ABSTRACT

REACTIVE MODIFICATION OF POLYESTERS AND THEIR BLENDS

by
Chen Wan

As part of a broader research effort to investigate the chemical modification of polyesters by reactive processing a low molecular weight (MW) unsaturated polyester (UP) and a higher MW saturated polyester, polyethylene terephthalate (PET), alone or blended with polypropylene (PP) were melt processed in a batch mixer and continuous twin screw extruders. Modification was monitored by on-line rheology and the products were characterized primarily by off-line rheology, morphology and thermal analysis. Efforts were made to establish processing/property relationships and provide an insight of the accompanying structural changes. The overall response of the reactively modified systems was found to be strongly dependent on the component characteristics, blend composition, type and concentrations of reactive additives and processing conditions.

The work concluded that UP can be effectively modified through reactive melt processing. Its melt viscosity and MW can be increased through chemical reactions between organic peroxides (POX) and chain unsaturation or between MgO and carboxyl/hydroxyl end groups. Reactive blending of PP/UP blends through peroxide modification gave finer and more uniform morphology than unreacted blends and at a given PP/UP weight ratio more thermoplastic elastomers-like rheological behavior. This is due to the continuously decreasing viscosity ratio of PP/UP towards unity by the competing reactions between POX and the blend components and formation of PP-UP copolymers which serve as *in-situ* compatibilizers to promote better interfacial adhesion. Kinetics of the competing reactions were analyzed through a developed model.

In addition to POX concentration and mixing efficiency, rheology and morphology of UP/PP bends were significantly affected by the addition of inorganic and organic coagents. Addition of coagents such as a difunctional maleimide , MgO and/or an anhydride functionalized PP during reactive blending offers effective means for tailoring the desired rheological and structural characteristics of the final products for potential applications such as low density extrusion foaming or compatibilization of immiscible polymer blends. Important modification conditions through coagents are identified and reaction mechanisms are proposed

A high MW saturated polyester, PET, can also be rheologically modified in extruders through low MW multifunctional anhydride and epoxy compounds by chain extension/branching. Several such modifiers were successfully screened in terms of their reactivity towards PET under controlled reactive extrusion conditions. A dianhydride with medium reactivity was then successfully used in a one-step reactive modification/extrusion foaming process to produce low density foams. A similar process was successfully used to produce small cell size foams from a four component system containing PET, PP and lesser amounts of a low molecular weight multifunctional epoxy compound and an acid functionalized polyolefin, the latter acting as compatibilizers.

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by
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家

唤出一轮明月
映我满怀杯雪

Dedicated to my beloved family

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LIST OF ACRONYMS

BGPM	N, N'-bis [3(carbo-2', 3'epoxypropoxy) phenyl] pyromellitimide
BTDA	3,3', 4,4' Benzophenone tetracarboxylic anhydride
DMT	dimethyl terephthalate
DSC	differential scanning calorimeter
EG	ethylene glycol
EVOH	ethylene vinyl alcohol
EVA	ethylene vinyl acetate
FTIR	Fourier transform infrared spectrophotometer
GMA	glycidyl methacrylate
I. V.	intrinsic viscosity
MA	maleic anhydride
MFI	melt flow index
MWD	molecular weight distribution
PBT	poly (butylene terephthalate)
PB3200	Polybond 3200
PDMI	N,N'-1,3-phenylenedimaleimide
PE	poly (ethylene)
PET	poly (ethylene terephthalate)
PMDA	pyromellitic dianhydride
POX	peroxide
PP	poly (propylene)
SEBS	styrene-ethylene-butadiene elastomer

TGA	thermogravimetric analysis
TGDDM	tetraglycidyl-4’, 4”-diamino diphenyl methane
TGG	triglycidyl glycerol
TGIC	triglycidyl isocyanurate
THF	tetrahydrofunan
UP	unsaturated polyester

CHAPTER 1

INTRODUCTION

The term polyester encompasses a very wide selection of thermoplastic and thermosetting polymers. A polyester resin can be made up of one or more dihydric or polyhydric alcohols (or their derivatives), one or more saturated dibasic or dicarboxylic acids (or their derivatives), and one or more unsaturated dibasic or dicarboxylic acids and their derivatives (Doyle, 1969). Of each of those basic components, there are literally dozens from which to choose, and when combinations of one or more of each are used, there are many thousands of completely different resins possible, each with properties unique within itself. There are many additives, usually used in minute quantities, which also have quite definite effects on the properties. It is believed that, at the present time, there are few other organic polymers or groups of polymers that can have this wide versatility (Maréchal, 2002). Quite apart from the versatility of properties obtainable with polyesters, there are other advantages such as low cost, processability and great availability, especially in the market of thermoset polymers (Goodman, 1986), that make polyesters the organic polymers of choice for a variety of applications.

However, polyesters are not prescribed as the answer to all products and processes in the plastics field, far from it. There are many processes and end products for which polyesters simply would not be suitable. In order to extend their applications, post-reactor modification or blending with one or more components to improve or tailor their properties for certain purposes are gaining more and more interest. Extensive research and development work has been conducted and reported in these areas (Brown, 1992, Xanthos, 2002).

In the present work, two types of polyesters, namely, high molecular weight (MW) saturated polyesters exemplified by poly(ethylene terephthalate) (PET) and low MW unsaturated polyesters exemplified by the reaction product of a glycol with saturated/unsaturated acids, have been selected to study the properties of post reactor modification products for novel applications. The following sections serve as an introduction to these two types of polyesters.

