 66) and poly(butylene terephthalate) (PBT) was studied by Huang et al. [116]. Blends of nylon 6 with acrylonitrile/butadiene/styrene (ABS) materials and with its styrene/acylonitrile copolymer (SAN) matrix used a series of glycidyl methacrylate/methyl methacrylate (GMA/MMA) copolymers as compatibilizing agents were studied by Kudva et al. [117]. Polymer blends of PA6 and poly(2,6-dimethyl-1,4-phenylene ethynyl) (PPE) by poly[methylene(phenylene isocyanate)] (PMPI) coupler were investigated by Chiang et al. [118].

Inhomogeneous interface grafting in melts of maleinated polystyren (SMA) and polyamides (PAs) was explored by Steurer et al. [119]. Phase morphology and mechanical properties of the blends of nylon 6 with scrap poly(vinyl butyral) (PVB) film and poly[styrene-block-(ethylene-co-butene)-block-styrene] (SEBS) were investigated by Cha et al. [120]. Miscibility behavior of poly(vinyl alcohol)/nylon 6 blends and their reactive blending with poly(ethylene-co-ethyl acrylate) were studied by Koulouri et al. [121]. Phase structure in polypropylene (PP)/PA6/SEBS blends was studied by Wilkinson et al. [122]. Reactive compatibilization of the immiscible and highly incompatible blends of ethylene rubber (EPR) and nylon 6 by addition of maleic anhydride grafted EPR (EPR-g-MA) as a compatibilizer was studied by Thomas et al. [123]. It was found that the addition of EPM-g-MA reduces the domain size of the dispersed phase followed by a leveling off at high concentrations; the leveling off is an indication of interfacial saturation. The optimum amount of the compatibilizer required to saturate unit volume of the interfacial zone was estimated from the emulsification curves. This optimum concentration of the compatibilizer can be considered as the so-
called critical micelle concentration (CMC) above which micelles of the copolymer are formed in the bulk phase, which is highly undesirable.

The effects of the concentration, viscosity and functionality of the maleated polyethylenes (PE-g-MA) on the rheological, and mechanical properties of nylon 6/PE-g-MA blends were investigated over a range of compositions by Kudva et al. [124]. A low viscosity maleated polyethylene was shown to be ineffective in toughening nylon 6 because of the propensity of polyethylene to become continuous even when nylon 6 was the majority. The higher viscosity maleated polyethylene was able to produce blends with high impact strength and excellent low temperature toughness over a range of compositions. In general, the impact properties of these blends improved as the nylon 6 molecular weight increased and as the ratio of maleated polyethylene to nonmaleated polyethylene increased. The dispersion of glycidyl methacrylate (GMA) funtionalized methacrylate-butadiene-styrene (MBS) core-shell particles in polyamide 6 (PA6) was explored by Aerts et al. [125]. The grafting efficiency on different nylons (6, 11, 12, 6,10 and 6,12) of ethylene-glycidyl methacrylate copolymer (PE-g-GMA) and ethylene-ethyl acrylate copolymer at a composition of 85/15 was investigated by Koulouri et al. [126].

The phase inversion and morphology of polyamide 1010/ PP/PP-g-GMA blends were studied by Zhang et al. [127-128]. It was observed that the smaller was the viscosity ratio (PP/PA) the smaller was the polypropylene concentration at which the phase inversion took place and polypropylene became the continuous phase. The compaibilizer induced a sharp reduction of particle size, but did not have a major effect on the phase-inversion point. By changing the content of GMA in PP-g-GMA, it was
possible to introduce significant changes of morphology. The reaction product between PA1010 and PP-g-GMA to be located at interface as a surrounding layer around domain particles was observed by a matrix removal TEM method. SEM observation on the interface showed that for the PA1010/PP blends the adhesion between PA 1010 and PP is very weak and their interface boundary is sharp. For the PA1010/PP/PP-g-GMA, it was found that the interface is not so obvious, and the reaction between PA1010 and PP-g-GMA strengthens the interface significantly.

Seadan et al. showed that a mixture of a peroxide (Perkadox 14) and a reactive monomer (maleic anhydride) was induced to two different blends: polypropylene/polyamide (PP/PA6) and ethylene-propylene rubber copolymer/polyamide (EPR/PA6). It appears that if the resulting blend made of PP and PA6 exhibited good adhesion, the final mechanical properties were affected by the molecular weight degradation related to the β-scission in the presence of free radicals. The EPR/PA6 reactive blends showed a very finely dispersed phase of the elastomeric copolymer (particle diameter less than 1μm) which corresponded to a very high level of impact resistance [129]. The reactive blending of PP/copolyamide 6/6.9 immiscible blends through compatibilization, which was achieved by peroxide decomposition in the melten blend in the presence of triallyl cyanurate (TAC), at low concentration levels, without gel formation, was studied by Tzur et al. [130]. Blends of nylon 6 and ethylene-propylene rubber grafted with maleic anhydride, (EPR-g-MA) were studied by Okada et al. [131]. The addition of magnesium oxide causes significant improvement in tensile properties of these blends. Blends consisting of a PA 66 matrix (75wt%) and a dispersed iPP phase (25wt%) with maleicanhydride-grafted isotactic polypropylene compatibilizers were examined by
Duvall et al. [132]. Micro-structural characterization of PA 6/PP blends formed during reactive extrusion of ε-caprolactam was investigated by Hornsby et al. [133].

The miscibility, phase behavior and cure kinetics of the reactive blends of an alcohol-soluble nylon with diglycidyl ether of bisphenol A (DGEBA) were studied by Zhong et al. [134]. Blends of PA 6 and epoxidised ethylene propylene diene (eEPDM) rubber were investigated by Wang et al. [135]. The in situ reactive compatibilization of PA 6/PS blends using anhydride functionalized PS was examined by Park et al. [136]. The high speed fracture characterization of various PA 6/ maleic anhydride grafted styrene-(ethylene-co-butylene)–styrene (SEBS-g-MA) and PA 6/EPR-g-MA blends was studied by Kayano et al. [137]. The blends of PA 6/PP (90/10) and PA 6/EPR (90/10) by polymerization of ε–caprolactam in the presence of a secondary polymeric phase through a reactive extrusion compounding procedure were examined by Prasad et al. [138]. Blends of aromatic/aliphatic polyamides of varying compositions were studied by Xanthos et al. [139]. Rheology and morphology of the blends containing PA6/ liquid crystalline copolyesters (LCPs) compatibilized by PP-g-MA were studied by Meng et al. [140].

Miscibility behavior of poly(vinyl alcohol) (PVOH)/PA 6 blends and their reactive blending with poly(ethylene-co-ethyl acrylate) (PEEA) was studied by Koulouri et al. [141]. The blends of poly(vinylidene fluoride) (PVDF) with PA 6 were examined by Liu et al. [142]. Compatibilization of PVDF/PA 6 blends by Zinc acetyl acetonate (ZnAcAc) was studied by Mascia et al. [143]. Reactive compatibilization of the incompatible and immiscible blends of PA 6 and polybutylene terphthalate (PBT) through N,N,N′,N′-tetraglycidyl-4,4′-diaminodiphenyl methane (TGDDM) was
investigated by Chiou et al. [144]. Effect of ABS type, effects of imidized acrylic (IA) as a compatibilizer, processing history and fracture behavior on the PA 6/ acrylonitrile-butadiene-styrene (ABS) blending system were intensive studied by Kudva et al. [145-147].

2.2.3.5 Other polymer blends

The impact fracture of the blends of PP/BaSO4/maleinated PP(MAPP) and PP/BaSO4/ maleinated EPR (MAEPR) was studied by Molnar et al. [148]. The results showed that impact resistance increased with higher degree of encapsulation, but the crucial factor determining toughness was the prevailing micromechanical deformation process and the deforming volume. Separate distribution of the components and weak adhesion of the filler to the matrix lead to a better impact resistance than does significant encapsulation. The ternary blends of PP/ethylene-octene copolymer/talc with core-shell structured fillers were examined by Ou et al. [149]. The effect of compounding conditions and composition on the properties of the blends of PP/ethylene-octene copolymer/talc using PP-g-MA as a compatibilizer was investigated by Huneault et al. [150-151]. It was observed that the mechanical properties of the compounds were not significantly affected by the mixing conditions. The use of 30 wt% of talc provided a two-fold increase in tensile modulus compared with pure PP. Impact resistance of filled and unfilled compounds was found to increase rapidly once the copolymer concentration reached around 20 wt% based on the polymer phase. Modulus and tensile strength decreased linearly with copolymer concentration. In the best cases, a slight tensile strength increase was observed when using between 2 and 10 wt% of modified PP.
The blends of styrene and maleic anhydride (MAH) modified high-density polyethylene (HDPE)/ethylene-propylene-diene monomer (EPDM) rubber/carbon black(CB) with ditertiary butyl peroxide (DYBP) as the initiator through the reactive extrusion were studied by Ou et al. [41]. In these blends, a dispersed phase of rigid particle as a core and elastomer as a shell that had a good interfacial adhesion with the matrix was found. The carbon-black-loaded natural rubber (NR)/cis-polybutadiene (BR) blend was examined by Bauer et al. [152]. Morphology, resistivity and flow properties of high impact polystyrene/ethylene vinyl acetate/carbon black (HIPS/EVA/CB) blends were investigated by Breuer et al. [42]. The mechanical properties and morphology of polypropylene/wood flour (PP/WF) composites with EPDM, maleated EPDM, maleated styrene-ethylene/butylene-styrene triblock copolymer (SEBS-MA) as impact modifiers and maleated polypropylene (MAPP) as a compatibilizer were studied by Oksman et al. [43]. Antony et al. showed that ionomeric polyblends of the zinc salt of maleated EPDM rubber (Zn-mEPDM) and the zinc salt of maleated polypropylene (Zn-mPP) in the composition range from 90/10 to 60/40 wt% had synergism behavior in physical properties as ionic thermoplastic elastomers (ITPE) [153]. The polyblend fiber constituted of PP and ethylene-vinyl acetate copolymer modified with mercapto groups was examined by Dutra et al. [154]. Molecular structure evolution in the ethylene vinyl acetate and dicumyl peroxide, EVA/DCP, and metallocene polyolefin elastomer, m-PE/DCP cross-linking systems was studied by H.J. Tai [155].

Blends of a poly(styrene-co-acrylonitrile) (SAN) with ethylene-octene elastomer (POE) were investigated by Mader et al. [156]. An improved toughness-
stiffness balance was obtained when adding a compatibilizer consisting of oxazolin-functionalized POE prepared by grafting EOR with oxazolin-functional maleinate, and poly(styrene-co-maleic anhydride) (SMA), which is miscible with SAN into the blend. It was evidenced that the dispersion of the POE in the SAN matrix was improved and the glass transition temperature of the dispersed POE phase was reduced. The formation of an inter-phase between the matrix and the rubber particles was revealed by TEM studies. Curry et al. showed that an amido ester cross-link formed when oxazoline-grafted PS (OPS) was mixed with acid-grafted PE (APE). The cross-link builds melt viscosity and stabilizes product morphology [158]. The blending system of PE/PS, using a peroxide, Lupersol 101, and a series of vector fluids, i.e., low molecular weight ethylene propylene copolymer, styrene monomer, para-chlorostyrene, polyisobutylene, two different molecular weight polybutadienes, low molecular weight acrylonitrile butadiene rubber and an organofunctional silane, was studied by Flaris et al. [159]. A vector fluid that has low viscosity, insoluble, non-reactive, and non-fugitive appears to be most effective in directing a reactive ingredient to the interface. Monomeric vector fluids can interpenetrate one phase and influence the interfacial reactions and morphology.

The blends of a low-density polyethylene/polystyrene (LDPE/PS) (70/30) with various compatibilizers, poly(styrene-b-ethylene) (SE), poly(styrene-b-butadiene) (SB), poly(styrene-b-ethylene-b-styrene) (SES), poly(styrene-b-butadiene-b-styrene) (SBS), poly(styrene-b-ethylene/butene-b-styrene) (SEBS) and styrene-b-ethylene/propylene (SEP) copolymers, were studied by Guo et al. [160]. Sun et al. indicated that a copolymer of PE-g-PS could be formed during melt blending of polyethylene
polystyrene (PE/PS) blends via a Friedel-Craigs benzene ring alkylation of the PS. This in situ compatibilization technique has potential in recycling of mixed polymer wastes [161]. Blends containing PS/EPR (90/10) and PS/EPR (80/20) compatibilized by SEB and SEBS interfacial modifiers using melt processing were investigated by Cigana et al. [162]. The emulsification curve, which relates the minor phase particle average diameters to the concentration of emulsifier, is used to compare the efficacy of these modifiers for the interface. At 10% minor phase, the SEBS acts as a more efficient emulsifier than the SEB, as evidenced by the lower equilibrium diameter (0.35 μm for SEBS, as opposed to 0.6 μm for SEB) and the lower critical concentration for emulsification (C_{crit}) and equilibrium particle diameter. The blends compatibilized by SEB, however, showed the same equilibrium diameter and critical concentration for emulsification for both blend compositions, indicating that even at 20% minor phase, all SEB modifier migrates to the interface [162]. Pagnoulle et al. showed that SAN (or part of SAN) was modified by various amounts of primary amines or carbamate groups (which are nothing but primary amine precursors) and used in conjunction with commercially available EPR-g-maleic anhydride (EPR-g-MA) pre-blended with EPDM. SAN-g-EPR may be formed at the interface through an imide bonding. A 10 fold increase in the impact energy was obtained [163].

The in situ compatibilization of immiscible polypropylene/poly(butylene terphthalate) (PP/PBT) blends with three monomers, acrylic acid (AA), maleic anhydride (MA) and glycidyl methacrylate (GMA), which are potentially reactive towards the carboxylic and/or hydroxyl groups at the chain ends of the PBT, melt grafted onto the PP through free-radical reactions studied by Sun et al. [164]. It was
found that GMA is more effective in compatibilizing the PP/PBT blends. Compatibilized PP/PBT blends with a fifteen-to-twenty-fold improvement in elongation at break and impact strength over an uncompatibilized PP/PBT blend were obtained [164]. Effects of processing parameters on the in situ compatibilization of PP/PBT blends through the free radical grafting of glycidyl methacrylate (GMA) onto PP were investigated by Hu et al. [165]. Results showed that elongation at break and impact strength were increased virtually linearly with decreasing feed rate (Q) or screw speed (N). For a particular specific throughput (Q/N), they decreasing almost linearly with a concomitant increase both in Q and N.

Binary blends of PP/PBT and PP/liquid crystalline polyester (LCP) based on 6-hydroxy-2-naphthoic acid (HNA) and p-hydroxy benzoic acid (HBA) using ethylene/ethyl acrylate/glycidyl methacrylate (EEAGMA) terpolymer as a compatibilizer were studied by Riitta et al. [166]. It was observed that the binary blends exhibited increasing viscosity during blending, changing in the crystallization of the PBT phase, and intimate contact between the blended polymers, which pointed to strong interactions or chemical reactions between the compatibilizer and both PBT and LCP. In both blends, the compatibilizer increased the impact strength, reduced the size of the dispersed domains and caused them to attach better in the matrix. FTIR study of graft copolymers of PP functionalized with 6wt% of acrylic acid (PPAA) and a liquid-crystalline polyester (SBH) derived from sebacic acid, 4,4'-dihydroxybiphenyl and 4-hydroxybenzoic acid prepared under various conditions, as well as fractionation products of the graft copolymers were investigated by Sek et al. [167].
The compatibilizing effect of thermoplastic elastomers, styrene-ethylene butylene-styrene (SEBS), maleic anhydride grafted SEBS (MA-SEBS), and maleic anhydride grafted polypropylene (MA-PP) on the mechanical properties and morphology of the thermotropic liquid crystalline polymer (TLCP)/PP composite films was investigated by Sauvarop et al. [168]. It was found that SEBS provided a higher value of tensile modulus than MA-SEBS, which in turn was higher than MA-PP, despite the expected stronger interaction between the MA chain and TLCP. All three compatibilizers helped improve the dispersion of the TLCP fibers and increased the fiber aspect ratio to a different extent. The fractured surface of the specimens showed more fiber breakage than pull-out when a compatibilizer was added, which suggested the improvement of interfacial adhesion. It is suggested that the increase in the viscosity ratio of TLCP/PP due to the added elastomeric compatibilizer, SEBS and MA-SEBS, compared with the thermoplastic compatibilizer, MA-PP, is more effective in improving the composite mechanical properties.

The blends of PP/LLDPE with SEBS as a compatibilizer were examined by Cser et al. [169]. It was observed that the dimension of the spherulites decreases with increasing PE content within the blends. The crystallization temperature of PP is increased in the presence of the other phase. The crystallization temperature of PP is increased in the presence of the compatibilizer. Smaller portions of SEBS can be found on the surface of the two olefinic phases as dispersed spheres, with an average diameter of 50-90 nm. The methods of 2,5-dimethyl-2,5 di(t-butyperoxy) hexane addition and effects of the peroxide treatment on polymer molecular structure and processability in the reactive processing of LLDPEs through corotating intermeshing and non-
intermeshing twin-screw extruder were studied by Lachtermacher et al. [31-33]. The development in phase separation of the melt blends of PP, PE, LDPE and LLDPE were studied by Crist et al. [170].

2.3 Summary and Conclusions

Compatibilization of polymer blends is becoming a rapidly growing field since it provides a convenient procedure to change the mechanical, thermal or chemical properties of existing materials without the expense of synthesis of new polymers. To achieve compatibility in phase-separated polymer blends, different procedures may be employed. The effect is to lower the interfacial tension and to increase the adhesion between the components. The different methods are employed, for instance, the use of a block or graft copolymer that can be added as a third component or generated in situ through chemical reactions by means of proper functional groups. The addition of a block copolymer whose segments are chemically identical to or miscible with the corresponding homopolymers provides the efficient way of compatibilization. Multi-block copolymers have been demonstrated to be as efficient as di-block and tri-block copolymers. However, suitable block copolymers are often difficult to synthesize; for this reason, the use of a less effective graft copolymer may be preferred. On the other hand, through reactive blending, it is possible to produce the tailored graft copolymers in situ by a more versatile and often less expensive process. The control of the concentration of reactive functional groups allows the desired microstructure to be obtained. Finally, the reactive blending process has a remarkable effect on phase dispersion, and in turn, can cause substantial modification in physical properties. The
blends and compatibilizers mentioned in this chapter are summarized in the appendix.

The abbreviations used in this dissertation are listed in the abbreviations.
CHAPTER 3
PHYSICAL BLENDS OF NOVEL POLYOLEFIN ELASTOMERS

3.1 Introduction

Linear low-density polyethylene (LLDPE) is an important class of polymer because of the specific properties that can be obtained according to the comonomer content and the copolymerization method. In the ethylene-olefin copolymerization, the incorporated α-olefins produce short branches and the catalytic system influences not only the structure but also other characteristics like molecular weight distribution, density and comonomer distribution of the copolymers. The development of metallocene catalysts (homogeneous single-site catalysts) made it to be possible for the synthesis of copolymers with structure and properties completely different from those of traditional linear polyethylene (LPE) catalysts. They have well defined structures, homogeneous comonomer distribution and narrow molecular weight distribution if compared with copolymers obtained by traditional Ziegler-Natta catalysts [1-4].

In 1993 the Dow Chemical Company commercialized a new class of liner low-density polyethylene, metallocene liner low density polyethylene (m-LLDPE), under the trade name Engage®. This copolymer of ethylene and octene is synthesized using the new, homogeneous and single-site metallocene catalysts resulting in a uniform length of the branches, a very random distribution of the comonomer along the backbone, a unique
distribution of the comonomer in different chains, and a very narrow molecular weight distribution. The distribution of the comonomer along the backbone, the length of the branches, and the comonomer concentration are important parameters of the chain configuration. They are determining the crystallinity behavior, including the ultimate crystallinity of the polymer and the macroscopic properties [3-5].

Due to the availability of m-LLDPE copolymers with the well-defined chain architecture, investigations were performed to correlate the chain configuration with the type, amount, and quality of the crystalline and amorphous phases as well as the macroscopic properties. The chain configuration is directly correlated to the density, which can be used to classify the copolymers: (i) a density higher than 0.93 g cm\(^{-3}\) (no comonomer) is correlated to m-LLDPE with a typically lamellar and spherulitic superstructure; (ii) a density between 0.930 and 0.910 g cm\(^{-3}\) (up to 3 mol% comonomer) show a finer lamellar and spherulitic morphology; (iii) in the density range between 0.910 and 0.890 g cm\(^{-3}\) (up to 8 mol % comonomer), the material contains a mixture of lamellar and bundle-like crystals; (iv) finally, in the class of m-LLDPE, which has a density lower than 0.890 g cm\(^{-3}\), is related exclusively to fringed-micellar structures. Also it has unique elastomeric behavior. This class of m-LLDPE is called POE. Taking into account the density 0.852 g cm\(^{-3}\) of completely amorphous m-LLDPE, the crystallinity can reach values of nearly zero, resulting in extraordinary macroscopic properties [5, 55].

In the case of m-LLDPE, the presence of the comonomer decreases significantly the degree of crystallinity. Highly branched chains may lead to molecular segregation. Both the degree of cristallinity and the molecular segregation have great influence on the thermal and mechanical properties of ethylene copolymers. The thermal behavior of such
copolymers is strongly influenced by the comonomer content [56, 58, 64]. In the investigation of Bensason et al. the melting temperature decreases systematically with increasing octent content from 411K in the homopolymer with a density of 0.955 g cm\(^{-3}\) to 331K in the copolymer with a density of 0.8724 g cm\(^{-3}\) (12.3 mol% octene). In addition, the melting range was broadened towards lower temperatures allowing recrystallization/aging at ambient temperature. For the samples with a lower comonomer content, the heat of crystallization showed an increase with decreasing cooling rate, although the heat of fusion was not affected systematically, probably caused by recrystallization/aging at ambient temperature. In copolymers with a higher octene content (> 8.2mol%), no effect of the cooling rate on the thermal behavior was measured [59, 48]. The recrystallization of ethylene-octene copolymers was investigated in more detail by Minick et al. [63]. Samples were annealed for 1 h at various temperatures within the melting range, quenched to 223 K and characterized via the subsequent differential scanning calorimetry (DCS) heating scan. The occurrence of a broad endotherm above the annealing temperature were explained by the incorporation of longer ethylene sequences in crystallites which are present at the annealing temperature. The heat of melting does not vary with the annealing temperature.

The morphology of homogeneous copolymers of ethene and α-octene studied as a function of the short chain branching content (SCBC) and the molar mass by Peeters et al. showed that samples with an increase in molar mass result in an increase of the long period and the crystalline lamella thickness. A decrease of cooling rate results in an increase of the melting temperature, the long period, the crystalline lamella thickness and an evolution from spherulitic structures to perfectly stacked lamella. For the branched
samples, increasing the SCBC results in a decrease of the melting and the crystallization temperature, crystallinity, spherulite radius, the long period, and the crystalline lamella thickness. On the other hand, an increasing the cooling rate affects only the crystallinity of the least branched samples. Furthermore, decreasing the cooling rate results in smaller spherulites. It has a minor influence on the lamellar parameters and reduces the dimensions of the basal plane of the unit cell. Increasing the molar mass of the branched sample results in a drop of the crystallinity, and a deterioration of the superstructure. It enlarges the amorphous layer thickness and the different crystallization regimes being applicable when different molar masses, SCBC, and cooling rates are used [77].

Simanke et al. observed that as the comonomer content increases, there is an increase in the intensity of $\beta$-transition, meanwhile it was observed a decrease in the intensity of $\alpha$-transition. From Raman spectroscopy and DSC data, it was also observed that as an increase in the comonomer, a decrease in the melting temperatures and crystallinity, indicating that the changes observed in $\beta$-transition region are probably related to movements of the chain segments that are located in the interfacial region [62]. A linear polyethylene (LPE) blended with a series of random ethylene-octene copolymers of differing octene content studied by Hill et al. showed that melts of blends containing the lowest octene contents (2,3,5 and 8 mol%) had liquid-liquid phase separation at some temperatures as well as for some compositions. The phase-separated regions were in the shape of closed loops and asymmetrically placed at low LPE content. This behavior has been found previously for LPE/branched PE blends. However, unexpectedly, the phase-separated loops became smaller as the content of the copolymer
increased. Blends of LPE with a 12mol% octene copolymer showed extensive separation and different morphologies [49, 65-70, 31, 170].

Polymer blends have provided an efficient way to fill new requirements of material properties. The alternative to blending is synthesizing new polymers which not only involves forbidding costs but also can not fulfill industrial demands. Blending is done for a variety of reasons including creating new materials with enhanced thermal and mechanical behavior. When two immiscible polymers are blended during melt extrusion, one phase is mechanically dispersed inside the other. The size and shape of the dispersed phase depend on several processing parameters including rheology, interfacial properties, and the composition of the blend. The great majority of useful blends are immiscible. In these blends, multiphase materials are usually developed in order to give combinations of properties that are superior to single component material [9-12].

Many synthetic polymers including polystyrene (PS), polypropylene (PP) etc., become brittle under severe conditions of deformation, such as at or below room temperature or high strain rates. They can undergo a sharp ductile-to-brittle transition. Therefore, these polymers need additives to expand their toughness over a broad temperature range. It frequently is a straightforward matter to increase the toughness of a polymer by decreasing its glass transition temperature. For example, we are able to toughen our material by using a dispersed toughening phase, such as elastomers, which can absorb a lot of energy. The excellent impact property should be obtained. Unfortunately, due to the poor interfacial adhesion between the matrix and the elastomer phase as well as separated phases in these blends, the stress is hard to be transferred from the matrix to the elastomer phase. In the blends, the elastomer does not act as an energy
absorbent. But otherwise, it makes the bulk property of the matrix worse. That is why the mechanical properties of binary blends are usually unsatisfactory [6-7, 78].

It is well known that there are a few of polymers, which are thermodynamically miscible as mentioned before. Fortunately, to some blends, even although they are thermodynamic immiscible, they are still able to be mechanically compatible. For instance, high-impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene terpolymer (ABS) have been successfully found commercial applications although they are, in fact, not miscible [6-11]. In this chapter, the physical blends of POE with different commercial polymers, including PP, HDPE, PS, PMMA, PA66, and PC, were investigated and the basic purposes of this chapter are as follows:

1) Mechanically compatible property of POE was studied by the mechanical behavior of the physical blends of POE with different commercial polymers.

2) The phase segregation behavior of POE was explored by the morphology study of the blends.

3) The thermodynamic miscible property of POE was investigated through differential scanning calorimetry (DSC) and dynamic mechanical spectroscopy (DMS).

4) Finally, comparing with synthetic properties of the blends of POE, promisingly blended systems were selected.

3.2 Experimental
3.2.1 Materials

All of polymers used in this study are commercial grades. Engage® polyolefin elastomers (POEs) are ethylene-octene copolymers. The POEs synthesized through the INSITE™ technology, were generously donated by the Dupont Dow Elastomers in pellet form. The density range of the copolymers was from 0.860 to 0.888 g/cm³. The pellet density, mole percent comonomer, Mooney Viscosity and melt flow index of the copolymers, which were provided by the manufacturer, and the comonomer is identified by octene, are listed in Table 3.1.

The INSITE™ technology polymers are identified through the initial constrained geometry catalyst technology (CGCT). REXENE resins 31S4A of polypropylene (PP) in pellet form, which had a melt-flow index (MFI) of 4.0 g/10min, was kindly supplied by Huntsman Corporation. Polymethyl methacrylate (PMMA) of ENVIOR resins in pellet form was provided through General Polymers, Division of Ashland Chemical. AFFINITY* resin in pellet form is the product of Dow Chemical Company. High-density polyethylene (HDPE) resin in pellet form is the product of Eastman Chemical Company. The polyethylene (PE) and linear low-density polyethylene (LLDPE) of Dow polyethylene (PE) resins, are the products of Dow Chemical Company in pellet form. LLDPE has a melt-flow index (MFI) of 6.0 g/10min. STYRON* polystyrene (PS) and STYRON* high impact polystyrene (HIPS) resins in pellet form are the products of Dow Chemical Company. LEXAN* glass fiber reinforced bisphenol-A polycarbonate (PC) resin in pellet form is the product of General Electric Co. Polyamide 6,6 (PA6,6) in pellet form is the product of Monsanton. The other materials used in this study are listed in table 3.2.
Table 3.1 Characteristics of polyolefin elastomers (POEs)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>POE-1</th>
<th>POE-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical M(_w) (g/mol)</td>
<td>146000</td>
<td></td>
</tr>
<tr>
<td>Density (g/cm(^3))</td>
<td>0.863</td>
<td>0.885</td>
</tr>
<tr>
<td>Melt index (g/10 min)</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Mooney viscosity, ML 1+4</td>
<td>35</td>
<td>22</td>
</tr>
<tr>
<td>Comonomer content (wt%)</td>
<td>28</td>
<td>18</td>
</tr>
<tr>
<td>Crystalline character</td>
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<td>Semi-crystalline</td>
</tr>
<tr>
<td>Supplier</td>
<td>Dupont Dow Elastomers</td>
<td>Dupont Dow Elastomers</td>
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</table>

Table 3.2 Other polymers used in this study

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Trade name</th>
<th>MFI (g/10min)</th>
<th>Crystal</th>
<th>Supplier</th>
</tr>
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<tr>
<td>POE</td>
<td>Affinity</td>
<td></td>
<td>Semi-crystalline</td>
<td>Dow Chemical</td>
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<tr>
<td>HDPE</td>
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<td></td>
<td>Semi-crystalline</td>
<td>Eastman</td>
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<tr>
<td>LLDPE</td>
<td>Dow PE</td>
<td>6.0</td>
<td>Semi-crystalline</td>
<td>Dow Chemical</td>
</tr>
<tr>
<td>PE</td>
<td>Dow PE</td>
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<td>4.0</td>
<td>Amorphous</td>
<td>Huntsman</td>
</tr>
<tr>
<td>HIPS</td>
<td>STYRON*</td>
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<td>Amorphous</td>
<td>Dow Chemical</td>
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<tr>
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<td></td>
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<td>Dow Chemical</td>
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<td>General</td>
</tr>
<tr>
<td>PC</td>
<td>LEXAN*</td>
<td></td>
<td>Amorphous</td>
<td>GE</td>
</tr>
<tr>
<td>PA6,6</td>
<td></td>
<td></td>
<td>Semi-crystalline</td>
<td>Monsanton</td>
</tr>
</tbody>
</table>

3.2.2 Methods
3.2.2.1 Physical blending process

All of polymers used in these studies are commercial grades. The polymer resins used in the physical blending were pre-mixed in a mixer about 10 minutes with desired ratios before vacuum drying. The mixture of polymer resins were dried in vacuum ovens over night at temperature in the range between 45-80°C and the vacuum pressure of 28 mmHg prior to blending. The temperature and time for drying the polymer resins used in this study are listed in table 3.3.

Table 3.3 Drying temperature and drying time for polymer resins

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Drying temperature (°C)</th>
<th>Drying time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POE</td>
<td>45-59</td>
<td>16-24</td>
</tr>
<tr>
<td>LLDPE</td>
<td>45-59</td>
<td>16-24</td>
</tr>
<tr>
<td>HDPE</td>
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<tr>
<td>PE</td>
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<td>16-24</td>
</tr>
<tr>
<td>HIPS</td>
<td>65-75</td>
<td>24-48</td>
</tr>
<tr>
<td>PS</td>
<td>65-75</td>
<td>24-48</td>
</tr>
<tr>
<td>PMMA</td>
<td>65-75</td>
<td>24-48</td>
</tr>
<tr>
<td>PC</td>
<td>70-80</td>
<td>24-48</td>
</tr>
<tr>
<td>PA6,6</td>
<td>56-69</td>
<td>24-32</td>
</tr>
</tbody>
</table>

The physical blending of POEs was carried out in a 34 - mm non-intermeshing and co-rotating twin screw extruder, APV Chemical Machinery Inc., which length-to-diameter ratio L/D is 34. The temperature of the extruder was regulated by electrical
resistance and water circulation in the barrels. The dried pre-mixing polymer resins were introduced into the extruder from the hopper of the extruder through a screw dry material feeder, Accu Rate, Inc. In the blending, the following process parameters were employed: processing temperature ranging from 160 to 300°C, screw speed ranging from 100 to 300 rpm, estimated residence time ranging from 0.5 to 1.5 minutes, feeding rate ranging from 50 to 150 grams per minute. For all experimental runs, devolatilization was carried out by a vacuum pump, VPS-10A, Brooks Equipment Company. This pump was placed near the die and it created a pressure of about 25 mmHg. The extruder was always starved to feed. The output and screw speed were varied in order to assess their influence on the properties of the physical blends of POEs [35-37]. The processing parameters used in physical blending of POEs are shown in table 3.4.

Table 3.4 Processing parameters used in the blending of POEs

<table>
<thead>
<tr>
<th>Blending system</th>
<th>Processing temperature (°C)</th>
<th>Screw speed (rpm)</th>
<th>Residence time (min)</th>
<th>Feeding rate (g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE/POE</td>
<td>140-190</td>
<td>100-300</td>
<td>1.5-1.0</td>
<td>100</td>
</tr>
<tr>
<td>PE/POE</td>
<td>140-180</td>
<td>100-300</td>
<td>1.2-0.8</td>
<td>100</td>
</tr>
<tr>
<td>PP/POE</td>
<td>180-240</td>
<td>100-300</td>
<td>1.5-1.0</td>
<td>100</td>
</tr>
<tr>
<td>PS/POE</td>
<td>200-250</td>
<td>100-300</td>
<td>1.5-1.0</td>
<td>100</td>
</tr>
<tr>
<td>PMMA/POE</td>
<td>200-250</td>
<td>100-300</td>
<td>1.5-1.0</td>
<td>100</td>
</tr>
<tr>
<td>PC/POE</td>
<td>220-300</td>
<td>100-200</td>
<td>1.5-1.0</td>
<td>100</td>
</tr>
<tr>
<td>PP/PA6.6/POE</td>
<td>200-260</td>
<td>100-200</td>
<td>1.5-1.0</td>
<td>100</td>
</tr>
</tbody>
</table>

3.2.2.2 Mechanical properties
The extrudates were pelletized and the resulting pellets of the blends were dried under vacuum overnight at temperature in range between 45-65°C in order to remove the absorbed water on the pellets. Then, the dried pellets were molded through compression molding for the test specimens of mechanical properties. The recommend process of Izod impact, tensile and flexural test specimens was based upon ASTM D4703. Test bars were prepared using a Carver compression molding machine, Fred S. Carver Inc. with processing temperature ranging from 150 to 300°C and molding pressure ranging from 1600 to 2600 psi. The procedure of compression molding is as follows:

1) Place the dried pellets into the mold;

2) Heat the resin and mold to the desired temperature;

3) Put pressure slowly on the molten polymer into the desired value;

4) Keep the temperature and pressure on the molten resin for some time;

5) Keep the pressure and cooling the resin to room temperature;

6) Relieve the pressure and removing the test specimens from the mold.

The processing parameters of compression molding for Izod impact, tensile and flexural test specimens used in these studies are listed in table 3.5. The processing temperature and pressure with time used in the procedure of compression molding are shown in table 3.5. All test bars were dried and handled according to exactly the same procedure and processing conditions as above mentioned in compression molding prior to mechanical testing.
Table 3.5 Processing parameters for compression molding procedure

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temp (°C)</th>
<th>Pressure (psi)</th>
<th>Time (min)</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE/POE</td>
<td>160</td>
<td>1800</td>
<td>5</td>
<td>Air</td>
</tr>
<tr>
<td>PE/POE</td>
<td>150</td>
<td>1600</td>
<td>5</td>
<td>Air</td>
</tr>
<tr>
<td>PP/POE</td>
<td>180</td>
<td>2000</td>
<td>5</td>
<td>Air</td>
</tr>
<tr>
<td>PS/POE</td>
<td>220</td>
<td>2500</td>
<td>6</td>
<td>Air</td>
</tr>
<tr>
<td>PMMA/POE</td>
<td>220</td>
<td>2500</td>
<td>6</td>
<td>Air</td>
</tr>
<tr>
<td>PC/POE</td>
<td>280</td>
<td>2600</td>
<td>6</td>
<td>Air</td>
</tr>
<tr>
<td>PP/PA6,6/POE</td>
<td>260</td>
<td>2600</td>
<td>6</td>
<td>Air</td>
</tr>
</tbody>
</table>

For Izod impact test, the rectangular test bars, which are about 32 mm long, 12.7 mm wide and 6.35 mm high, were molded and center-notched using a notching cutter, Testing Machines Inc. The notched Izod impact test were conducted utilizing a TMI impact test machine according to ASTM D256 at ambient temperature and liquid nitrogen temperature, respectively. Tensile testing of dried dog-bone-shaped test bars, type V test specimens which had 7.26 mm gauge length, 3.18 mm width and 3.18 mm thickness, was done using an INSTRON 1125 testing machine at strain rate in range between 50 mm/min and 2 mm/min for modulus of elasticity, yield strength measurements and elongation at break in reference to ASTM D638 under ambient conditions. Four-point flexural test of rectangular test bars which had 64 mm length, 12.7 width and 3.18 mm thickness, was evaluated through the same test machine used in the tensile test for flexural strength and modulus of elasticity at cross-head speed of 2 mm/min and room temperature in accordance with ASTM D790.
3.2.2.3 Morphological observation

Morphologies of the physical blends of POEs were studied through scanning electron microscopy (SEM) and atomic force microscopy (AFM). The cryofracturing surface of the notched Izod samples for SEM were prepared through the Izod impact test at liquid nitrogen temperature. In order to prevent electron charging on insulating surfaces, the cryofracturing surfaces of Izod sample were sputter coated with gold-palladium alloy (Au-Pd) through a Hummer V coating system about 30 seconds. Jeol JSM-6400 and Jeol Jeol JSM-35CF, equipped with tungsten filament, were used in this study. The accelerating voltage of the microscopes was usually set to be in the range of 5 kV. The basic procedures for the SEM observations are as follows:

1) Place the notched Izod sample into the liquid nitrogen about 15 minutes, and then performing Izod impact test immediately;

2) Cut the cryofractureing surface from the Izod sample and mounting the surface onto a metal cylinder by conductive paint;

3) Coat Au/Pd onto the cryofracturing surface;

4) Observe the cryofracturing surface through SEM.

The surface morphology and nanostructure of physical blends of POEs was examined through atomic force microscopy (AFM). AFM samples were prepared in film form through compression molding. The compression molding parameters for a blend of POE are the same as corresponding one listed in table 3.5. The sample films posses flat surface with thicknesses in the range of 0.05-0.2 mm. For AFM observation, a scanning
probe microscope Nanoscope III, Digital Instruments Inc., equipped with Lateral Force and Multi-Mode heads was used. Tapping mode imaging was performed using crystal silicon nanoprobe cantilevers. Phase imaging was performed simultaneously with the topographical imaging.

3.2.2.4 Thermal analyses and x-ray diffraction (XRD) measurements

In order to detect the glass transition temperature (Tg) and the grade of crystallisation of the physical blends, differential scanning calorimetry (DSC) was used. DSC was performed on a Seiko SII DSC 220C-SSC/5200, Seiko Instruments, equipped with a data RHEOL. station. The sample mass was in range of 10-15mg in all experiments. The sample was sealed into a standard aluminum pan and crimping cover through a crimper. The sample was purged with dry nitrogen at a flow rate of 100ml/min. For cooling, the liquid nitrogen accessory of the device was used. Calibration was carried out with an sapphire standard. The Tg was defined as the midpoint of the change in the heat capacity for the transition. The melting temperature was taken as the temperature corresponding to the peak in heat flow during heating. Enthalpies of crystallization and melting were obtained by integrating the heat flow curve to a flat baseline. Using the heat of fusion of a perfect iPP (209J/g) and a perfect PE (277J/g) crystal, the weight fraction crystallinity (Xc) was caculated as:

\[ Xc = \frac{\Delta H_{melt}}{f\Delta H^*_{melt}} \]  

(3.1)
Where $\Delta H_{\text{melt}}$ is the measured enthalpy of melting, $\Delta H^*_{\text{melt}}$ is the ideal enthalpy of melting a perfect crystal of polymer X, and $f$ is the weight fraction of polymer X in the blend. The heating rate was 10$^\circ$C/min. The basic programs used in DSC are showed in table 3.6. The data was analyzed by the equipment analysis programs.

For X-ray diffraction (XRD) observation, samples were prepared in film form through compression molding. The compression molding parameters for a blend of POE are the same as corresponding one listed in table 3.5. The sample films posses flat and parallel surface with thicknesses in the rang of 0.5 – 0.8 mm. The solid film samples, which size are 1cm x 3cm, are mounted on 2.7cm x 4.6cm glass slides to go into the sample holder. XRD data were obtained using Ni-filter Cu Kα radiation obtained from a Philips APD 3720 X-ray generator operating at 40kV and 20 mA. A quantitative evaluation of the intensity in the angular range between 10 and 90$^\circ$ 2θ was measured. The measurement of XRD was programmed by a controller. All measurements were performed under ambient conditions.

3.3 Results and Discussion

3.3.1 Fracture behavior

The fracture behavior of the physical blends of polyolefin elastomers (POEs) was characterized by conventional testing, notched Izod impact test. The notched Izod impact strength values (J/m) of the physical blends of POE-1 and POE-2 are reported as a function of the POE content (wt%), under room temperature and liquid nitrogen.
Table 3.6 Basic programs used in DSC

<table>
<thead>
<tr>
<th>No</th>
<th>Polymers</th>
<th>Step 1</th>
<th>Step 2</th>
<th>Step 3</th>
<th>Step 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PP, POE,</td>
<td>25 to 200°C,</td>
<td>200 to 150°C,</td>
<td>-150 to 200°C,</td>
<td>200 to 25°C,</td>
</tr>
<tr>
<td></td>
<td>PP/POE,</td>
<td>+20°C/min,</td>
<td>-10°C/min,</td>
<td>+10°C/min,</td>
<td>-50°C/min,</td>
</tr>
<tr>
<td></td>
<td>PS/POE,</td>
<td>N₂ gas,</td>
<td>N₂ gas,</td>
<td>N₂ gas,</td>
<td>N₂ gas</td>
</tr>
<tr>
<td></td>
<td>PC/POE,</td>
<td>Hold 2min</td>
<td>Hold 10min</td>
<td>Hold 2min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PMMA/POE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>PA6,6, PC, PS,</td>
<td>25 to 300°C,</td>
<td>300 to 25°C,</td>
<td>25 to 300°C,</td>
<td>300 to 25°C</td>
</tr>
<tr>
<td></td>
<td>PMMA,</td>
<td>+20°C/min,</td>
<td>-50°C/min,</td>
<td>+10°C/min,</td>
<td>-50°C/min,</td>
</tr>
<tr>
<td></td>
<td>PP/PA6,6/</td>
<td>N₂, gas,</td>
<td>N₂ gas,</td>
<td>N₂ gas,</td>
<td>N₂ gas</td>
</tr>
<tr>
<td></td>
<td>POE</td>
<td>Hold 2min</td>
<td>Hold 5min</td>
<td>Hold 2min</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>HDPE, POE,</td>
<td>-150 to 180°C,</td>
<td>180 to 150°C,</td>
<td>-150 to 180°C,</td>
<td>180 to 25°C,</td>
</tr>
<tr>
<td></td>
<td>PE, LLDPE</td>
<td>+20°C/min,</td>
<td>-50°C/min,</td>
<td>+10°C/min,</td>
<td>-50°C/min,</td>
</tr>
<tr>
<td></td>
<td>HDPE/POE,</td>
<td>N₂ gas,</td>
<td>N₂ gas,</td>
<td>N₂ gas,</td>
<td>N₂ gas</td>
</tr>
<tr>
<td></td>
<td>PE/POE,</td>
<td>Hold 2min</td>
<td>Hold 15min</td>
<td>Hold 2min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LLDPE/POE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PP, POE,</td>
<td>-150 to 200°C,</td>
<td>200 to 150°C,</td>
<td>-150 to 200°C,</td>
<td>200 to 25°C,</td>
</tr>
<tr>
<td></td>
<td>PP/POE,</td>
<td>+20°C/min,</td>
<td>-50°C/min,</td>
<td>+10°C/min,</td>
<td>-50°C/min,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N₂ gas,</td>
<td>N₂ gas,</td>
<td>N₂ gas,</td>
<td>N₂ gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hold 5min</td>
<td>Hold 15min</td>
<td>Hold 5min</td>
<td></td>
</tr>
</tbody>
</table>
temperature. Figure 3.1 presents the notched Izod impact strength (Is) of the elastomer-modified HDPE measured at room and liquid nitrogen temperature for the different content of POEs. The values of Is obtained at room temperature show a synergistic behavior of impact properties of the physical blends of HDPE with POEs. In addition, the samples of plain HDPE broke nearly completely, while the behavior of samples of elastomer-modified HDPE was always of the non-break type. After the impact test a relatively large plastic deformation zone could be easily observed in the blend samples near the fracture flank. In this zone the material showed whitening.

Figure 3.2 illustrates the notched Izod impact strength, Is, of the elastomer-modified PP evaluated at room and liquid nitrogen temperature for the different concentration of POEs. The values of the physical blends obtained at room temperature demonstrates an impressive jump when modified with 20 weight percentage of POEs. Moreover, the samples of plain PP broke completely, while the behavior of samples of elastomer-modified PP was always of the non-break type. After the impact test a relatively large plastic deformation zone could be easily observed in the blend samples near the fracture flank. In this zone the material showed whitening. In addition, a reduction of the sample thickness close to the fracture flank was frequently observed. The whitened deformation zone in samples modified with rubber extended up to approximately 1 mm away from the fracture surface, whereas in unmodified PP no such deformation zone was observed.

Figure 3.3, 3.4 and 3.5 present the notched izod impact strengths, Is, of the elastomer-modified PS, PMMA and PC measured at room and liquid nitrogen temperature for the various content of POEs, respectively. The results of the physical blends obtained
Figure 3.1 Notched Izod impact strength of the blends of HDPE/POE versus the POE content

Figure 3.2 Notched Izod impact strength of the blends of PP/POE versus the POE content
Figure 3.3 Notched Izod impact strength of the blends of PS/POE versus the POE content

Figure 3.4 Notched Izod impact strength of the blends of PMMA/POE versus the POE content
Figure 3.5 Notched Izod impact strength of the blends of GFR-PC/POE versus the POE content at room temperature indicate an incompatible behavior. All samples of plain PS, PMMA, PC and their physical blends broke completely. Moreover, after the impact evaluation, a plastic deformation zone could be observed in the samples near the fracture flank. In this zone the material showed whitening. The reduction of the sample thickness close to the fracture surfaces were not found in the tested samples of blends.

3.3.2 Tensile properties

The tensile properties of POEs, Affinity and LLDPE and their stress-strain behavior at 50 mm/min crosshead speed are respectively shown in the table 3.7 and
figure 3.6. Here, the stress-strain diagram serves as a basis for classification of polymers. LLDPE exhibited highest modulus of elasticity, high ultimate tensile strength, narrowest yield region and relative lower elongation. Yielding, in which a large and sudden load drop in the stress-strain curve, produces a fairly sharp neck profile, is localized. The stress increases during cold drawing. The stress-strain curve of LLDPE illustrates a ductile polymer behavior. Affinity has the highest ultimate tensile strength, medium modulus of elasticity, broader yield region and relative high elongation. The increase in the stress after the neck stabilized is associated with strain hardening of the necked material. Affinity shows plastomer characteristics. The stress-strain curves of POE-1 and POE-2 are distinctive from others. POE-1 and POE-2 have low ultimate tensile strength and modulus of elasticity, and highest elongation. There is no indications of a yield in the stress-strain curve. The deformation has elastomeric characteristics with a low initial modulus, a gradual increase in the slop of the stress-strain curve at higher strains but less steep than in strain hardening of LLDPE and Affinity.

The results presented in Figure 3.7 and 3.8 demonstrate that the incorporation in the range of weight fraction between 0.1 and 0.3 of POEs into HDPE matrix causes a decrease in the modulus of elasticity (E) by 17%-46%, a decrease in the yield tensile strength (σy) by 21%-40%, relative to the unmodified HDPE. In contrast, the ultimate elongation of the blends is usually higher by 73% - 1060%, compared to the virgin HDPE. The commercial HDPE and blends of HDPE/POE-1 undergo some whitening in the necked zone. They start to whiten later in the deformation process, when strain hardening occurs and the stress rises. Strain energy per unite volume is represented as the
Table 3.7 Tensile properties of POE, Affinity and LLDPE at 50 mm/min crosshead speed

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Yield Tensile Strength (MPa)</th>
<th>Modulus of Elasticity (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POE-1</td>
<td>1.16±0.17</td>
<td>1.36±0.14</td>
<td>&gt;2500</td>
</tr>
<tr>
<td>POE-2</td>
<td>4.65±0.33</td>
<td>4.85±0.15</td>
<td>&gt;2500</td>
</tr>
<tr>
<td>LLDPE</td>
<td>11.77±0.73</td>
<td>44.82±2.78</td>
<td>&gt;1800</td>
</tr>
<tr>
<td>Affinity</td>
<td>12.05±0.24</td>
<td>29.98±0.61</td>
<td>&gt;1800</td>
</tr>
</tbody>
</table>

Figure 3.6 Stress-strain behavior of the blends of POE, Affinity and LLDPE at 50 mm/min crosshead speed
area under the stress-strain curve which is related to toughness of the material. The stress-strain behaviors of the blends of HDPE/POE-1 shown in figure 3.9 indicate that the introduction of POE leads to increasing the strain energy per unit volume, W, of the blends. From the point of view of strain energy per unit volume, the results suggest that the POEs introduced into the HDPE matrix cloud lead to increasing impact resistance of the blends. In fact, they are in accord with the results mentioned in 3.3.1.

The effect of increasing POE content in the PP/POE system manifests itself in a decrease in the yield tensile strength (σy) and modulus of elasticity (E) as illustrated in Figure 3.10. As expected, with introduction of the POE-1 content ranging from 10 to 30 wt%, both yield tensile strength (σy) and modulus of elasticity (E) are decreased by 14.4%-33.3% and 21.7% - 47.3%, respectively, comparing with virgin PP. However, in the blends containing 10wt% and 30% of POE-1, the elongation of the blends of PP/POE-1 presented in Figure 3.12. is increased by 22.6% - 166.5% relative to a homopolymer of PP. The stress-strain curves of PP and PP/POE blends at room temperature shown in Figure 3.11 display a clear characteristic transformation from brittleness to ductility. The formation of the blends has characteristics common to many semicrystalline thermoplastics with localized yielding and cold drawing while the homopolymer of PP does not have yielding and cold drawing. With a increase of POE content into the PP matrix, the yielding region and cold drawing of the blends become border and longer, respectively. During the yielding, the stress-whitening was easily observed in the blends of PP/POE. However, it did not find in the homopolymer of PP. For the blends of PP/POE, fairly sharp neck profiles are also produced during yielding. The areas under the stress-strain curves, strain energy per unit volume, are increased with
a increase of POE into the PP matrix. It is suggested that to some extent there exists a phase separation phenomenon in the blending and impact resistance is increased with putting more POE phase into PP. They go with the results mentioned in 3.3.1.

The results shown in Figure 3.13. illustrate that the incorporation of a weight fraction in the range between 0.1 and 0.3 of POE into PS and PMMA matrix causes a decrease in the yield tensile strength (σ_y) by 15.6% - 37.1% for PS as well as 15.1% - 51% for PMMA and modulus of elasticity (E) by 2.5% - 47.2% for PS as well as 35.9% - 62.6% for PMMA, relative to the virgin PS and PMMA. In contrast, the ultimate elongation of the blends is usually higher comparing with the homopolymer of PS and PMMA. The stress-strain behaviors of the blends of PS/POE and PMMA/POE presented in Figure 3.14 and 3.15 indicate that in both cases the broad yield region is found when 10 weight percentage of POE is put into the PS and PMMA matrix phase. The cold drawing did not appear until 20wt% POE introduced into the PS and PMMA matrix. The areas under the stress-strain curves of the blends, strain energy per unit volume, go up with a increase of POE content in the matrix phase. Stress-whitening was found during yielding. This suggests that there exists a phase separation in the blends. The homopolymers of PS and PMMA possess brittle characteristic behaviors. It is suggested that the blends of PS and PMMA could be toughened by incorporation of POE if phase separation is improved.

The effect of increasing POE content in the PC/POE system mainfests itself in a decrease in the yield tensile strength (σ_y), and modulus of elasticity (E) as illustrated in Figure 3.16. Incorporating POE weight concentration in the range from 10% to 30% into the PC matrix, both yield tensile strength (σ_y) and modulus of elasticity (E) are decreased
by 30.7% - 52.8% and 47.2% - 63.1%, respectively, comparing to virgin PC. However, at
the blends containing 10wt% and 30wt% of POE, the elongation of the blends
presented in Figure 3.12 is increased by 32.9% - 44.5% relative to homopolymer of PC.
The stress-strain curves of PC and PC/POE blends at room temperature shown in Figure
3.17 display a clear characteristic transformation from brittleness to ductility. The
deformation of the blends is similar to the characteristics behavior of PC with no
yielding and cold drawing. With a increase of POE content into the PC matrix, the areas
under the stress-strain curves, strain energy per unit volume, are decreased. At the break
, stress-whitening was easy observed in the blends of PC/POE. However, it did not find in
the PC. It is suggested that there may exist a phase separation in the blends and

![Figure 3.7 Elongation of the blends of HDPE and PP with POEs](image)

Figure 3.7 Elongation of the blends of HDPE and PP with POEs
Figure 3.8 Yield tensile strength and modulus of elasticity of the blends of HDPE versus POE-1 at 50 mm/min crosshead speed

Figure 3.9 Stress-strain behavior of the blends of HDPE/POE-1 at 50 mm/min crosshead speed
Figure 3.10 Yield tensile strength and modulus of elasticity of the blends of PP versus POE-1 at 50 mm/min crosshead speed.

Figure 3.11 Stress-strain behavior of the blends of PP/POE-1 at 50 mm/min crosshead speed.
Figure 3.12 Elongation of the blends of PS, PMMA and PC with POE-1

Figure 3.13 Yield tensile strength and modulus of elasticity of the blends of PS and PMMA versus POE-1 at 2 mm/min crosshead speed
Figure 3.14 Stress-strain behavior of the blends of PS/POE-1 at 2 mm/min crosshead speed

Figure 3.15 Stress-strain behavior of the blends of PMMA/POE-1 at 2 mm/min crosshead speed
Figure 3.16 Ultimate tensile strength and modulus of elasticity of the blends of GFR-PC versus POE-1 at 2 mm/min crosshead speed

Figure 3.17 Stress-strain behavior of the blends of GFR-PC/POE-1 at 2 mm/min crosshead speed
the impact resistance of the physical blends could not be improved with incorporating POE phase into PC matrix due to the phase-separated phenomenon. They are in accord with the results mentioned in 3.3.1.

3.3.3 Morphology

SEM and AFM observations of the blend of HDPE/POE-1 presented in Figure 3.18 and 3.19 demonstrated that the blends investigated do not exhibit distinct phase boundaries between HDPE and POE-1. In these, HDPE constitutes a topologically continuous matrix in which the rubber inclusions are homogeneously dispersed. The diameter of the elastomer phase in the blends generally does not exceed 100 nm. It is interesting to note that the blend of HDPE/POE-1 could possess a nano-structure with some level of interfacial adhesion. It also stands to reason that this kind of blend has synergistic behavior of impact resistance due to the unique nano-structure. It is rarely reported in the classic polymer blending text books [9, 11-12].

SEM micrographs of the blends of PP/POEs illustrated in Figure 3.20 indicate that the blends with PP matrix show a separately dispersed morphology. The diameter and shape of the elastomer inclusions in the blends depend on the particular type of the elastomer, but usually does not exceed 3.5 μm. In the blend of PP/POE-1 constituted PP matrix, spherical-shaped particles of POE-1 are included while oval-shaped particles of POE-2 include in the blend of PP/POE-2. In both cases, the elastomer phase is bound to the PP matrix to a certain extent. It is suggested that the synergistic property of impact resistance of the blends due to the interfacial adhesion between the elastomer and PP matrix. The phenomenon of coalescence is easily found in the blends. This morpholoical
observation matches the predicted morphology, which is based on the stress-whitening during tensile testing.

The morphology of PS and the blend of PS/POE (90/10) shown in Figure 3.21 demonstrate that there exists a phase separated behavior. Dispersed droplets of the minor POE phase in the PS matrix are easily observed. It is interesting to note that the physical blend of PS/POE exhibit evidence of some level of interfacial adhesion. The domain size of elastomer varies within a range between 5 μm and 10 μm. The blend also is experiencing coalescence and particle-particle interactions. Representative SEM micrographs of blend of PMMA/POE are shown in Figure 3.22. It is observed that a two phase morphology is comprised in discrete, uniformly distributed POE spherical particles of size 1 to 8.5 μm without exhibiting a significant agglomeration. The discrete interface between the two phases suggests poor interfacial adhesion. It stands to reason that the impact behavior of the blends of PS/POE and PMMA/POE is incompatible due to the phase separation and agglomeration.

The SEM micrograph of GFR-PC and the physical blend of GFR-PC/POE (90/10) shown in Figure 3.23 is typical for PC material made up of three incompatible phases. The POE dispersed phase appears in the form of droplets of 2-12 μm, with no adhesion to the PC matrix. In the PC-rich ternary blends, the POE is preferentially located in the PC matrix. The significant phenomena of agglomeration are also found in the blends. The morphologic observation suggests that the blend of GFR-PC with POE is not mechanical compatible because of the poor interfacial adhesion and coalescence
Figure 3.18 Scanning electron micrographs of HDPE/POE-1 blend: a) HDPE x 2000; b) 70/30 x 5000
Figure 3.19. Atomic force micrographs (AFM) of HDPE/POE-1 (70/30) blend: a) (500x500 nm) AFM height image (z-range = 25 nm) and phase image (phase=50°); b) 3-D AFM image
Figure 3.20 Scanning electron micrographs of PP/POEs blends: a) PPx 500; b) PP/POE-1 (80/20) x 2000; c) PP/POE-2 (70/30) x 2000
Figure 3.21 Scanning electron micrographs of PS/POE-1 blend: a) PS x 200; b) PS/POE-1 (70/30) x 500
Figure 3.22 Scanning electron micrographs of PMMA/POE-1 blend: a) PMMA x 200; b) PMMA/POE-1 (80/20) x 200; c) PMMA/POE-1 (80/20) x 2000
Figure 3.23 Scanning electron micrographs of glass fiber reinforced PC (GFR-PC)/ POE-1 blend: a) GFR-PC x 500; b) GFR-PC/POE-1 (90/10) x 500; c) GFR-PC/POE-1 (90/10) x 2000
3.3.4 Differential scanning calorimetry (DSC)

The DSC thermograms and thermal characterization of POEs, Affinity and LLDPE that were slowly heated from \(-130^\circ\text{C}\) at \(10^\circ\text{C/min}\) are shown in Figure 3.24 and table 3.8. It is observed that the thermal behavior of the POEs has a glass transition temperature (Tg) and a single endotherm correlated to melting temperature (Tm) while the thermal behavior of Affinity and LLDPE possess a single endotherm corresponding to melting temperature. The glass transition temperature of POE-1 and POE-2 are \(-52.1\) and \(-45.2^\circ\text{C}\). The Peak melting temperature of POE-1, POE-2, Affinity and LLDPE are \(63.3, 83.0, 113.1, 125.3^\circ\text{C}\), respectively. The melting endotherm of POEs are broadened
and shifted to lower temperature with decreasing crystallinity (Xc). The melting endotherm peaks of Affinity and LLDPE are very narrow and sharp, while the melting range of the POEs are broad. It is interesting to note that the crystallinity of POE-1 is so small, only about 0.008, that it could be considered as an amorphous material.

The DSC thermograms and thermal characterization of neat HDPE and blends of HDPE/POE-1 presented in Figure of 3.25 and table of 3.9 illustrate that the behavior of the blend of HDPE/POE-2 has a glass transition (Tg) and a single endotherm correspond melting temperature ( Tm ) of POE-1 while only a endotherm is found in neat HDPE. In the heating scan, one can see that one melting peak appears at 136.1 °C, which corresponds to the melting point of HDPE crystallinity. The blend of HDPE/POE has a slightly lower melting point than that of neat HDPE. The Tm depression may be attributed to the mixing with POE or smaller size and disordering of the HDPE. It is found that not only Tg of the blends is shifted to lower temperature relative to neat POE but also the crystallinity (Xc) of HDPE in the blend varies with the POE content. It is interesting to note that the Xc of the blend of HDPE/POE (80/20) is 0.628 while the Xc of the blends of HDPE/POE (90/10) as well as HDPE/POE (70/30) has higher value. It is suggested that the impurity (POE) in the HDPE phase affects not only Xc of PP but also the crystalline ordering of PP in the blends. The lower Tg effect and a variety of crystallinity of the blend may be ascribed to the HDPE mixing with POE.

The DSC studies of neat PP and PP/POEs were carried out essentially to study the glass transition, melting and crystallization behavior of the neat PP and blends of PP/POEs. Figure 3.26 and table of 3.10 represent the thermal behavior and characterization during heating of the virgin samples and blending samples resulting from
mixing in APV extruder. The blends of PP/POE possess a glass transition temperature (Tg of POE) and a bimodal endotherm, i.e. the low endotherm (denoted by Tm of POE-2) and the high endotherm (denoted by Tm of PP). The shape of endotherm of the blend is the same as that of the neat PP. It is observed that in both cases, Tg and Tm of the blends of POE is slightly shifted to lower temperature relative to neat POE and PP. Tm depression may be caused by the partial miscibility of PP and POE. The crystallite (Xc) of the blends of PP/POE varies with POE content. It is interesting to note that the Xc of PP/POE goes up with an increase in POE weight fraction, suggesting that the impurity (POE) in the PP phase affects not only Xc of PP but also the crystalline ordering of PP in the blends.

The DSC thermograms and thermal characterization of PS, PMMA, GFR-PC and their blends with POE are plotted in Figure 3.27 and listed in table 3.11, respectively. The thermal behaviors of neat PS, PMMA, GFR-PC indicate that they are a typical amorphous materials which only have a glass transition temperature (Tg). The glass transition temperatures (Tg) of PS, PMMA and GFR-PC are 104.4 °C, 98.2 °C and 149.0 °C, respectively. However, in the blending case, the blends of PS/POE, PMMA/POE and GFR-PC/POE possess two Tg and an endotherm which is very shallow and broad. It easily is observed that not only the Tg of elastomer but also the Tg of matrix are shifted to lower temperature comparing to the neat POE, PS, PMMA and GFR-PC. The lower Tg effect of the blends may be ascribed to the PS, PMMA and GFR-PC mixing with POE. The two glass transition temperatures (Tg) in the thermograms indicates the immiscibility of the blends of PS/POE, PMMA/POE and GFR-PC/POE.
Table 3.8 Thermal characterization of POEs, Affinity, PE and LLDPE by DSC

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>ΔHm (J/g)</th>
<th>Xc</th>
</tr>
</thead>
<tbody>
<tr>
<td>POE-1</td>
<td>-52.1</td>
<td>63.3</td>
<td>2.3</td>
<td>0.008</td>
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<tr>
<td>POE-2</td>
<td>-45.2</td>
<td>83.0</td>
<td>52.9</td>
<td>0.182</td>
</tr>
<tr>
<td>Affinity</td>
<td>113.1</td>
<td>108.8</td>
<td>0.375</td>
<td></td>
</tr>
<tr>
<td>PE</td>
<td>125.9</td>
<td>116.5</td>
<td>0.402</td>
<td></td>
</tr>
<tr>
<td>LLDPE</td>
<td>125.3</td>
<td>114.2</td>
<td>0.394</td>
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</tr>
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</table>

Table 3.9. The thermal characterization of the blends of HDPE/POE-1 by DSC

<table>
<thead>
<tr>
<th>HDPE/POE-1</th>
<th>Tg POE-1 (°C)</th>
<th>Tm HDPE (°C)</th>
<th>ΔHm HDPE (J/g)</th>
<th>Xc HDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>136.1</td>
<td>208.7</td>
<td>0.720</td>
<td></td>
</tr>
<tr>
<td>90/10</td>
<td>134.9</td>
<td>189.1</td>
<td>0.724</td>
<td></td>
</tr>
<tr>
<td>80/20</td>
<td>-59.5</td>
<td>145.8</td>
<td>0.628</td>
<td></td>
</tr>
<tr>
<td>70/30</td>
<td>-53.9</td>
<td>182.5</td>
<td>0.899</td>
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</table>
Table 3.10. The thermal characterization of the blends of PP/POE by DSC

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Tg POE (°C)</th>
<th>Tm PP (°C)</th>
<th>ΔHm PP (J/g)</th>
<th>Xc PP</th>
</tr>
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<tbody>
<tr>
<td>PP</td>
<td></td>
<td>168.5</td>
<td>86.1</td>
<td>0.411</td>
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<tr>
<td>PP/POE-1 (90/10)</td>
<td>-58.8</td>
<td>167.5</td>
<td>105.8</td>
<td>0.562</td>
</tr>
<tr>
<td>PP/POE-1 (80/20)</td>
<td>-62.5</td>
<td>166.8</td>
<td>84.8</td>
<td>0.507</td>
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<tr>
<td>PP/POE-1 (70/30)</td>
<td>-53.1</td>
<td>167.2</td>
<td>67.8</td>
<td>0.463</td>
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<tr>
<td>PP/POE-2 (80/20)</td>
<td>-52.9</td>
<td>167.2</td>
<td>74.9</td>
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<tr>
<td>PP/POE-2 (70/30)</td>
<td>-53.3</td>
<td>166.8</td>
<td>62.5</td>
<td>0.427</td>
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Table 3.11 Thermal characterization of the blends of PS/POE, PMMA/POE and GFR-PC/POE by DSC

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Tg elastomer (°C)</th>
<th>Tg matrix (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td></td>
<td>104.4</td>
</tr>
<tr>
<td>PS/POE-1 (90/10)</td>
<td>-58.8</td>
<td>103.4</td>
</tr>
<tr>
<td>PMMA</td>
<td></td>
<td>98.2</td>
</tr>
<tr>
<td>PMMA/POE-1 (70/30)</td>
<td>-55.8</td>
<td>96.8</td>
</tr>
<tr>
<td>GFR-PC</td>
<td></td>
<td>149.0</td>
</tr>
<tr>
<td>GFR-PC</td>
<td>-57.4</td>
<td>146.2</td>
</tr>
</tbody>
</table>
Figure 3.24 DSC thermograms for POEs in heating mode

Figure 3.25 DSC thermograms for the blends of HDPE/POE in heating mode
Figure 3.26 DSC thermograms for the blends of PP/POEs in heating mode: a) PP/POE-1; b) PP/POE-2
Figure 3.27 DSC thermograms for the blends of PS/POE, PMMA/POE and GFR-PC/POE in heating mode

3.3.5 X-ray diffraction (XRD)

The X-ray diffraction (XRD) diagrams of POE, Affinity, HDPE and HDPE/POE illustrated in Figure 3.28 and 3.29 indicate that these polymers possess typical semi-crystalline scattering features while POE is lower and broader peaks than that of Affinity and HDPE. It is interesting to note that the X-ray diffraction of POE-1 has double features between amorphous scattering and semi-crystalline scattering. In other words, it is hard to say whether POE-1 is a semi-crystalline material or an amorphous material exactly. It is in accord with the results which the Xc of POE-1 is 0.0008. It may be
suggested that POE-1 could be considered as an amorphous material in the later chapters. It is easily observed that the XRD diagrams of the blend of HDPE/POE are formed through simply superimposing the XRD diagram of HDPE onto XRD diagram of POE. It is suggested that the impurity of POE does not affect the type of crystallinity of HDPE.

The diffractograms of neat PP and the blend of PP/POE are presented in Figure 3.30. It is found that the XRD pattern of neat PP is $\alpha$-form while that of PP in the blend is $\gamma$-form. In contrast to the pattern of the blend of HDPE by superimposition of HDPE and POE, the transformation of crystalline form in the blends is not trivial. The crystal unit cell of the monoclinic lattice of $\alpha$-form was reported to be $a=0.666$ nm, $b=2.078$ nm, $c=0.6495$ nm, $\beta=99.62^\circ$ and $\alpha=\gamma=90^\circ$, with a crystallographic symmetry (space group) of $P2_1/c$. The number of repeating units involved in each unit cell is twelve, and crystallographic density is $0.946$ g/cm$^3$. The crystal structure and unit cell geometry of the triclinic lattice of $\gamma$-form in PP are known only approximately. The proposed triclinic unit cell parameters are $a=0.654$ nm, $b=2.140$ nm, $c=0.650$ nm, $\alpha=89^\circ$, $\beta=99.6^\circ$ and $\gamma=99^\circ$. This unit cell appears to result from the monoclinic $\alpha$ form by a simple shear along the $a$ axis. The $\gamma$-form can be observed in low molecular weight i-PP or crystalization of i-PP at elevated pressure above 200MPa [171-172]. In our case, during the extrusion, the high shear speed and pressure may lead to the transformation from $\alpha$-form to $\gamma$-form in the blend of PP/POE.

3.4 Conclusions

Immiscibility of POE with amorphous polymers was examined by physical blends of POE with PS, PMMA and GFR-PC. These blends of POE illustrate thermodynamic
Figure 3.28 X-ray diffraction diagrams of POEs and Affinity

Figure 3.29 X-ray diffraction diagrams of the blends of HDPE/POE
Figure 3.30 X-ray diffraction diagrams of the blends of PP/POE

immiscibility. Thermal behavior of the blends was examined by DSC. There exist two glass transition temperatures (Tg) in the DSC traces of the blends. Morphology of the blends was studied by SEM. SEM results of the blends show a two-phase morphology with poor interaction between the POE phase and the matrix. The domain sizes of the blends are in the range between 50 and 3 μm. These evidences indicate the thermodynamic immiscibility in the blends of PS/POE, PMMA/POE and GFR-PC/POE. The mechanical properties of the blends of PMMA/POE are decreased while that of the blends of PS/POE and GFR-PC/POE are slightly improved. There is no evidence to show synergistic mechanical behaviors in these blends.

The mechanical behavior, morphology and crystallization from the blends of PP/POE were investigated. The mechanical behavior of the blends changes drastically compared to pure PP, and for POE concentration between 10 and 30 wt%, neck formation
is observed. For all investigated blends, demixing occurs and an island-like morphology of POE domains in a PP matrix is found. A fair interface adhesion between the phases is observed. The domain size of minor POE phase is in the range of a few micron. This blending system is an excellence candidate for further compatibilization. The glass transition temperature (Tg), melting temperature (Tm) and crystalinity (Xc) of the blends were studied by DSC. Using X-ray diffraction (XRD), the crystallization of the PP phase in the blends was investigated.

Polyolefin elastomer (POE) blends with HDPE is thermodynamically immiscible but mechanically compatible. Synergistic behavior of impact resistance is observed in the blends of HDPE/POE, which reminds us of the old idea that “like dissolves like” is also valid in this polyolefin blend. Morphological results are interpreted that this blend system is thermodynamically immiscible because a two-phase morphology is observed by SEM and AFM in the blends. A nanometer morphological structure with good interfacial adhesion between the two components is also found in the blends. Thermal behavior of the blends was investigated by DSC. The semi-crystalline features of the HDPE/POE blends was explored by XRD.
CHAPTER 4
FUNCTIONAL POE-BASED POLYPROPYLENE BLENDS

4.1 Introduction

Polypropylene (PP) is a semi-crystalline polymer with very interesting mechanical and thermal properties. Based on worldwide consumption, polypropylene (PP) is the second highest volume of thermoplastic. Also, PP is a low-cost material providing good mechanical properties for moderate temperature applications. PP is predominately used for applications requiring high modulus [82-83]. However, for application as engineering plastic its toughness and in particular its notch toughness is not sufficient. PP is basically characterized by a poor impact behavior at low temperature because of its relatively high glass transition temperature Tg. The incorporation of elastomer particles offers a classical solution of this problem [35-37, 84-85]. It is well known that as the temperature is reduced below 0°C, the mechanical properties of PP rapidly decline and a highly energy-absorbent crazing failure mode is exchanged for a brittle failure mode. In contrast, POE has a ductile to brittle transition temperature well below that of PP, resulting in dutile failure at most subambient service temperatures. Combining the low temperature ductility of POE with the high stiffness of PP has the potential to significantly expand the applications base of these two polyolefins. Attempts to enhance the low temperature performance of PP by introducing a dispersed phase that has a low glass-transition temperature (Tg) have been successful. Heterophasic PP blends with increased toughness were first developed by melt compounding PP with different
polyolefines, such as HDPE, ethylene-propylene copolymers (EPR), as well as ethylenediene terpolymers (EPDM) [84-98].

The morphologies and mechanical properties of the blends of syndiotactic polypropylene (sPP) with HDPE studied by Loos et al. indicated that the mechanical behavior of the blends changes drastically compared to pure HDPE and sPP. In the blends with HDPE concentrations between 10 and 70 wt%, no neck formation is observed. For all investigated blends, demixing occurs. It results for low HDPE concentrations in a island-like morphology of HDPE domains in a sPP matrix. A good interface adhesion between the phases was observed. Using in-situ Raman spectroscopy, the crystallization of the sPP phase in the blends was investigated. The start temperature of crystallization increases more than 10°C higher if HDPE is present, which reflects the favored nucleation of sPP in the blends of sPP/HDPE [82].

The morphologies of the blends of isotactic polypropylene (iPP) with HDPE examined by Montes et al. illustrated that TEM method works equally well for iPP/HDPE blends as for iPP/LLDPE blends. Phase ripening was observed, and it can be used to reveal phase separation when the driving force is low. The phase separation is found for a wide range of compositions for temperatures in the range between 170 and 200°C. However, the phase-separated region narrows slightly as the melt temperature is reduced within this range. It is easier to detect the larger HDPE crystals in a matrix of fine iPP crystals than vice versa. For this reason there is more uncertainty in the phase boundary on the HDPE rich side of the phase diagram. However, there is no doubt that in both the iPP/LLDPE and iPP/HDPE systems phase separation was seen over a very wide range of composition [99].
Morphology and elastomeric properties of iPP/ hydrogenated poly(styrene-co-butadiene) blends studied by Yang et al. exhibited that melt blending of iPP with hSBR yields a phase-separated material in which hSBP-rich domains with a uniform diameter of 20 nm are dispersed in an iPP-rich matrix. The blend shows good strain recovery after large deformation, suggesting a potential for a new class of TPE. The presence of rubbery (hSBR-rich) domains may provide a favourable contribution to the good strain recovery mechanism. The strain recovery mechanism may also originate from the characteristic morphology of iPP crystallites in the matrix. An optimum crystal size for good strain recovery was found [86].

Toughening of PP by addition of an elastomeric component consisting of ethylene-propylene (EPR) and/or ethylene-butene rubber (EBR) with different molecular weights studied by Yokoyama et al. showed that for a constant level of the total rubber content, the incorporation of EBR in the elastomeric component strongly enhanced the fracture toughness of PP blends. Improvement of the fracture resistance was also obtained by increasing the molecular weight of the elastomers. The higher efficiency of EBR with respect to EPR to toughen PP is due to a higher capability to induce extensive shear yielding within the matrix, in spite of a low tendency to cause cavitation. Such an effect is attributed to a different interaction exhibited by EBR and EPR with the PP matrix [84].

The blends of PP with EPDM studied by Wal et al. indicated that polypropylene can effectively be toughened by blending with EPDM. The brittle-ductile transition temperature (T_{bd}) decreases with 40% rubber to −50°C, which is comparable to PP with a decrease of 135°C. The T_{bd} on notched samples of the higher concentration blends are
much lower than the \( T_{bd} \) of PP unnotched. Thus the function of the rubber is much more than to reduce the notch sensitivity of the sample. The function of the rubber is thus next to relieve the volume strain and thereby the multi-axial stress, also to act as a stress concentrator which enhances the shear banding. The yield stress and the modulus decrease linearly with decreasing rubber content. The rubber content has a very strong effect on the deformation behavior of notched PP/EPDM blend [92-95].

Elastomer particle size and elastomer/matrix adhesion are two important factors determining the impact properties of elastomer-toughened plastics. These two factors are usually interrelated as a result of the complex dynamics of the blend preparation process. It is difficult to alter the dispersed phase size without simultaneously altering blend composition, the amount of interfacial chemical bonding, the molecular weights of blend components, and so forth. Elastomer-toughened polymers may be classified into two broad categories, brittle or pseudoductile, according to the chain flexibility and entanglement density of a polymer. Brittle polymers, such as polystyrene (PS) and poly(methy methacrylate) (PMMA), have stiff polymer chains and are toughened mainly by increased crazing. Pseudoductile polymers, such as polyamide (PA) and polypropylene (PP), have more flexible polymer chains and are toughened by mechanisms mainly involving delocalization of shear yielding in the matrix and elastomer particle internal cavitation. Strong interfacial adhesion is generally believed to be required for toughening a brittle polymer, while the role of interfacial chemical bonding in toughening a pseudoductile matrix polymer is not as clear [17-19].

The chemical nature of PP is non-polar materials with a very good chemical and solvent resistance. These are attractive features for most applications. But it has drawback
that PP has poor adhesion to toughening agent, polar polymers and particulate fillers. This has prompted the development of chemically modified PPs that were grafted with maleic anhydride (MA), acrylic acid (AA) or other polar species [7-13, 38-39, 172]. Variable quantities of functionalized peroxides bearing carboxylic acid groups reacted with polypropylene in a twin-screw extruder studied by Assoun et al. indicated that PP can be functionalized to contain grafted carboxylic acid group via a reactive extrusion process using functional peroxides. Moreover, the specific grafting process can be affected by molecular structure of the peroxides. By affecting the reactive of the radicals generated form the peroxides, the grafting efficiency of the carboxylic acid group onto the PP backbone and the polymer degradation may be controlled [25].

PP functionalized by maleic anhydride (MA) investigated by Nachtigall et al. illustrated that in the performed experimental design, the main effects for the analyzed parameters are [MA], [DCP], reaction time, and temperature. The degree of functionalization and the molecular weights depend on [MA], [DCP], and temperature. Reaction times have no significant effect. Interaction effects between [MA] and temperature play an important role on both the degrees of functionalization and molecular weights. At 180°C, higher degrees of functionalization could be obtained with an [MA] between 1.4 and 2.6 wt%. Functionalization also increases with [DCP]. Increasing the degree of functionalization was directly related to the decrease in molecular weight, suggesting that maleic anhydride incorporation occurred mainly at the chain ends, after or before reactions of chain scission [25-26].

Liu et al. observed that PP containing a basic functional group, oxazoline, had been successfully prepared by the melt grafting of 2-iso-propenyl-2-oxazoline onto PP.
The rubber particle size of PP/NBR blends can be effectively controlled by carefully varying either the processing conditions or the amount of interfacial reaction or a combination of both. Blends with the same rubber particle size can be obtained by using different combinations of processing conditions and the amount of interfacial reaction such that the role of interfacial chemical bonding on toughening can be differentiated from that of rubber particle size. Without any interfacial chemical bonding, the impact energies of PP/NBR blends were about the same as pure PP. Interfacial chemical bonding is required for ductile failure to occur in toughened PP. The improvement in impact energies of PP/NBR blends above the brittle-tough transitions was up to 13.5-fold for notched samples. The impact improvement is consistent with a mechanism, which involves cavitation within the rubber particles followed by plastic flow in the ligaments of the matrix phase. More generally, interfacial chemical bonding plays an important role in toughening pseudoductile polymers just as it does in brittle polymers [17-18].

Melt grafting of glycidyl methacrylate (GMA) onto polypropylene (PP) and reactive compatibilization of rubber toughened PP studied by Chen et al. illustrated that the GMA can be melt grafted onto polypropylene with via a free radical initiation. But it is accompanied by β-scission of the PP molecules. The extent of GMA grafting (DGg) and the molecular weight of the functionalized PP copolymers can be controlled by carefully manipulating various reaction factors, such as monomer concentration, initiator concentration, reaction temperature as well as the molecular weight of the starting PP homopolymer. The addition of a second monomer to the reaction environment, namely styrene, permits one to increase the GMA grafting levels and to reduce the extent β-
scission. The GMA grafted PP copolymer can effectively compatibilize the blends of PP homopolymer with acid-functionalized NBR rubber. Up to an eight-fold improvement in the impact energy of the PP/NBR blend has been obtained over those blends without the grafted copolymer. The compatibilizing capacity of the reactive copolymer is not exclusively dependent on the total reactive group concentration in the blend. The properties of the reactive copolymer are not found to have a significant influence on the compatibilizing capacity. A large amount of moderately functionalized copolymer offers better compatibilization performance than a small amount of high functionalized copolymer. Furthermore, reducing the molecular weight of the functionalized copolymer lowers its compatibilizing efficiency. The effect of adding styrene as a comonomer in the grafting process is to reduce the effectiveness of the GMA modified copolymers as blend compatibilizers [21].

Sun et al. observed that the performance of a co-rotating twin screw extruder as a chemical reactor for the free radical grafting of GMA onto melten PP is similar to that in a batch mixer. The GMA grafting in the presence or absence of styrene proceeds rapidly as it has gone to complete halfway downstream of the extruder. Additionally, the presence of styrene, as a second monomer, increases the GMA grafting yield greatly with a significant reduction in PP chain degradation. The GMA grafting yield increases with increasing concentration of the peroxide, 1,3-bis (tert-butyl-peroxy-isopropyl) benzene. An increase in screw speed or feed rate causes a decrease in GMA grafting yield due to a decrease in residence time distribution. At a particular specific throughput (the ratio of throughput to screw speed), an increase in throughput with a increase in screw speed
brings about a decrease in GMA grafting yield. This is again due to a corresponding decrease in residence time distribution [20].

Up to date, the blending system of PP with POE was rarely reported [47]. As mentioned in chapter three, this blending system is thermodynamically immiscible. It exhibits the phase-separated phenomenon in the physical blends. Under the stress, the sample is failed due to the poor adhesion between the PP matrix and the POE toughening phase. Glycidyl methacrylate (GMA), which had epoxy functional groups, was introduced into the interface via reactive extrusion. Thus the impact property of the blends of PP with modified POE could be improved because the interfacial reaction was enhanced. The overall objectives of this chapter are as follows:

1) A family of POE based PP alloys functionalized by peroxide initiated, free radical melt grafting of glycidyl methacrylate (GMA) onto POE and PP via a reactive extrusion process with a wide range of tailored and reactive group contents was prepared.

2) The effect of processing parameters and the role of interfacial bonding on the impact property of the alloys of PP toughened by functional POE as well as on the morphology of the alloys were investigated.

3) The effects of processing parameters on degree of grafting of GMA onto the PP alloys were studied by $^1$H-NMR and FTIR. The effects on the mechanical properties of the alloys were also examined. And the domain size of POE in the alloys was explored by statistical method.
4.2 Experimental

4.2.1 Materials

The polymers used in these studies are commercial grades. The used POE-1 and POE-2, which had melt-flow index of 0.5 and 1.0 g/10min respectively, were generously provided by the Dupont Dow Elastomers in pellet form. They are ethylene-octene copolymers. The used polypropylene (PP), REXENE 31S4A, was a homopolymer resin in pellet form. It had a melt-flow index of 4.0 g/min and was kindly supplied through Huntsman Corporation. They are the same as ones listed in table 3.1 and 3.2.

All of the peroxides and monomers used in these studies were regent grade chemicals. GMA monomers, molecular weight (MW) of 142, which were 97wt% solution and were inhibited with 50 ppm p-methoxy phenol, were purchased from Aldrich Chemical Company. Styrene monomers, MW of 104, which were 99wt% solution and were inhibited with 15 ppm 4-tert-butylcatechol, were also the product of Aldrich Chemical Company. Peroxide initiators, tert-butyl hydroperoxide and dicumyl peroxide, which have half-life of 1 hour at 140°C and 137°C, respectively, were used as received from Witco Corporation. 2, 5-dimethyl-2, 5-di (t-butyldperoxy) hexane, which has a half-life of 1 hour at 140°C, was used as received from Elf Atochem North America, Inc. The chemical used in these studies is listed in table 4.1.

4.2.2 Methods

4.2.2.1 Free radical melt grafting
Prior to reactive extrusion, all of polymer resins used in these studies were dried in a vacuum to remove sorbed water. The drying temperature and time for POE and PP are listed in table 3.3. In order to remove the inhibitors in purchased monomers, the monomers were purified through chromatographic columns containing activated alumina before using. The melt grafting of the GMA monomer onto the POE

Table 4.1. Chemicals used in these studies

<table>
<thead>
<tr>
<th>Chemical</th>
<th>MW</th>
<th>1 hr $T_{1/2}$</th>
<th>Description</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycidyl methacrylate (GMA)</td>
<td>142</td>
<td>97% solution, monomer</td>
<td>Aldrich Chemical</td>
<td></td>
</tr>
<tr>
<td>Styrene</td>
<td>104</td>
<td>99% solution</td>
<td>Aldrich Chemical</td>
<td></td>
</tr>
<tr>
<td>t-Butyl hydroperoxide</td>
<td>140</td>
<td>70% liquid, initiator</td>
<td>Witco Corporation</td>
<td></td>
</tr>
<tr>
<td>Dicumyl peroxyde (DCP)</td>
<td>137</td>
<td>Crystalline solid</td>
<td>Witco Corporation</td>
<td></td>
</tr>
<tr>
<td>2, 5-Dimethyl-2,5-di-(t-butylperoxy)</td>
<td>140</td>
<td>91-93% liquid, initiator</td>
<td>Elf Atochem North America,</td>
<td></td>
</tr>
</tbody>
</table>

was carried out in a 34 - mm co-rotating twin screw reactive extruder, APV Chemical Machinery Inc., which length-to-diameter ratio L/D is 34. The temperature of the extruder was regulated by electrical resistance and water circulation in barrels. The dried PP and POE were mixed in a mixer about 10 minutes with desired ratios before reactive
extrusion. The amount of peroxide was measured by an analytical balance and put into the purified monomers. The peroxide and purified monomers were mixed through a magnetic stirring apparatus with a stirrer bar about 2 minutes. The pre-mixed PP and POE as well as the mixture of peroxide and monomers were introduced into the reactive twin screw extruder from the hopper of the extruder through a screw feeder and a gear pump, respectively. The pellets of PP and POE were moistened with a chosen amount of a liquid mixture of monomers and peroxide when introduced from the hopper. The free radical melt grafting processing was performed at temperature in range between 210 and 270 °C, with screw speed in a range between 100 and 300 rpm, and feeding rate in range between 50 and 150 g/min. For all experimental runs, devolatilization was carried out by a vacuum pump. This pump was placed near the die and it created a pressure of about 25 mmHg. The extruder was always starved to feed. Thus, the screw speed (N), feed rate (Q), and specific throughput (Q/N) could be varied independently.

4.2.2.2 High-temperature NMR and FTIR measurements

The reactive extrudates were pelletized. The pellets of the crude graft copolymer were dissolved in refluxing toluene at a concentration of ca 4% (wt/vol). The hot solution was precipitated into ten volumes of acetone. The unreacted monomers, GMA homopolymer, and GMA-styrene copolymer remained soluble in acetone and were separated out from the grafted POE. The precipitated graft modified PP and POE was filtered, washed and then vacuum dried at 75°C for 48 hours. Fourier Transform Infrared (FTIR) measurements showed that DG level remained unaltered upon further rounds of purification. Therefore, one purification step was sufficient for removal of all the residual impurities.
The degree of grafting (DG) was defined as the weight percentage of the reactive component bound onto the graft copolymer as shown in (4.1).

\[
DG(\text{wt}%) = \frac{\text{Mass of monomer grafted onto polymer}}{\text{Mass of polymer}} \times 100
\] (4.1)

The purified copolymers were compressed into thin films, 0.1-0.2 mm in thickness, at 210°C under a pressure of 2000psi for 1 min. FTIR spectra of these thin films were recorded on a Nicolet MR-740 FTIR spectrometer at room temperature using 128 scans with a resolution of 4cm\(^{-1}\). Solution suitable for NMR measurements were prepared by dissolving 30-40 mg of the purified grafted copolymers in 0.75 ml of toluene-d\(_8\) with heating. \(^1\)H-Nuclear Magnetic Resonance (NMR) spectra of the purified grafted polymers were recorded at 104°C on an Inova 500 NMR spectrometer (500 MHZ), which was equipped with a high temperatre probe and a heating device.

4.2.2.3 Rheological measurements

All of polymers used in this rheological study was dried in a vacuum oven for overnight at 50°C before use. Rheological measurements were made by melt compounding a variety of dried polymers, purified monomers and initiators in a Brabender torque rheometer, Roller Type V, with a 50cm\(^3\) mixing head and standard rotors, which was driven by a Plasti-Corder PL-2000, C.W. Brabender Instruments, Inc. The rate of rotation of the blades was fixed at 30 rpm, the total residence time in the cell was about 20 minutes, and the temperatures were used at 220°C, 240°C and 270°C, respectively. 30 grams of sample were exactly employed in all runs. The initiators were introduced into the melt mixture when after an equilibrium torque was reached. The
Brabender torque of the melt mixture was recorded continuously as a function of mixing time. The basic procedure used in this rheological study is showed as follows:

1) Heat the cell of the rheometer to the desired temperature;

2) Put 30 grams of sample into the heated cell;

3) Run the rheological measurements;

4) Introduce the initiators into the melt mixture when the equilibrium torque reached;

5) Monitor the whole procedure;

6) Clean the cell for next the run.

4.2.2.4 Morphology characterization

In order to characterize the particle size of the disperse phase, its distribution and the extent of interfacial bonding in the blend, cryogenically fractured surfaces of the samples were observed by using a scanning electron microscopy (SEM), JEOL 6400, operated at 5 kV. The test specimens for SEM were first cryo-fractured from liquid nitrogen. The resulting fracture surface was then sputter coated with a thin layer of gold-palladium alloy to avoid charging under the electron beam prior to SEM examinations. The detail of SEM observation has already been described in 3.2.2. The particle size of dispersed phase was characterized by two quantities: number average diameter ($D_n$) and weight average diameter ($D_w$). The apparent diameter of the 2D image was measured and
individually outlining the particles to calculate their dimensions. The $D_n$ and $D_w$ were calculated from the following relationships:

$$D_n = \frac{\sum n_d}{\sum n} \quad (4.2)$$

$$D_w = \frac{\sum n_d^2}{\sum n_d} \quad (4.3)$$

Where $n_i$ is the number of particles with diameter $D_i$.

4.2.2.5 DSC and DMS measurements

The thermal behavior of the blends was analyzed by means of a differential scanning calorimeter (DSC), Seiko SII DSC 220, Seiko Co. Samples weighing approximately 10-15 mg were used. The samples encapsulated in standard aluminium pans were heated at a scanning rate of 10°C/min in a dry nitrogen atmosphere. Also they were cooled through liquid nitrogen. Thermal data were determined during the last heat scan. Analysis of the curves was performed using the equipment analysis programs. The glass transition temperature was defined as the midpoint of the change in the heat capacity for the transition. The melting temperature and the enthalpy of fusion were obtained from the maximum and the area of the endothermic peak, respectively. The crystalinity, $X_c$, was calculated by:

$$X_c = \frac{\Delta H_{\text{melt}}}{f \Delta H_{\text{melt}}} \quad (4.4)$$
Where $\Delta H^*$ is the enthalpy of fusion per gram of iPP or that in the blend, and $\Delta H^{0}_{iPP}$ is the heat of fusion per gram of 100% crystalline iPP (209J/g). The detail of DSC measurements have been described in 3.2.2.

In order to decide the glass transition temperatures (Tg) of amorphous PP and POE in the blends, dynamic mechanical spectroscopy (DMS) was employed. The dynamic mechanical behaviour was evaluated using a Seiko SII DMS 110, Seiko Co. The samples for DMS were molded by compression molding. The processing parameters were the same with corresponding ones listed in 3.2.2. The samples were rectangular strips measuring 4.5 x 1.2 x 0.3 cm$^3$. The frequencies were selected at 1Hz. All the scans were carried out from −130°C to 150°C at the heating rate of 2°C/min in a flexural mode. Temperature dependence of the storage modulus (E’), loss modulus (E’’) and dynamic loss (tanδ) were obtained. The data was analyzed by the equipment analysis programs.

4.2.2.6 Mechanical testing

Prior to every processing step and testing, in order to ensure removal of sorbed water, all samples used in these studies were dried under vacuum overnight at temperature of 56°C in order to ensure removal of sorbed water. The extrudates were pelletized and the resulting pellets of the blends were molded through compression molding for the test of mechanical properties. Test bars were prepared using a Carver compression molding machine, Fred S. Carver Inc., at temperature of 210°C and pressure 2000psi. The detail of the procedure and parameter of compression molding for Izod impact, tensile and flexural test bars used in this study are the same as the corresponding one listed in 3.2.2.
For the Izod impact test, the samples, rectangular test bars with 32 x 12.7 x 6.35 mm$^3$ were notched using a notching cutter, Testing Machines Inc. The notched Izod impact measurements were made using a TMI pendulum type impact test machine in accordance with ASTM D256 at ambient temperature and liquid nitrogen temperature, respectively. Tensile testing of dry dog-bone-shaped test bars, type V test specimens having 7.26mm gauge length, 3.18mm width and 3.18mm thickness, was done using an INSTRON 1125 tensile testing machine at cross-head speed in range between 50 mm/min and 2 mm/min for modulus and yield strength measurements and elongation at break in reference to ASTM D638 under ambient conditions. Four-point flexural test of rectangular test bars with 64 x 12.7 x 3.18 mm$^3$, was determined utilizing the same test instrument as was the tensile test for flexural strength and modulus of elasticity at 2mm/min strain rate under room temperature according to ASTM D790.

4.3 Results and Discussion

4.3.1 Melt Grafting of Glycidyl Methacrylate (GMA) onto POE

The proposed mechanism and chemical reactions of melt grafting of glycidyl methacrylate (GMA) onto PP and POE are schemed in Figure 4.1 and in equations (1) – (22), respectively. They describe some of the main reactions taking place during the melt grafting of a GMA monomer onto PP or POE in the presence of a free-radical initiator, such as peroxide.

Initiator decomposition:

\[ I \rightarrow R^* \]  \hspace{1cm} (1)
Attacking of monomer and its homopolymerization:

R* + mM → Mm* (m>1)  \hspace{1cm} (2)

Hydrogen abstraction:

\[-(CH_2CH_2)_i-CH_2CH(CH_2)_jCH_3- + R* → \]
\[-(CH_2CH_2)_i -CH_2C*(CH_2)_jCH_3- (3PR*) + RH \hspace{1cm} (3)\]

\[-(CH_2CH_2)_i -CH_2CH(CH_2)_jCH_3- + R* → \]
\[-(CH_2CH_2)_i -C*HCH(CH_2)_jCH_3- (2PR*) + RH \hspace{1cm} (4)\]

\[-(CH_2CH_2)_i -CH_2CH(CH_2)_jCH_3- + R* → \]
\[-(CH_2C*H)_i -CH_2CH(CH_2)_jCH_3- (PR*) + RH \hspace{1cm} (5)\]

β-Scission:

\[-(CH_2CH_2)_i -CH_2C*(CH_2)_jCH_3- CH_2CH(CH_2)_jCH_3- \rightarrow \]
\[-(CH_2CH_2)_i -CH_2C*H(CH_2)_jCH_3 (2PR*) + CH_2=C(CH_2)_jCH_3- \hspace{1cm} (6)\]

Cross-linking:

\[PR* + PR* → EO-EO \hspace{1cm} (7)\]

Monomer grafting:

\[3PR* (2PR* or PR*) + nM → PRMn* (n > 1) \hspace{1cm} (8)\]

Chain transfer:

\[-(CH_2CH_2)_i -CH_2CH(CH_2)_jCH_3- + PR* → 3PR* (2PR* or PR*) + PR \hspace{1cm} (9)\]

\[-(CH_2CH_2)_i -CH_2CH(CH_2)_jCH_3- + PRMn* → \]
\[3PR* (2PR* or PR*) + PRMn \hspace{1cm} (10)\]

\[-(CH_2CH_2)_i -CH_2CH(CH_2)_jCH_3- + Mm* → 3PR* (2PR* or PR*) + Mm \hspace{1cm} (11)\]

Termination by combination:

\[Mn* + R* → Mn-R \hspace{1cm} (12)\]
\[ 3^{\text{PR}} \left( 2^{\text{PR}} \text{ or } \text{PR}^* \right) + \text{R}^* \rightarrow \text{PR-R} \quad (13) \]

\[ 2^{3^{\text{PR}}} \left( 2^{\text{PR}} \text{ or } \text{PR}^* \right) \rightarrow \text{PR-PR} \quad (14) \]

\[ 2\text{PRMn}^* \rightarrow \text{PRMn-MnPR} \quad (15) \]

\[ 3^{\text{PR}} \left( 2^{\text{PR}} \text{ or } \text{PR}^* \right) + \text{PRMn}^* \rightarrow \text{PRMn-PR} \quad (16) \]

\[ \text{PRMn}^* + \text{Mm}^* \rightarrow \text{PRMn-Mm} \quad (17) \]

\[ 3^{\text{PR}} \left( 2^{\text{PR}} \text{ or } \text{PR}^* \right) + \text{Mm}^* \rightarrow \text{PR-Mm} \quad (18) \]

\[ \text{PRMn}^* + \text{R}^* \rightarrow \text{PRMn-R} \quad (19) \]

Termination via disproportionation:

\[ 3^{\text{PR}} \left( 2^{\text{PR}} \text{ or } \text{PR}^* \right) + \text{PRMn}^* \rightarrow \text{PRMn + PR} \quad (20) \]

\[ 3^{\text{PR}} \left( 2^{\text{PR}} \text{ or } \text{PR}^* \right) + \text{Mm}^* \rightarrow \text{PR + Mm} \quad (21) \]

\[ 2 \cdot 3^{\text{PR}} \left( 2^{\text{PR}} \text{ or } \text{PR}^* \right) \rightarrow 2\text{PR} \quad (22) \]

Here, I and R* represent initiators and free radicals decomposed from initiators. \(3^{\text{PR}}\), \(2^{\text{PR}}\) and \(\text{PR}^*\) represent the tertiary, secondary and primary radicals of ethylene segments from hydrogen abstraction, respectively. \(\text{Mm}^*\) represents the radicals from the attacking of the monomer by primary radical and homopolymerization of the monomer, \(\text{PRMn}^*\) illustrates the macro-radical after monomer grafting, and \(\text{Mm}, \text{PR}, \text{PRMn}, \text{PR-PR}, \text{PRMn-PR}, \text{and PR-Mn-MnPR}\) show the corresponding dead polymers (linear, branched, or cross-linked). \(M\) represents GMA. When \(i\) and \(j\) are equal to 0 and 1, the macromolecule is polypropylene while when \(i\) and \(j\) are equal to 1 and 5, it is POE. Reaction (6) would obviously result in the degradation of PP or POE while reactions (7) and (14) – (16) would cause the crosslinking of PP or POE. Grafting of GMA onto PP or POE may be realized by reactions (8) and (15) – (19).
The purified grafted blend of PP/POE is characterized using FTIR and $^1$H-NMR spectroscopy. The characteristic signals in the FTIR spectrum presented in Figure 4.2 are found at $\nu = 1730$ cm$^{-1}$ for the C=O stretching vibration of GMA and $\nu = 1380$ cm$^{-1}$ for the C-H bending vibration of POE. For the C=O stretching vibration and the C-H bending vibration the integration limits are 1690-1760 cm$^{-1}$ and 134-1470 cm$^{-1}$, respectively. The signals are well separated from other bands. The FTIR spectra represent a strong band at 1380 cm$^{-1}$, which is characteristics of POE and a peak at 1730 cm$^{-1}$, which is the characteristic of GMA structure. Comparing to POE, the physical blend and reactive blend, a new peak at 1730 cm$^{-1}$ is observed in the reactive blend relative to the POE, physical blend. It is confirmed that the grafting process is successful. High temperature $^1$H-NMR spectroscopy of GMA grafted POE represented in Figure 4.3 is confirmed the success in melt grafting of GMA onto the POE again. High temperature $^1$H-NMR is also employed as an absolute method in order to determine the grafting degree (DG) of GMA onto the POE beside the relative FTIR measurement. The degree of grafting (DG) of GMA onto the blend of PP/POE is determined by quantitative high temperature $^1$H-NMR analysis as an absolute method. It is observed that the peaks between 4.00 and 4.35 ppm assign the two hydrogen atoms that are adjacent to the ester oxygen atom while the peaks between 0.8 and 1.8 ppm assign nineteen hydrogen of POE. The constitution of POE-g-GMA is shown in Figure 4.4.

The DG is evaluated from the ratio of the integral of the relative peak areas located between 4.00 and 4.35 (A$_{4.00-4.35}$) to the integral of the relative peak areas occurred between 0.8 and 1.8 ppm (A$_{0.80-1.80}$). It is also found that E/GMA copolymers consisting of the GMA functional units are responsible for the similar characteristic
signals in the FTIR spectra and $^1$H-NMR spectrum to the blend of PP/POE grafted with GMA. While GMA is not grafted but co-polymerized, it may be assumed that the related FTIR spectra and $^1$H-NMR spectrum show the same properties. Therefore, they can be employed as external standard materials in order to calibrate the DG. The grafted material itself is also used as standard material. With comparing the DG of GMA onto POE and the ratio intensity of absorption at 1730 cm$^{-1}$ to the intensity of absorption at 1380 cm$^{-1}$, the calibration curve of FTIR measurements for grafting degree (GD) of GMA onto POE is plotted in Figure 4.5. This calibration curve may be applied to other systems, such as PP-g-GMA, HDPE-g-GMA, LLHDPE-g-GMA, PE-g-GMA and so on due to their similar molecular structures.

The effect of POE on DG of GMA onto POE in the blend of PP/POE shown in Figure 4.6 indicates that the highest DG of GMA is correspond to 20 weight percentage of POE2 while DG of GMA varies as the weight concentration of POE1. In the range between 10 and 20 weight percentage of POE, DG of GMA of the reactive blend of PP/POE2 is higher than that of the reactive blend of PP/POE1. At 30 weight percentage of POE1 the DG of GMA of reactive the blend has a great jump while that of the reactive blend of POE2 has a depression. The effect of GMA on DG of GMA in the blend of PP/POE (70/30) illustrated in Figure 4.7 present that the DG of GMA varies greatly as the weight concentration of GMA. The GMA monomer has a significant effect on the melt grafting GMA onto POE. Also this results suggest that the amount of POE and GMA monomer may be main factors in the reactive extrusion.

The effect of peroxide and concentration of peroxide on the DG of GMA in the blend of PP/POE are shown in Figure 4.8 and 4.9, respectively. The results represent that
the DG of GMA in the blend of PP/POE varies with different peroxide. The effectiveness of peroxide used in this study is shown in regular order as following:

2,5-dimethyl-2,5-di-(t-butylperoxy) hexane > t-butyl hydroperoxide > dicumyl peroxide.

Addition of styrene monomer also enhances the DG of GMA in the blend of PP/POE with 0.3 molar ration of styrene monomer to GMA monomer. In agreement with the finding reported in previous work concerning the same free radical grafting carried out for PP, the presence of styrene monomer enhances the DG of GMA in the blend of PP/POE with 0.3 molar ratio of styrene monomer to GMA monomer [17-24]. The processing temperature effect on DG of GMA in the blend of PP/POE (70/30) is illustrated in Figure 4.10. It is interesting to note that the highest, medium and lowest level of DG of GMA in the blend are 210°C, 240°C and 270°C, respectively. The significant change in the DG of GMA suggests the processing temperature may be another main factor in the reactive compounding. The present study has the similar results as reported by Liu, Sun, Chen and Roux [17-22].

![Figure 4.1 Proposed scheme of melt grafting GMA onto POE](image-url)
Figure 4.2 FTIR spectrum of: (a) PP, POE-1 and GMA grafted POE-1; (b) PP, POE-2 and GMA grafted POE-2
Figure 4.3 $^1$H-NMR spectrum of GMA-grafted POE

Figure 4.4 Constitution of POE-g-GMA
Figure 4.5 Calibration curve of FTIR measurements for GD of GMA onto POE

Figure 4.6 Effect of POE on the DG of GMA onto POE in the blend of PP/POE
Figure 4.7 Effect of GMA on the DG of GMA onto POE in the blend of PP/POE (70/30)

Figure 4.8 Effect of peroxide on DG of GMA onto POE in the blend of PP/POE
Figure 4.9 Effect of concentration of peroxide on DG of GMA onto POE in the blend of PP/POE (70/30)

Figure 4.10 Effect of processing temperature on DG of GMA onto POE in the blend of PP/POE (70/30)
4.3.2 Melt Rheology of the Functional Blend of PP/POE

Effect of POE on the evolution of the torque as a function of mixing time for the blend of PP/POE is depicted in Figure 4.11. For POE, PP and their blends, they have a similar rheological behavior which first the torque decreases as the polymer melts and then remains almost constant for the rest of the mixing time, steady state, in which the torque is very reproducible. In the GMA and peroxide presence, the steady-state torque rises, a positive deviation that is relative to that of the physical blend, reflecting the melt grafting reaction of GMA on the interface between PP and POE. It is confirmed that the melt grafting of GMA onto the blend of PP/POE is successful. Effect of GMA on the rheological property of the blend of PP/POE (70/30) shown in Figure 4.12 indicates that there exists a positive deviation of torque in steady state relative to the torque curve of the physical blend in all compounding investigated. The positive deviations vary with the weight concentration of GMA. The blend illustrates little decline in steady state torque with increasing GMA concentration. It is suggested that there is a well-known $\beta$-scission along with the melt grafting.

Effect of peroxide and concentration of peroxide on the rheological behavior of the blend of PP/POE is presented in Figure 4.13 and 4.14, respectively. In the blend, the steady state torque is depressed a little, suggesting the degradation of the PP and POE. The decline goes slowly up with increasing the concentration of peroxide. According to the depression on the steady state torque, the effect of peroxide used in this study on degradation in the blends may be in regular order as following:

t-butyl hydroperoxide $>$ 2,5-dimethyl-2,5-di-(t-butylperoxy) hexane $>$ dicumyl peroxide .
It is observed that addition of styrene monomer reduces the degradation of PP and POE during the reactive extrusion. Effect of temperature on the rheological property of the blend represented in Figure 4.15 indicates that the steady state torque at 240°C has positive deviation while those at 210°C and 270°C have negative deviation, suggesting degradation and no interfacial reaction in the blends, respectively. This is in accord with the results mentioned in effect of temperature on DG of GMA. The results point out that during melt grafting of GMA onto PP and POE, it is difficult to avoid the degradation. However, the point is how to balance the two sides. In other words, we make a sacrifice on degradation in order to obtain more grafting onto PP and POE.

Figure 4.11 Effect of POE on the evolution of the torque as a function of mixing time for the blend of PP/POE at 240°C and 30 rev/min
Figure 4.12 Effect of GMA on the evolution of the torque as a function of mixing time for the blend of PP/POE at 240°C and 30 rev/min

Figure 4.13 Effect of peroxide on the evolution of the torque as a function of mixing time for the blend of PP/POE at 240°C and 30 rev/min
Figure 4.14 Effect of concentration of peroxide on the evolution of the torque as a function of mixing time for the blend of PP/POE at 240°C and 30 rev/min

Figure 4.15 Effect of temperature on the evolution of the torque as a function of mixing time for the blend of PP/POE at 30 rev/min
4.3.3 Dynamic Mechanical Spectroscopy (DMS) and DSC

The thermal behavior of the blend of PP/POE measured by DMS and DSC is shown in Figure 4.16 and 4.17. It is believed that the slopes of storage modulus \((E')\) and peaks of loss modulus \((E'')\) located at around 22.1°C are related to the glass transition of PP matrix in the blend. The other ones correspond to about -38.2 °C or -17.4 °C are determined to be related to the glass transition of POE phase in the blend. The glass transition temperatures \((T_g)\) for the blend are summarized in the table 4.2. It is found that in both cases of physical blending and reactive blending, the two glass transition temperatures \((T_g)\) correlated to PP and POE are shifted to lower temperature, relative to the neat PP and POE. However, through comparing with two blending systems, the Tg of PP matrix in the reactive blending is shifted lower than that in the physical blending. It is suggested that there exist separated phases of PP matrix and POE minor phase in the blend while the grafted PP and POE show the effect of compatibilization.

The resulting DSC thermograms for the blend of PP/POE in heating mode are shown in Figure 4.18 and table 4.3 gives a summary of the corresponding values of melting temperature \((T_m)\), enthalpy of melting \((\Delta H_m)\) and the degree of crystallinity \((X_c)\). The reactive blend has the similar thermal behavior to the physical blend which has one glass transition, two endotherms correlated to POE minor phase and PP matrix. The two endotherms indicate a phase separation is formed in the blend. In addition, there is a difficulty with respect to the calculation of the crystallinity from the melting endotherm area of the POE in the blend due to the very broad melting range. According to the peak
area determination method, the drawing of a baseline to integrate the endotherm is often ambiguous and may introduce considerable error in the crystallinity values. It is observed that the reactive blend has lower melting temperature (Tm) of PP matrix than that of the corresponding one of physical blend. And the Xc of the PP matrix varies inversely as concentration of GMA.

Table 4.2. Glass transition temperatures (Tg) by DMS for the blend of PP/POE

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg of POE phase (°C)</th>
<th>Tg of PP matrix (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td></td>
<td>22.1</td>
</tr>
<tr>
<td>POE-1</td>
<td>-38.2</td>
<td></td>
</tr>
<tr>
<td>POE-2</td>
<td>-17.4</td>
<td></td>
</tr>
<tr>
<td>PP/POE-1 (80/20)</td>
<td>-47.3</td>
<td>21.2</td>
</tr>
<tr>
<td>PP/POE-1 (80/20) + 5%</td>
<td>-46.6</td>
<td>19.2</td>
</tr>
<tr>
<td>GMA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP/POE-1 (70/30)</td>
<td>-39.6</td>
<td>22.1</td>
</tr>
<tr>
<td>PP/POE-1 (70/30) + 5%</td>
<td>-45.3</td>
<td>20.6</td>
</tr>
<tr>
<td>GMA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP/POE-1 (70/30) + 9%</td>
<td>-42.0</td>
<td>19.1</td>
</tr>
<tr>
<td>GMA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP/POE-2 (80/20)</td>
<td>-33.6</td>
<td>21.7</td>
</tr>
<tr>
<td>PP/POE-2 (70/30)</td>
<td>-33.6</td>
<td>21.7</td>
</tr>
<tr>
<td>PP/POE-2 (70/30) + 5%</td>
<td>-35.4</td>
<td>20.9</td>
</tr>
</tbody>
</table>
Table 4.3. Thermal characterization by DSC for the blend of PP/POE

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tm (°C)</th>
<th>ΔHm (J/g)</th>
<th>Xc</th>
</tr>
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<td>PP</td>
<td>168.5</td>
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<tr>
<td>PP/POE-1 (90/10) + 5% GMA</td>
<td>166.8</td>
<td>73.2</td>
<td>0.389</td>
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<tr>
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<td>84.8</td>
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<td>62.9</td>
<td>0.430</td>
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<td>58.7</td>
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</tr>
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<td>166.2</td>
<td>63.8</td>
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<td>166.1</td>
<td>60.7</td>
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Figure 4.16 Dynamic mechanical spectroscopy behaviors of the physical blend of PP/POE as a function of temperature at 1 Hz: a) storage modulus; b) loss modulus
Figure 4.17 Dynamic mechanical spectroscopy behaviors of the reactive blend of PP/POE as a function of temperature at 1 Hz: a) storage modulus; b) loss modulus
Figure 4.18 The heating traces measured by DSC for the blend of: a) PP/POE-1; b) PP/POE-2
4.3.4 Morphology

Figure 4.19, 4.20, 4.21 and 4.22 represent scanning electron micrographs of fractured surfaces for the physical blend of PP/POE and reactive blend of PP/POE, respectively. The morphology of reactive blend of PP/POE illustrated in Figure 4.20 and 4.22, compared to that of the mechanical blend shown in Figure 4.19 and 4.22, provides further evidence in favor of the presence of POE-g-GMA copolymer in the materials. It is observed that the physical blend of PP/POE-2 has a distinct two-phase morphology comprising agglomerated and oval-like domains of POE-2, with little adhesion to the PP matrix. The mechanical blend of PP/POE-1 possesses a two-phase morphology that consists of discrete, non-uniformly distributed spherical particles of POE-1, without effectively binding to the matrix. By comparison, a more homogeneous dispersed and smaller spherical-shape domain of POE, as well as less agglomerated phase of POE and strong interfacial adhesion between the phase of POE and the PP matrix are found while being two phases in the reactive blending system. It is suggested that there must exist grafted copolymers acting as effective surfactant, compatibilizers, for the two phases. This is consistent with the results from FTIR, DMS and DSC. The number-average domain size (Dn) and weight-average domain size (Dw) as function of the concentration of GMA is illustrated in Figure 4.23. It is observed that there is an impressive drop for the domain size of POE when reaching up to the Critical Micelle Concentration (CMC), about 0.5 wt% DG of GMA in the reactive blending system. After CMC, the domain sizes of POE maintain constant in the system. It further accounts for the existence of POE-g-GMA as an effective ‘surfactant’.
Figure 4.19 Scanning electron micrographs of fracture surfaces of the physical blend of PP/POE-2 (70/30): a) X200; b) X5000
Figure 4.20 Scanning electron micrographs of fracture surfaces of the reactive blend of PP/POE-2 (70/30): a) X200; b) X5000
Figure 4.21 Scanning electron micrographs of fracture surfaces of the physical blend of PP/POE-1 (70/30): a) X200; b) X2000
Figure 4.22 Scanning electron micrographs of fracture surfaces of the reactive blend of PP/POE-1 (70/30): a) X200; b) X2000
Figure 4.23 Effect of DG of GMA on the domain size of POE in the blend of PP/POE

4.3.5 Tensile Properties

The effect of melt grafting in the PP/POE system manifests itself in a decrease in the yield tensile strength ($\sigma_y$), modulus of elasticity (E), flexural strength (W) and tangent modulus of elasticity ($E_{\text{flex}}$) as illustrated in Figure 4.24 and 4.25. As expected, with introduction of melt grafting, yield tensile strength ($\sigma_y$), modulus of elasticity (E), flexural strength (W) and tangent modulus of elasticity ($E_{\text{flex}}$) of reactive blends are
decreased by 7.5%-20.0%, 4.2% - 39.0%, 4.6%-7.6% and 4.5%-8.1, respectively, comparing with the physical blends of PP/POE. However, the elongation of the reactive blends of PP/POE presented in Figure 4.26 is increased by 4.0% - 138.5% relative to the physical blends. Effect of GMA and processing temperature on tensile properties of the blend are illustrated in Figure 4.27 and 4.28. It is found that with increasing of initial GMA concentration, the yield stress ($\sigma_y$) and modulus of elasticity ($E$) of reactive blends are decreased by 7.3%-21.2% and 16.3%-39.0%, relative to the physical blends. The yield stress ($\sigma_y$) and modulus of elasticity ($E$) vary inversely as the processing temperature. The stress-strain behavior of the reactive blends of PP/POE at room temperature shown in Figure 4.29 clearly displays a typical deformation of strong and tough thermoplastics which has a localized yielding and cold drawing. With melt grafting, the yielding region and cold drawing of the blends become border and longer, respectively. For the reactive blends of PP/POE, fairly sharp neck profiles are also produced during yielding. And the yield stress ($\sigma_y$), modulus of elasticity ($E$) and elongation vary slightly with the type of peroxide. The areas under the stress-strain curves, strain energy per unit volume, are increased by reactive blending, relative to no melt grafting ones. It is suggested that the reactive blends are tougher than that of the correlated physical blending ones.

4.3.6 Impact Behavior

Figure 4.30. shows the effect of the melt grafting on the impact strength of the PP/POE blends. In both cases of the blend of PP/POE-1 and PP/POE-2, the un-notched and notched Izod impact strength of PP/POE blends are significantly improved when the
Figure 4.24 Effect of melt grafting on the tensile properties of the blend of PP/POE: a) tensile strength; b) modulus of elasticity
Figure 4.25 Effect of melt grafting on flexural properties of the blend of PP/POE: a) flexural strength; b) tangent modulus of elasticity
Figure 4.26 Effect of melt grafting on elongation of the blend of PP/POE: a) PP/POE-1; b) PP/POE-2
Figure 4.27 Effect of GMA on the tensile properties of the blend of PP/POE (70/30): a) tensile strength; b) modulus of elasticity
Figure 4.28 Effect of processing temperature on the tensile properties of the blend of PP/POE (70/30)

Figure 4.29 Stress-strain behavior of the blend of: a) PP/POE-1; b) PP/POE-2
initial GMA is introduced into the interface between the POE and PP matrix, relative to the corresponding physical ones. This improvement may be due to the interfacial interaction between the two phases by POE-g-GMA as compatibilizers. Effect of GMA on the Izod impact strength of the blend of PP/POE is illustrated in Figure 4.31. The notched Izod impact strength of the reactive blend of PP/POE (70/30) is dramatically increased by about 10-fold to 25-fold with increasing the concentration of initial GMA relative to the virgin PP. There is an impressive jump when the concentration of GMA reaches up to a level of about 3 wt% for notched impact strength while at 1wt% of concentration of GMA, there is another great jump for un-notched one. Figure 4.32 presents the effect of peroxide on the impact strength of the blends of PP/POE. The un-notched and notched Izod impact strength vary with the type of peroxide. Effect of on improvement of the impact resistance is in approximately regular order as following:
2,5-dimethyl-2,5-di-(t-butylperoxy) hexane > t-butyl hydroperoxide > Dicumyl peroxide

It is also found that styrene monomer could be in favor of the impact resistance in the reactive blending.

Effect of processing temperature on notched impact strength of the blend of PP/POE-1 (70/30) is represented in Figure 4.33. At processing temperature of 240°C, the Izod impact strength of the blend has the highest value while it has lower values at 220°C and 270°C, respectively. Number-average domain size (Dn) of POE and the Izod impact strength as function of DG of GMA in the blend of PP/POE-1 (70/30) is illustrated in Figure 4.34. It is interesting to note that the impact strength could be dramatically enhanced with a decrease of the number-average domain size of minor POE phase in PP matrix. The PP/POE blends undergo a brittle-ductile transition as the DG of GMA and number-average domain size (Dn) of POE reach a level of c.a. 0.5 wt% and 0.8 μm, respectively. It is suggested that the impact property could be significantly improved through controlling the morphological structure by POE-g-GMA as an effective compatibilizer. They are consistent with the results mentioned in 4.3.

4.4 Conclusions

The glycidyl methacrylate (GMA) can be successfully melt grafted onto polyolefin elastomer (POE) via a free radical initiation but is accompanied by β-scission of the POE molecules. The extent of GMA grafting (DG) and the molecular
Figure 4.30 Effect of melt grafting on the Izod impact strength of the blend of: a) PP/POE-1, notched; b) PP/POE-2, notched; c) PP/POE, unnotched
Figure 4.31 Effect of GMA on the Izod impact strength of the blend of PP/POE (70/30):

a) notched; b) unnotched
Figure 4.32 Effect of peroxide on the Izod impact strength of the blend of PP/POE: a) notched; b) unnotched
Figure 4.33 Effect processing temperature on the notched Izod impact strength in the blend of PP/POE-1 (70/30)
Figure 4.34 Number-average domain size of POE and the Izod impact strength as a function of DG of GMA in the blend of PP/POE-1 (70/30)

weight of the functional POE copolymers can be controlled by carefully manipulating various reaction factors such as monomer concentration, initiator concentration and reaction temperature as well as the molecular weight of the starting POE. The addition of a second monomer to the reaction environment, namely styrene, permits one to increase the GMA grafting levels and reduce the extent of β-scission. The GMA grafting yield increases with increasing concentration of the peroxide and GMA monomer. This similarity is related to the fact that the peroxide concentration and its half lifetime govern the overall grafting rate and ultimate yield.

The GMA grafted POE copolymer can effectively compatibilize the blends of PP/POE. Up to a 25-fold increase in impact strength of PP/POE has been observed over the neat PP with the toughened blends going through a brittle-ductile transition at
relatively low concentrations of functional POE in the PP matrix phase. The POE particle size of PP/POE blends can be effectively controlled by carefully varying either the processing conditions or the amount of interfacial reaction or a combination of both. It is observed that more grafting degree (DG) of GMA it has, the smaller domain size of POE it has in the blends. The brittle-ductile transition of the blends happens to 0.6 wt% DG of GMA and 0.8 micron of POE particle size. Generally speaking, the smaller domain size of the minor phase in the blends it has, the better impact properties it has. Compatibilizing capacity of the reactive copolymer is not exclusively dependent on the total reactive group concentration in the blend. The properties of the reactive copolymer are found to have a significant influence on the compatibilizing capacity. A large amount of moderately functionalized copolymer offers better compatibilization performance than a small amount of highly functionalized copolymer.
CHAPTER 5
APPLICATIONS OF FUNCTIONAL POE AND POE-BASED BLENDS

5.1 Introduction

Multiphase polymer blend systems offer interesting possibilities for obtaining optimum property combinations if the phase morphology and the interfacial interactions are properly controlled. These factors are crucial properties of blend materials [7-15]. Added block or graft copolymers as interfacial agents to control the morphology and to strengthen the interfaces of immiscible blends have been used successfully. However, industrially more interesting would be the formation of the block or graft copolymer in situ during melt mixing through interfacial reaction of added functionalized polymeric components. Even more interesting would be to have graft copolymer with functional groups on the surface. Nevertheless, reactive blending has gained a lot of interest since the commercialization of super-tough alloys [41, 148-151].

The morphology and mechanical properties of PP/PC blends using compatibilizer PP-g-GMA studied by Yin et al. indicated that PP-g-GMA is an effective compatibilizer for the PP and PC blending system. With addition of PP-g-GMA, the size of PP domains is significantly reduced and the interaction between different phases is greatly improved. The crystal form of crystalline PP changes from a mixture into a unique crystal form when PP is incorporated with PC. GMA grafted onto PP molecular chains can act as a
nucleating agent which enhances the crystallization temperature of PP. Due to the compatibilization of PP-g-GMA, the glass transition temperature of PC in the ternary blends shifts towards lower temperature. The apparent viscosities and mechanical properties of PP/PC/PP-g-GMA, such as modulus of elasticity, tensile strength, elongation at break and Izod impact strength, are improved comparing with PP/PC at the same content of PC [30].

Yu et al. observed that super-tough nylon 6 was prepared by using polyethylene-octene elastomer (POE) grafted with maleic anhydride as a toughening agent. The maleic anhydride grafting of POE results in significant improvements of compatibility and interfacial adhesion between nylon 6 and POE as well as in a sharp reduction of the particle size of the dispersed phase due to the in situ formation of a graft copolymer during melt processing. The use of POE-g-MA significantly improves notched Izod impact strength of nylon 6/POE blends so as to reach a level of super tough, whereas the unmodified POE has hardly any contribution to toughness of nylon 6. Furthermore, the addition of a small amount of a multifunction epoxy compound (CE-96) to the nylon 6 promotes the toughening effect of POE-g-MA and shifts the brittle-ductile transition to a lower POE-g-MA contents [50-51].

Li et al. found that in the blends of PP and PA 6 with PP-g-MA as a compatibilizer, compatibility is an important factor influencing the orientation of the dispersed phase in the matrix. The compatibility is advantageous for fibrillation. In order to maintain the fibrillar morphology, the temperature in the secondary process should be lower than the melt point of the fibril-forming component. Otherwise, the fibrillar morphology would disappear. The fibrillation of thermoplastic PA 6 occurs easily in PP
in the simple shear field. When processed with a single screw extruder, the equilibrium of dispersion and deformation is established in the compression zone of the screw channel. The mechanical properties, such as tensile strength, impact strength, and modulus of an in-situ fibrillation composite, are different in the different direction. The fibrillation benefits mechanical properties in its oriented direction [111-112].

The compatibilization of PA 6/ABS blends using glycidyl methacrylate/methyl methacrylate copolymers studied by Kudva et al. indicated that the effect of a series of glycidyl methacrylate/methyl methacrylate (GMA/MMA) copolymers on the behavior of PA 6/SAN and PA 6/ABS blends was investigated. Incorporation of these copolymers can reduce the dispersed phase domain size of PA 6/SAN blends if the GMA content is above a certain level. These changes in the dispersed phase morphology stem from reactions between the end groups of PA 6 and the copolymer. This occurs to some degree by steric stabilization of the SAN domains against coalescence. Incorporation of the copolymer generally does not promote effective toughening of nylon 6/ABS blends in a single screw extruder. At low GMA contents in the copolymer, the Izod impact strength actually becomes somewhat worse than that of a binary nylon 6/ABS blend. While there are marginal improvements in impact strength when the GMA content is increased, all blends had poor low-temperature toughness. The addition of GMA/MMA copolymers to PA 6/ABS blends appears to break up the co-continuity of the ABS phase and to promote the formation of two populations of ABS domains. One group of ABS domains consisting of large clusters becomes large with increasing GMA content in the copolymer, while the other group consists of small ABS domains. The morphological rearrangements in PA 6/ABS blends caused by the incorporation of the GMA/MMA
copolymer lead to a non-uniform distribution of rubber particles within the blend. Reactions of both the acid and the amine end groups of PA 6 with the epoxide ring of GMA induce cross-linking effects through a two-point grafting mechanism [117].

Morphological studies of PA 1010/PP blends studied by Zhang et al. showed that the morphology of binary and ternary blends of PA 1010, PP and PP-g-GMA were examined. With the increase of mixing time, the larger particle size deceased. Binary blends of PA 1010 with PP-g-GMA showed that the PP-g-GMA particle sizes decreased as the GMA content of PP-g-GMA increased as the GMA content of PP-g-GMA increased. The morphology of ternary blend of PA1010/PP/PP-g-GMA showed that the dispersed phase diameter decreased as the GMA content of PP-g-GMA increased from 0.26% to 0.57%. When the PP-g-GMA containing 1.07% GMA was used in the ternary blends, it was found that the dispersed phase diameter increased and two distribution ranges of particle sizes was observed. The resulting morphology was dependent on the GMA content in PP-g-GMA and on the miscibility of PP with PP-g-GMA. Due to the different GMA content in PP-g-GMA, their corresponding morphology showed various patterns. The results of the matrix indicated that the copolymer formed by PP-g-GMA and PA1010 located at the interface between PP and PA 1010, and acted as a compatibilizing agent which strengthened the adhesion between two phases [127-128].

Multi-component polypropylene (PP) composites are used in large quantities in the automotive industry, among other applications also for the preparation of bumpers. They usually contain elastomers to improve the fracture, especially the impact resistance of PP, and filler to increase stiffness. This obvious route to improve stiffness and toughness simultaneously created much interest both industrially and academically in a
number of polymers. Numerous studies have been carried out on such and similar systems in preceding years. Two types of structures, namely separated dispersion of the minor components (elastomer, and filler) in the matrix polymer and embedding of the filler by the elastomer, can be formed in three-component polymer/elastomer/filler systems. In polymer/polymer/filler composites, a third structure was also observed where the inter-phase was enriched in the filler particles. The prevailing structure is primarily determined by thermodynamics and by surface characteristics. But it is also influenced by the rheological properties of the components and that of the composite, as well as by processing conditions. Although much effort has been put into the determination of structure-property relationships in multi-component polymer systems, much less is known about their impact resistance, in spite of the practical importance of this property. Hardly any systematic study has been carried out and the published results are contradictory [7-13, 148-151].

Toughening and reinforcing PP with core-shell structure fillers studied by Ou et al. illustrated that using a core (talcum powder) - shell (POE) structured filler, a ternary PP/POE/talc composite with high toughness and high modulus was created. A one-step process was used to prepare the ternary composite and it showed little difference compared to the two-step process. The rheological behavior of PP was changed and the mechanical properties were improved. SEM observation showed that the core-shell structured filler dispersed better in the blends than in PP [149].

The effects of process conditions and composition on the properties of blends of talc/POE/PP investigated by Huneault et al. showed that mechanical properties were not affected significantly by the operation conditions of the twin-screw process. Dispersion,
evaluated visually on thin film, was satisfactory even though the talc grade was relatively fine with a median particle size of 2µm. The use of 30 wt% of talc provided a two-fold increase in modulus. The use of POE provided a significant improvement in impact resistance when used at levels over 20wt% based on the polymer phase (PP). This critical level was identical in both filled and unfilled PP. Maleated polypropylenes varying with molecular weight were evaluated as adhesion promoter. In the best case, 2wt% of PP-MA can provide 9% and 16% increases in tensile stress and impact resistance, respectively [150-151].

The growth of xerography illustrates a classic example of the successful commercialization of task specific scientific development. The xerographic toner used in copy machines has been refined and perfected to allow extremely inexpensive methods of image reproduction with very little demand upon the user. However, it is estimated that a few million tons of post-consumer waste xerographic toner is collected annually in the world. A waste stream of such magnitude will no doubt contribute to eventual ecological problems, which will only be augmented with increased demand and use. The design of successful recycling techniques could provide an alternative method of disposal that is potentially beneficial economically as well as ecologically [44].

Xerographic toner basically consists of a carbon black in a binder resin, such as polystyrne-n-butyl methacrylate, or polystyrne-n-butyl acrylate, etc. The molecular weight ranges from 50,000 to 60,000. Toner particle sizes are generally in the range between about 10µm and 20µm in diameter. Since usually 85% or more of the toner is polymer, the mechanical property of toner is mainly dependent on it. It is well known that the mechanical property of xerographic toner is very brittle due to the rigid molecular
structure of binder resin [44]. There are few papers talking about how to recycle used toner as a structural material.

Polymer blends are homogeneous or heterogenous mixtures of two chemically different polymers. It is well known only few polymers are miscible, or soluble in one another. When polymer pairs are immiscible, separated phases are formed in the mixture. In a blend, droplets may be formed in the final product. A major factor determining droplet size is its surface tension. A reduction in interfacial tension typically leads to smaller particle size and better physical properties. A chemical way to accomplish this is to add a compatibilizer to the mixture, which makes the polymers in a blends less incompatibile, as soap does in an oil/water mixture. Basically, compatibilizers are molecules that anchor themselves to the polymer pairs across their interfaces. They may have either a block or graft structure. Graft compatibilizers are more usually employed because of manufacturing economics. Reactive extrusion is now an efficient continuous manufacturing method that combines the two traditionally separated operations: compatibilization and extrusion into a single process carried out on an extruder [9-13].

It is well known that the final morphology of blend has a controlling influence on the mechanical properties of the blends. Compatibilizers have been used successfully as interfacial agents to control the morphology and to strengthen the interfaces in blends of immiscible polymers. Beside component properties and adhesion, the particle size of the reinforced filler also can influence to the properties. The purposes in this chapter are as follows:
1) Four new families of ternary blending system of POE, which were PP/PC, PP/PA 6,6, POE/xerographic black toner (BT), and PP/xerographic black toner (BT), were prepared by reactive extrusion process.

2) The mechanical properties of the ternary blends of POE were examined through Izod impact strength, tensile properties, and flexural properties.

3) The effects of process parameters on the mechanical properties and on the morphologic behavior were studied.

4) The relationship between the mechanical properties and the morphologic behavior was investigated.

5.2 Experimental

5.2.1 Materials

The pellets of POE-1 and POE-2, which had melt-flow index of 0.5 and 1.0 g/10min respectively, were generously donated through Dupont Dow Elastomers. They are ethylene-octene copolymers. The density range of the copolymers is between 0.860 and 0.888 g/cm³. The polypropylene (PP), REXENE 31S4A, was a homopolymer resin in pellet form. It had a melt-flow index of 4.0 g/min and was kindly provided through Huntsman Corporation. Polymethyl methacrylate (PMMA), ENVIOR resin, was supplied by General Polymers, Division of Ashland Chemical, in pellet form. AFFINITY* resin in pellet form is a product of Dow Chemical Company. High-density polyethylene (HDPE) resin in pellet form is the product of Eastman Chemical Company. Linear low-density polyethylene (LLDPE), Dow polyethylene (PE) resins, which has melt-flow index of 6.0
g/min, is the product of Dow Chemical Company in pellet form. STYRON* polystyrene (PS) and STYRON* high impact polystyrene (HIPS) resins in pellet form are the products of Dow Chemical Company. LEXAN* glass fiber reinforced bisphenol-A polycarbonate (PC) resin in pellet form is the product of General Electric Co. Polyamide 6,6 (PA6,6) in pellet form is the product of Monsanto. The materials above mentioned are also described in table 3.2.1-1 and 3.2.1-2. Xerographic Black toner (BT) in powder form, XP-808, which consists of styrene/butadiene copolymer (75-85wt%), iron oxide (15-20wt%), carbon black (<5wt%) and quaternary ammonium salts (<2wt%), was kindly supplied by Xerox Corporation.

All of the peroxides and monomers used in these studies were regent grade chemicals. GMA monomers, molecular weight (MW) of 142, which were 97wt% solution and were inhibited with 50 ppm p-methoxy phenol, were purchased from Aldrich Chemical Company. Styrene monomers, MW of 104, which were 99wt% solution and were inhibited with 15 ppm 4-tert-butylcatechol, were also the product of Aldrich Chemical Company. Peroxide initiators, tert-butyl hydroperoxide and dicumyl peroxide, which have half-life of 1 hour at 140°C and 137°C, respectively, were used as received from Witco Corporation. Lupersol 101 initiator, 2, 5-dimethyl-2, 5-di (t-butylperoxy) hexane, which has a half-life of 1 hour at 140°C, was used as received from Elf Atochem North America, Inc. The chemicals above mentioned are also listed in table 4.2.1-1.

5.2.2 Methods

5.2.2.1 Reactive extrusion
Prior to reactive extrusion, all of polymer resins and xerographic black toners used in these studies were dried in a vacuum to remove sorbed water. The drying temperature and time used in these studies are the same with the corresponding one described in table 3.1. In order to remove the inhibitors in purchased monomers, the monomers were purified through chromatographic columns containing activated alumina before using. The reactive extrusion was carried out in a 34-mm co-rotating twin screw reactive extruder, APV Chemical Machinery Inc., which length-to-diameter ratio L/D is 34. The temperature of the extruder was regulated by electrical resistance and water circulation in barrels. In these reactive extrusions, there are two schemes described as following.

In scheme one, the dried polymer resins were mixed in a mixer about 10 minutes with desired ratios before reactive extrusion. The amount of peroxide was measured by an analytical balance and put into the purified monomers. And the peroxide and purified monomers were mixed through a magnetic stirring apparatus with a stirrer bar about 2 minutes. The pre-mixed polymer resins as well as the mixture of peroxide and monomers were introduced into the reactive twin screw extruder from the hopper of the extruder through a screw dry material feeder and a Zenith gear pump, respectively. The dry material feeder is the product of Accu Rate Inc., and the Zenith gear pump is type ‘H’ pump, which is the product of Zenith Pumps Division, Parker Hannifin Corporation. The pellets of polymer resins were moistened with a chosen amount of a liquid mixture of monomers and peroxide when introduced from the hopper. The reactive extrusion processing was performed at temperature in range between 180 and 300 °C, with screw
speed in range between 100 and 300 rpm, and feeding rate in range between 50 and 150 g/min.

In scheme two, the dried polymer resins were introduced into the reactive extruder from the hopper of the extruder with two screw dry material feeders, Accu Rate Inc. The desired ratios between the two resins were performed through the different screw speeds on the two dry material feeders. The preparation of monomer and peroxides was the same as above mentioned. The mixture of monomers and peroxides was injected into the reactive extruder from the bottom of barrel by a Zenith high-pressure gear pump, Zenith Pumps Division, Parker Hannifin Corporation. The reactive extrusion processing was performed at temperature in range between 180 and 300 °C, with screw speed in range between 100 and 300 rpm, and feeding rate of feeder in range between 10 and 150 g/min. For all experimental runs, devolatilization was carried out by a vacuum pump. This pump was placed near the die and it created a pressure of about 25 mmHg. The extruder was always starved to feed. Thus, the screw speed (N), feed rate (Q), and specific throughput (Q/N) could be varied independently.

5.2.2.2 Mechanical properties

Prior to every step of processing and mechanical testing, in order to ensure removal of sorbed water, all samples used in these studies were dried under vacuum overnight at temperature in range between 50 and 76°C in order to ensure removal of the water. The extrudates were pelletized and the resulting pellets of the blends were molded through compression molding for the tests of mechanical properties. Test bars were prepared using a Carver compression molding machine, Fred S. Carver Inc., at
temperature in range between 160 and 210°C and pressure in range between 1600 and 2600psi. The detail of the procedure and parameter of compression molding for Izod impact, tensile and flexural test bars used in these studies are the same as the corresponding one described in 3.2.2.

For Izod impact test, the samples, rectangular test bars with 32 x 12.7 x 6.35 mm$^3$, were notched using a notching cutter, Testing Machines Inc (TMI). The notched Izod impact measurements were made using a TMI pendulum type impact test machine in accordance with ASTM D256 at ambient temperature and liquid nitrogen temperature, respectively. Tensile testing of dry dog-bone-shaped test bars, type V test specimens having 7.26mm gauge length, 3.18mm width and 3.18mm thickness, was done using an INSTRON 1125 tensile testing machine at cross-head speed in range between 50 mm/min and 2 mm/min for modulus and yield strength measurements as well as elongation at break in reference to ASTM D638 under ambient conditions. Four-point flexural test of rectangular test bars with 64 x 12.7 x 3.18 mm$^3$ was determined utilizing the same test instrument as was the tensile test for flexural strength and modulus of elasticity at 2mm/min strain rate under room temperature according to ASTM D790. The detail of the mechanical test mentioned above was also described in 3.2 as well as 4.2.

5.2.2.3 SEM observation

Morphology of the blends were observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The cryofracturing surface of the notched Izod samples for SEM were prepared through the Izod impact test at liquid nitrogen temperature. In order to prevent electron from charging on insulating surfaces, the cryofracturing surfaces of Izod sample were sputter coated with a thin layer of
gold/palladium alloy (Au/Pd) through a Hummer V coating system ca 30 seconds. Jeol JSM-6400 and Jeol JSM-35CF, equipped with tungsten filament, were used in this study. The accelerating voltage of the microscopes was usually set to be at 5 kV.

5.2.2.4 DSC measurements

In order to determine the glass transition temperature (Tg) and the grade of crystallisation of the physical blends, differential scanning calorimetry (DSC) was employed. DSC was performed on a Seiko DSC 220C, Seiko Instruments, equipped with a data station. The sample mass was in range between 10 and 15 mg. The sample was sealed into a standard aluminum pan and crimping cover through a crimper. The sample was pureed with dry nitrogen at a flow rate of 100 ml/min. For cooling, the liquid nitrogen accessory of the device was used. Calibration was carried out with a sapphire standard. The Tg was defined as the midpoint of the change in the heat capacity for the transition. The melting temperature was detected as the temperature corresponding to the peak in heat flow during heating. Enthalpies of crystallization and melting were obtained by integrating the heat flow cure to a flat baseline. Using the heat of fusion of a perfect iPP (209 J/g) and a perfect PE (277 J/g) crystal, the weight fraction crystallinity was calculated as:

$$X_c = \frac{\Delta H_{melt}}{f\Delta H^{*}_{melt}}$$

(5.1)

Where $\Delta H_{melt}$ is the measured enthalpy of melting, $\Delta H^{*}_{melt}$ is the ideal enthalpy of melting a perfect crystal of polymer X, and f is the weight fraction of polymer X in the
blend. The heating rate was 10°C/min. The basic programs used in these studies were described in table 3.6. The data were analyzed by the equipment analysis programs.

5.3 Results and Discussion

5.3.1 Blends of PP/Polycarbonate (PC) with POE-g-GMA

5.3.1.1 Mechanical properties

The mechanical properties of the physical and reactive blends are illustrated in Figure 5.1, 5.2 and 5.3. Compared with the mechanical blends, the Izod impact strength is improved by 2-fold. However, flexural strength and tangent modulus of elasticity of the reactive blends are reduced by 14.0%-28.2% and 14.0%-28.1% relative to the physical blends. In addition, The effect of POE-g-GMA on impact resistance is larger than that of POE-g-MA. The effect of GMA on the impact strength of the reactive blends reaches up to maximum at 1wt% GMA. The modification of mechanical properties of the ternary blends can be attributed to the contribution of the compatibilizer, POE-g-GMA, which acts as an 'interfacial agent', reduces the interfacial tension, minimizes and homogenizes the domain size, and increases the interfacial adhesion. The proposed mechanism of compatibilization in blend of PP/PC with POE-g-GMA is in Figure 5.4. The epoxy group of POE-g-GMA could react with the terminal hydroxyl group of PC.

5.3.1.2 Thermal behavior

Thermograms of PP/PC and PP/PC/POE-g-GMA blending systems are shown in Figure 5.5. In the PC/POE blends, two glass transitions are found. This indicates there
Figure 5.1 Effect of in situ POE-g-GMA on Izod impact strength of the blend of PP/GFR-PC

Figure 5.2 Effect of GMA on the impact strength of the blend of PP/GFR-PC/POE (80/10/10)
Figure 5.3 Flexural properties of the blend of PP/GFR-PC/POE-g-GMA

Figure 5.4 Proposed scheme of compatibilization with POE-g-GMA in the blend of PP/PC
is a phase separation in the blends. In the blends of PP/PC, the melting temperature (Tm) of PP matrix is shifted 1-2°C to lower temperature and the crystallinity of PP is decreased by 9%-17% in presence of POE-g-GMA and POE-g-MA. The features offer us a evidence that the copolymer POE-g-GMA may be an effective compatibilizer for the PP/PC blending system.

Figure 5.5 DSC thermograms of GFR-PC, GFR-PC/POE and PP/GFR-PC/POE in heating mode
5.3.1.3 Morphology

SEM micrographs of fracture surfaces of PP/PC, PP/PC/POE-g-GMA and PP/PC/POE-g-MA are illustrated in Figure 5.5, 5.6 and 5.7. The blend containing polycarbonate without compatibilizer shows a spherical dispersion of the PC phase in the PP matrix. A sharp interface in the blends is observed, which results from the fact that there is almost no interfacial adhesive between PC spheres and PP matrix. The diameters of PC domain are 2-5μm. On the other hand, the addition 10wt% POE-g-GMA and 10wt% POE-g-MA make the morphology undergo a considerable change in the dimension of the dispersion phase and the interfacial behavior. The domain sizes of PC become smaller and more homogeneous than that of physical blends by in-situ compatibilization. These results indicate that POE-g-GMA can act as an effective compatibilizer in PP/PC blends.

Figure 5.6 SEM micrograph of the blend of PP/GFR-PC/POE
Figure 5.7 SEM micrograph of the blend of PP/GFR-PC/POE-g-MA

Figure 5.8 SEM micrograph of the blend of PP/GFR-PC/POE-g-GMA
5.3.2 Blends of PP/Polyamide 6,6 (PA 6,6) with POE-g-GMA

5.3.2.1 Morphology

SEM micrographs of cryo-fracture surfaces of the PP/PA 6,6/POE blends are shown in Figure 5.9, 5.10, 5.11 and 5.12. It is interesting to note that the morphology of PA 6,6 fibrils is found in the mechanical blends. However, the dispersed POE phase of this uncompatibilized blends is unstable towards coalescence during melt processing and consequently forms a coarse morphology, consisting of both essentially spherical POE particles with size-scales of between 5 and 10 μm in diameter and larger as well as more complex domain structures. There is also an evidence of poor interfacial bonding in this system, with fibrils of PA 6,6 pulled from the PP matrix lying loose on the fracture surface. SEM micrographs of reactive blend reveal significance in not only change in the shape but also reductions in the size-scale of the dispersed phases. Cryo-fracture surfaces of the reactive blends reveal a not complex morphology in which smaller PA 6,6 and POE particles are well dispersed. It is clearly indicated a dramatic reduction in the size-scale of the PA 6,6 dispersed phase to lower than 0.5 μm, as a result of presence of in-situ POE-g-GMA.

5.3.2.2 Thermal behavior

DSC was employed to study the miscibility and phase behavior of the blends of PP/PA 6,6/POE. Figure 5.13 presents the DSC thermograms of PA 6,6, PP/PA 6,6/POE, and PP/PA 6,6/POE-g-GMA. The analysis of the melting behavior of a crystalline component in semi-crystalline polymer blends is an important tool in assessing polymer
Figure 5.9 SEM micrographs of the physical blend of PP/PA 6,6/POE (70/20/10): a) X500; b) X2000
Figure 5.10 SEM micrographs of the physical blend of PP/PA 6,6/POE (60/30/10):  

(a) X500;  
(b) X2000
Figure 5.11 SEM micrographs of the blend of PP/PA 6,6/POE-g-GMA (70/20/10): a) X500; b) X2000
Figure 5.12 SEM micrographs of the blend of PP/PA 6.6/POE-g-GMA (60/30/10): a) X500; b) X2000
Figure 5.13 DSC thermograms of PA 6,6, PP/PA 6,6/POE in heating mode

miscibility. In miscible blends, the melting point of a crystalline component is usually lowered with respect to the pure polymer as a result of thermodynamically favorable interactions. PA 6,6’s phase shows a reduced degree of crystallinity showing that crystallization of PA 6,6 is more difficult in the presence of the POE. PA 6,6’s phase shows a Tm’s depression in its blends with POE. In reactive blends, the degree of crystallinity is reduced and the Tm of PA 6,6’s phase is shifted to lower temperature relative to the physical blends. It is suggested that POE-g-GMA is an effective surfactant in the blends of PP/PA 6,6 due to the lower Tm’s effect. The proposed mechanism of compatibilization in the blend of PP/PA 6,6 with POE-g-GMA is shown in Figure 5.14.
Figure 5.14 Proposed scheme of compatibilization with POE-g-GMA in the blend of PP/PA 6,6

5.3.2.3 Tensile properties

Figure 5.15 and 5.16 show plots of yield stress, modulus and elongation of elasticity vs. POE content for the blends of PP/PA 6,6/POE, respectively. Although POE-g-GMA improves the yield strength and modulus of elasticity of the PP/PA 6,6 blends, the elongation of the blends is reduced. There are many factors affecting strength, modulus and elongation of a semicrystalline polymer, such as molecular weight, molecular weight distribution, crystal morphology and crystallinity. Compared with physical blends, reactive blends has lower crystallinity (Xc) and melt temperature (Tm),
Figure 5.15 Yield stress ($\sigma_y$) and modulus of elasticity (E) of the blend of PP/PA 6,6/POE.

Figure 5.16 Elongation of the blend of PP/PA 6,6/POE.
which should be one of the reasons for higher yield strength and modulus values. On the other hand, the crystal morphology, such as crystal size and form, the imperfection of spherulitic structure, and so forth, may also play important roles in influencing the strength and modulus of the blends.

5.3.3 Blend of PS/POE with POE-g-GMA as a Compatibilizer

5.3.3.1 Morphology

SEM micrographs of the blend of PS/POE without and with POE-g-GMA as an in-situ compatibilizer are illustrated in Figure 5.17 and 5.18, respectively. It is observed that the fracture surface of the mechanical blend displays phase-separated and somewhat coalesced. In the blend without POE-g-GMA, a compatibilizer, the fracture path occurs along the interface between the PS matrix and the minor POE phase. In contrast, in the blend with POE-g-GMA, there is broader phase boundary between the POE phase and PS matrix and the fracture occurs through the phase of elastomer, suggesting having better interfacial bonding. It is also found that with compatibilization not only the domain size of POE is significantly reduced from about 8 μm to 1 μm relative to the mechanical blends but also phase adhesion is improved.

5.3.3.2 Thermal behavior

Thermal characterization of glass transition and DSC thermograms of PS and PS/POE are illustrated in table 5.1 and Figure 5.19, respectively. The thermograms of the blends clearly present two glass transitions, suggesting the existence of two amorphous phases, a PS phase and a POE-1 phase. As shown in the DSC thermogram and table 5.1,
The Tg of PS in the reactive blend is shifted to lower temperature relative to mechanical one, suggesting the POE-g-GMA as an effective compatibiizer in this blending system. In other words, it stands to reason that the thermal miscibility of PS with POE is improved through the reactive blending.

Table 5.1. Thermal characterization of glass transition in neat PS and PS/POE

<table>
<thead>
<tr>
<th>Code</th>
<th>Tg of POE phase (°C)</th>
<th>Tg of PS matrix (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td></td>
<td>104.4</td>
</tr>
<tr>
<td>POE-1</td>
<td>-52.3</td>
<td></td>
</tr>
<tr>
<td>PS/POE-1 (90/10)</td>
<td>-58.8</td>
<td>103.4</td>
</tr>
<tr>
<td>PS/POE-1 (90/10) + 5%</td>
<td>61.1</td>
<td>95.4</td>
</tr>
<tr>
<td>GMA</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.3.3.3 Mechanical properties

The mechanical properties of the blend of PS/POE are represent in table 5.2. As shown in the reactive blend of PP/POE (90/10), the tensile strength at yield (σy) as well as modulus of elasticity (E) go up to 130% and 129% relative to the physical one. However, the elongation of the reactive blend is decreased by 33% comparing to the physical one. Stress-strain behavior of the blends of PS /POE (90/10) with the strain rate of 2 mm/min and at room temperature is illustrated in Figure 5.20. It is observed that the blend has typical behavior of rigid and tough materials. At break, the tensile strength of the reactive blend has higher value than that of non-reactive one. The areas under the stress-strain curves, the absorbed energy per unit volume, is the property that measures
Figure 5.17 SEM micrographs of the blend of PS/POE (90/10): a) X200; b) X2000
Figure 5.18 SEM micrographs of the blend of PS/POE-g-GMA (90/10): a) X200; b) X2000
Figure 5.19 DSC thermograms of PS and PS/POE (90/10) in heating mode

Figure 5.20 Stress-strain behavior of the blend of PS/POE (90/10)
Table 5.2. Mechanical properties of the blends of polystyrene (PS)/POE

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Tensile Strength (MPa)</th>
<th>Modulus of Elasticity (MPa)</th>
<th>Elongation (%)</th>
<th>Impact Strength at room temp. (J/m)</th>
<th>Impact Strength at Liquid N₂ temp. (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>28.69±1.43</td>
<td>468.1±23.40</td>
<td>6.12±1.22</td>
<td>7.763±0.388</td>
<td>13.35±0.56</td>
</tr>
<tr>
<td>PS/POE-1 (90/10)</td>
<td>18.23±0.912</td>
<td>346.9±17.3</td>
<td>15.31±3.06</td>
<td>10.44±0.522</td>
<td>9.93±0.30</td>
</tr>
<tr>
<td>PS/POE-1 (90/10) + 5% GMA</td>
<td>23.45±1.17</td>
<td>446.9±22.3</td>
<td>10.2±2.0</td>
<td>12.00±0.36</td>
<td>9.90±0.29</td>
</tr>
<tr>
<td>PS/POE-1 (80/20)</td>
<td>14.29±0.71</td>
<td>220.81±11.1</td>
<td>10.93±0.33</td>
<td>12.68±0.38</td>
<td>11.21±0.35</td>
</tr>
<tr>
<td>PS/POE-1 (70/30)</td>
<td>13.47±0.67</td>
<td>186.55±9.33</td>
<td>11.15±0.34</td>
<td>11.91±0.36</td>
<td>11.90±0.36</td>
</tr>
</tbody>
</table>

The ability of a material to withstand impact and is related to the toughness of the material. Based upon the more absorbed energy per unit volume, the blend of PS/POE with POE-g-GMA as a compatibilizer is tougher than that mechanical one. This is consistent with the result in impact test.
5.3.4 Application of In-situ Functional POE for Recycling of Xerographic Toners

5.3.4.1 Morphology

SEM micrographs of POE/BT blends without and with compatibilization are presented in Figure 5.21 and 5.22, respectively. In these SEM micrographs, it is illustrated that using compatibilization, the domain size of black toner (BT) is significantly reduced from 5μm and 1μm relative to the non-reactive blending (mechanical blending). The improvement in phase adhesion as a result of the compounding could be easily observed. In the blends, the fracture passes along the interface between the minor phase of black toner and the POE matrix. In contrast, to the blends with compatibilization, the phase of black toner is bound onto the POE matrix and the fracture occurs through the black toner phase. In addition, the coalescence is improved by using in situ POE-g-GMA due to reducing interfacial tensions while the mechanical mixing results in blend granules. It is also found that efficient dispersion is obtained with compatibilization whereas the phase of black toner is agglomerated in the interfaces without compatibilization.

In Figure 5.23, SEM micrographs of the blends of PP/BT (80/20) without functional POE as a modifier are illustrated, respectively. The fracture surface shows that the blend without functional POE as a modifier exhibits a separately dispersed morphology. The blend without the modifier constitutes the black toner (BT) phase, which includes spherical particles of size from 15μm to 5μm, does not effectively bind onto the PP matrix because of the sharp phase boundary. In addition, the mechanical blend is experiencing significant coalescence and particle-particle interactions. In the
Figure 5.24, the SEM micrographs of the blend of PP/BT (80/20) with functional POE as a modifier are presented. It is observed that in the presence of POE-g-GMA, the domain size of the dispersed particles of BT is smaller, closed to 1 to 2 μm. Not only the particles remains spherical shape without any agglomeration but also there is the interfacial adhesion between the BT and PP matrix with broader phase boundary. It is believed that in case of using functional POE as a modifier, the impact strength could be improved through enhancement in interfacial adhesion between the dispersed BT and PP matrix with the formation of interfacial in-situ compatibilizer at the phase boundary.

5.3.4.2 Tensile behavior

Modulus of elasticity of the POE/BT blend with varied amount of black toner is shown in Figure 5.25. Modulus of elasticity of POE-3 produced under the same processing condition is 26.12 MPa. As shown in Figure 5.23, the modulus of the blends of POE/BT with compatibilization is increased by 9%-39%, relative to the corresponding mechanical one. Stress-strain behavior of the blend of POE/BT (50/50) with the cross-head speed of 50 mm/min and at room temperature is represented in Figure 5.26. It is found that the blend has a typical behavior of tough material. The tensile strength at break and elongation of the blend with compatibilization are increased relative to the non-reactive blend. The areas under the stress-strain curves, absorbent energy per unit volume, indicate that the reactive blends are tougher than that of the blends without compatibilization. The tensile behavior of the blend of PP/BT is illustrated in Figure 5.27 and 5.28, respectively. It is observed that the tensile strength at yield (σy) and modulus of elasticity (E) of the reactive blends are reduced relative to the physical
Figure 5.21 SEM micrographs of POE/BT without compatibilization: a) X200; b) X2000
Figure 5.22 SEM micrographs of POE/BT with compatibilization: a) X200; b) X2000
Figure 5.23 SEM micrographs of PP/BT without functional POE as a modifier: a) X200; b) X2000
Figure 5.24 SEM micrographs of PP/BT with functional POE as a modifier: a) X200; b) X2000
Figure 5.25 Modulus of elasticity for the blend of POE/BT with varied amount of black toner

Figure 5.26 Stress-strain behavior of the blend of POE/BT (50/50) with the cross-head speed of 50 mm/min and at room temperature
Figure 5.27 Tensile properties of the blend of PP/BT with varied amount of black toner (BT): a) tensile strength at yield ($\sigma_y$); b) modulus of elasticity (E)
Figure 5.28 Stress-strain behavior of the blend of PP/BT (80/20) with the cross-head speed of 2 mm/min and at room temperature blending. The areas under the stress-strain curves of the reactive blends are larger than that of mechanical ones. It is suggested that the reactive blends of PP/BT have better impact resistance than that of correlated physical ones.

5.3.4.3 Impact strength

Results obtained from the impact test of the blends of POE/BT and PP/BT with and without compatibilization are presented in Figure 5.27 and 5.28, respectively. The notched Izod impact strengths in Joule/meter (J/m) are plotted against the black toner content in weight percentage. It exhibits a synergistic behavior for these blends. This suggests that these blending systems may be more mechanical compatible compared to other systems such as HDPE/BT, etc. The mechanical blends have lower impact strength
Figure 5.29 Impact properties of the blend of POE/black toner (BT) with and without compatibilization.
than that of the correlated reactive ones, suggesting the poor interfacial adhesion between the phase of BT and the matrix (POE or PP), in which under stress, the interface may be failed. However, there is an improvement of impact resistance when compatibilization is used. And it is consistent with SEM micrographs shown in 5.3.4.1 and the prediction mentioned in the stress-strain behavior. It is that the reactive blends should have better impact property than that of mechanical ones.

5.4 Conclusions

POE-g-GMA is an effective compatibilizer for the blending system of PP and PC. With addition of POE-g-GMA, the size of PC domains is significantly reduced and interaction between different phase is greatly improved. The mechanical properties of PP/PC/POE-g-GMA, such as Izod impact strength and flexural properties, are much higher than the values for the blending system of PP/PC at the same content of PC. These features can be tentatively attributed to the fact that the in-situ compatibilizer of PP-g-GMA-co-PC which can reduce the interfacial tension and promote the adhesion of the two phases. Compatibilizing capacity of the reactive copolymer is not exclusively dependent on the total reactive group concentration in the blend. The properties of the reactive copolymer are found to have a significant influence on the compatibilizing capacity. A moderately functionalized copolymer offers better compatibilization performance than a highly functionalized copolymer.

It has been found that compatibility is an important factor influencing the orientation of the dispersed PA 6.6 phase in the PP matrix. Incompatibility is
advantageous for fibrillation. The size of the dispersed phase (PA 6,6) undergoes a 100-fold reduction from 50 microns to sub-microns with the in-situ compatibilized blends with glycidyl methacrylate (GMA) modified POE (POE-g-GMA). Due to compatibilization, the reactive blends have the lower melting temperature (Tm) as well as crystallinity (Xc) of PA 6,6 than those of their mechanical counterparts. The mechanical properties of the reactive blends, such as yield stress (σy) and modulus of elasticity (E), are improved while the elongation is reduced relative to mechanical ones. It is also found that in presence of POE-g-GMA, the adhesion between PA 6,6 phase and PP matrix is improved.

The blending system of PS/POE was found to be incompatibilibe. All of the mechanical blends studied show a two-phase morphology. With compatibilization, the domain size and coalescence of POE are reduced significantly compared to the non-reactive blends of PS/POE. Due to the compatibilization of POE-g-GMA, the glass transition temperature (Tg) of PS matrix is shifted to lower temperature. In-situ compatibilization is also found to improve interfacial adhesion between the minor POE phase and PS matrix, giving rise to the enhancement of tensile strength, modulus of elasticity and impact strengths. It is conclude that the compatibilization can significantly improve the mechanical behavior of the blends of PS/POE. This improvement of impact property may be due to the action of POE as impact modifier since it is able to absorb impact energy.

The synergistic increase in the impact property with a surprise was found in the blends of POE for recycling of xerographic black toners (BT). It is indicated that the loss of mechanical properties, compared with the blend components, depends on not only the
domain sizes of the dispersed black toner phase but also interfacial adhesion. Compatibilization is also found to improve the dispersion and interfacial adhesion between the black toner phase and the matrix (POE or PP), giving rise to the enhancement of the impact strengths. The tensile strengths and modulus of elasticity of the reactive blends of POE/BT are increased while those of reactive blends of PP/BT are reduced. In the reactive blends of POE/BT and PP/BT, the domain sizes and coalescence of black toner are reduced significantly relative to the mechanical blends. Better dispersion and interfacial adhesion between black toner and the matrix (POE or PP) are observed with compatibilization. An additional advantage of in-situ functional POE is that it could dramatically improve the impact strength of the blend duo to its action as an effective impact modifier.
CHAPTER 6
CONCLUSIONS AND FURTHER RECOMMENDATION

6.1 Summary and Conclusions

Engage® polyolefin elastomers (POE) are novel ethylen-octene copolymers synthesized by single-site metallocene catalyst. This technology allows extraordinary control over molecular architecture, properties, and rheology. Because of the molecular geometry of single-site metallocene catalyst, POE has distinctive features such as high molecular weight (MW), narrow molecular weight distribution (MWD), homogenous comonomer distribution, and low cost relative to conventional Ziegler-Natta catalyst. Polymer blending is a economical way to create new materials. Blends of POE will open up new markets and applications because its rubber properties makes it possible to use polyolefin materials where they have never been used before. What are the benefits of using POE? POE can be employed as excellent candidates not only for low-cost impact modifiers but also for long-time plasticizer to some blending systems.

In polymer blends, there exist some phenomena such as miscibility and phase separation. It is well known that there are just serveral polymer pairs which are thermodynamical miscibility such as PS/PPO, PS/PPE, PVC/PBT, and so on. Most of polymer blends exist phase separation which goes along with poor interfacial adhesion as well as serious agglomeration. However, in these multiphase polymer blends, there exist the potential opportunities for combining the attractive features of each material or
improving the deficient characteristics of a particular mater. In order to approach the goals, the multiphase blends should have strong interfacial adhesion and desired morphological structures.

In order to investigate the immiscibility of POE with other polymers, physical blends of POE were studied. Morphology of the blends was studied by SEM and AFM. It is indicated that all of the blends have phase-separated, agglomeration, poor interfacial adhesion, and bigger domain size of POE except for HDPE/POE. The blends of HDPE/POE have an unique nano-structure which is rarely reported in typical text books of polymer blending. Thermal analysis was carried out by DSC and DMS. There exist two Tg in these blends, which reflect phase-separated. Crystalline structure of POE blending with semi-crystalline polymer was explored by XRD. XRD pattern of the blend of HDPE/POE is simply superimposed. It is illustrated that crystalline structure of HDPE phase does not change during mixing. However, crystalline structure of PP phase in the blend of PP/POE converts from α-form to γ-form during blending. On the basis of morphological and thermal analytical study, all of the blends of POE are thermodynamically immiscible.

Fracture behavior of all physical blends of POEs is increased except for PMMA/POE. It is of interest to note that notched Izod impact strength of HDPE/POE and PP/POE is improved by 7-fold and 10-fold respectively. It goes without saying that POE should be a very good candidate of low-cost impact modifier. Tensile behavior of all blends of POEs indicates that there are common characteristic such as decrease in yield strength and modulus of elasticity as well as increase in elongation. It is evident that POE
could be a good candidate of long-time plasticizer. According to mechanical behavior, the mechanical compatibility of physical blends of POE is as follows:

a) PMMA/POE is incompatible;
b) PS/POE and PC/POE are semi-compatible;
c) HDPE/POE and PP/POE are compatible.

On the basis of the study of physical blends of POE, POE should be an excellent candidate of low-cost impact modifier and long-time plasticizer for PP/POE. However, there still exist some problems such as agglomeration and interfacial adhesion. Grafting copolymer used as compatibilizing agent is an effective way to retard phase separation as well as improve interfacial adhesion. POE-g-glycidyl methacrylate (GMA) could be chosen as a compatibilizer employed for the blending system of PP/POE. POE-g-GMA was prepared by free radical melt grafting. From FTIR and $^1$HNMR spectroscopy, it is conformed that GMA is successfully grafted onto POE. We first report that GMA can be grafted onto POE. According to the calibration curve evaluated by $^1$HNMR, DG of GMA onto POE was calculated by FTIR spectroscopy. In order to simulate the process of interfacial modification and degradation, the rheological behavior of the blends were examined. A positive deviation of viscosity relative to the mechanical blending, reflecting GMA successfully grafted onto POE in the reactive compounding, is found in the torque curves of the blends. A degradation (β-scission) reflected by small decrease in viscosity in melting steady state, is also found during the melt grafting processing.

POE-g-GMA working effectively as compatibilizer in the blending system is confirmed by Tg of POE phase and Tg of PP matrix shifted inward. The reactive blends have lower Tm of PP matrix than that of physical blends. Xc of PP matrix varies
inversely as the concentration of GMA monomer. Morphology was studied by SEM. It is indicated that there are not only a more homogeneous dispersed and smaller spherical-shape domain of POE but also less agglomerated of POE and strong interfacial adhesion between POE and PP in the blends. On basis of the study of POE domain sizes, there is an impressive drop for the number-average domain size (Dn) and weight-average domain size (Dw) of POE phase when reaching to Critical Micelle Concentration (CMC), c.a. 0.6 wt% of DG of GMA.

According to the mechanical behavior of the blends, yield tensile strength (σy), modulus of elasticity (E), flexural strength (W) and tangent modulus of elasticity (E_{flex}) of the reactive blends are decreased relative to the mechanical ones. The results illustrated that POE could be an effective long-time plasticizer in this blending system. A typical deformation of strong and tough materials is displayed by the stress-strain behavior of the reactive blends at room temperature. Notched impact strength of the reactive blends can be dramatically increased by c.a. 25-fold relative to virgin PP. Un-notched impact strength of the reactive blends can reach to c.a. 1900 (J/m), which absolutely competes with PP modified by EPDM. Functional POE has lower cost comparing with commercial functional EPDM. It is also of interest to note that impact behavior of the blends can be significantly improved through controlling the morphological structures by functional POE as an effective impact modifier.

POE-g-GMA should have great potential applications for multiphase blending systems because epoxy functional group of GMA can be easily reacted with amine, carboxlic acid and alcohol groups in order to form in-situ compatibilizers on the interfaces. In order to investigate the feasibility of functional POE as compatibilizer used
in multiphasr blending, there are different blending systems which were initially examined such as PP/GFR-PC, PP/PA 6,6, PS/POE, POE/xerographic black toner (BT), and PP/BT. In all of the multiphase blending systems, there exist some common features of morphology for the reactive blends such as phase-separated morphology, less agglomeration, better interfacial adhesion and smaller domain size of minor phase relative to physical blends. It is illustrated that fuctional POE can be employed as effective compatibilizers for the multiphase blending systems. The results of thermal analysis indicate that there are lower Tm and Tg effects in the blending systems. Again, it is conformed that functional POE can be used compatibilizer in the blending. Mechanical properties of reactive multiphase blending can be improved comparing with the physical blends. It is conclude that functional POE can be used as a compatibilizer in the multiphase blending systems, such as PP/GFR-PC, PP/PA 6,6 and PS/POE. And they were successfully employed for recycling xerographic toners. The synergistic increase in impact behavior is found in these reactive blends.

6.2 Further Recommendation

Polyolefin elastomer (POE) will give us a whole new spectrum of design possibilities. On the basis of fundamental study for POE and its blending, it may be seen that POE can be used as low-cost impact modifier and long-time plasticizer. On the basis of previous study, we have some further recommendation as follows:

1. The screen test for thermodynamical miscibility and mechanical compatibility of POE should be further carried out at a wide range of commercial polymers by mechanical
mixing because the effects of chemical structure and molecular weight of other polymers on POE are different. From the point of view of thermodynamics, this examination is absolutely necessary. It will indicate which polymer is thermodynamically favorable with POE. There will exist some attractive properties of the new promising blends of POE, which can be predicted by mixing rules.

2. POE should be functionated with different functional groups through free radical melt grafting. POE could be grafted by maleic anhydride (MA), functional peroxides, oxazoline and so on. In order to control the reactive process, the mechanism and kinetics of grafting as well as degradation should be further studied. Low-cost functional POE can be commercialized by optimization to reach the best property-cost ratio.

3. Applications of functional POE employed in multiphase blending systems should be further explored. In these multiphase blends, there exists a lot of opportunities for combining attractive features of each material in order to reach the desired behavior. For example, very many different fillers, such as glass fibers graphite fibers, carbon blacks, aramid fibers and so on, have some surface groups after surface treatments. Functional POE could be used as compatibilizer to make multiphase blends or polymeric composites. Also functional POE could be employed as “surfactant” to make organic-inorganic nanocomposite, where the inorganic portion is so finely dispersed as to form transparent materials. There may exist some interfacial bonding between the inorganic and organic phases such as hydrogen bonding and covalent bonding.
4. Although the feasibility using functional POE as compatibilizer for polymer blending is a critical part in this whole plan, there still exists a gap between research and industry. Design of experiments (DOE) could be an important and effective tool for the gap in order to reach the optimal property-price ratio of the product. DOE is of particular value for product design, conducting tests and experiments, improving manufacturing processes or troubleshooting problems on the production line or in the field. Benefits of the modern statistical methods are the melding of the technical knowledge and experience of the scientist and engineer with the arts of statistical analysis and design to produce better products and services at lower costs.
APPENDIX:
SUMMARY OF THE BLENDS AND COMPATIBILIZERS MENTIONED

Table A.1 Physical blends of polyolefin elastomer (POE)

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<td>m-PE</td>
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Table A.3 Functional polymers with melt free-radical grafting

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Table A.5 Blends of polycarbonate (PC)

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REFERENCES


BIOGRAPHICAL SKETCH

Hui Tang was born in Beijing, in the People’s Republic of China. He received a B.S. degree in polymer material science from Beijing University of Aeronautics and Astronautics in July 1989. From September 1988 to December 1993, he worked in the Beijing Tainma Special Material Development Co., as an engineer. From August 1994 to December 1996, he studied analytical chemistry under the supervision of Professor Conttrell, and obtained an M.S. degree in chemistry from Florida A&M University in December 1996. He started the Ph.D. program in the Department of Materials Science and Engineering at the University of Florida in January 1997, under the supervision of Professor Beatty.

Hui Tang is married to Wei Lu. They have two daughters, Aubrey Y. Tang, who was born in Tallahassee, Florida, and Alicia Tang, who was born in Gainesville, Florida.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Charles L. Beatty, Chair
Professor of Materials Science and Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Ronald H. Baney
Associate Engineer of Materials Science and Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Stanley R. Bates
Associate Engineer of Materials Science and Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Assistant Professor of Materials Science and Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Arthur L. Fricke
Professor of Chemical Engineering
This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 2000

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Dean, College of Engineering

[Signature]
Dean, Graduate School