1.1 High Molecular Weight Thermoplastic Polyester (PET)

1.1.1 Synthesis, Properties, Applications

Among those polyesters, PET, first introduced as a material for synthetic fibers (Trevira,^{TM}) in 1953, has been widely used for nearly fifty years now and it has already carved out a leading position in applications as diverse as fibers, films, and molded products. Other high MW thermoplastic polyesters such as poly (butylene terephthalate) (PBT) and poly (ethylene naphthalate) (PEN) also share a market portion. But PET is the unquestioned leader and ranks quite high among thermoplastic polyesters. It seems worth recalling that in its classical application, the textile industry, PET fibers could resemble cotton, wool, or silk fibers and, what is more important, this could be effected without any chemical modification. While PET has rather limited use as an injection moldable engineering plastic, PET films (Mylar^{TM}, Hostafan^{TM}), because of their excellent electrical properties, find wide applications in the electronics and electrical industries. The application of PET for packaging purposes, especially for carbonated soft drinks, is still a monopoly and nowadays this is the main reason for its annual production growth of 10% (Fakirov, 2002). Such opportunities for PET applications are related to its unique properties, originating mostly from its chemical/structural characteristics. The high crystalline melting temperature (270°C) and stiff polymer chains of PET result in not only good mechanical properties up to 150-175°C, but also good chemical, solvent, and hydrolytic resistance (Odian, 1991).

Poly(ethylene terephthalate) can be prepared by several methods. Among them, two routes are mainly used in industry. The first is by transesterification from dimethyl terephthalate (DMT) and ethylene glycol (EG) (Figure1.1a) and the second by direct esterification from terephthalic acid (TPA) and EG (Figure 1.1b). Although producing the same polymer, they differ in the monomers used, the polymerization process details and the low MW by-products, as shown in the following reactions (Aharoni, 2002):

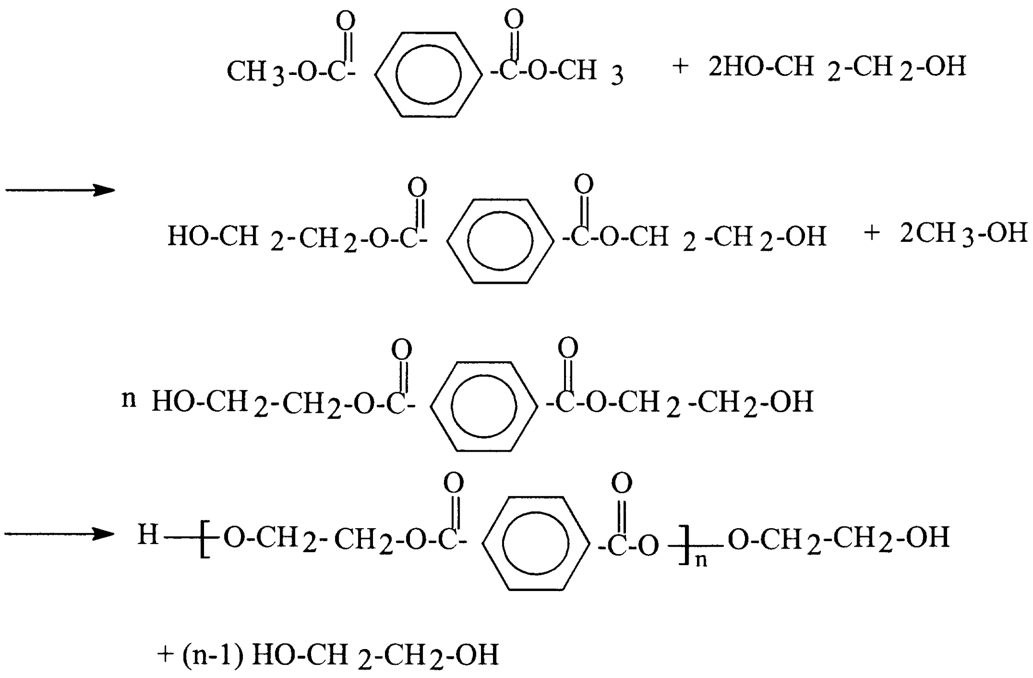

Figure 1.1a PET synthesis from dimethyl terephthalate and ethylene glycol.

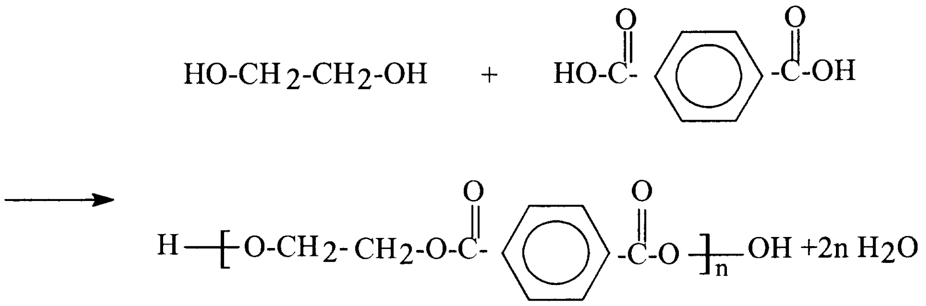

Figure 1.1b PET synthesis from terephthalic acid and ethylene glycol.

Poly(ethylene terephthalate) has several noteworthy properties that affect its processing behavior and also its modification products. It can be obtained in various states of order such as amorphous, “oriented mesomorphic”, spherulitically crystallized and oriented crystallized due to its distinct slow crystallization rate. The low melt strength of conventional low MW and narrow MWD PET also makes film blowing, extrusion blow molding and low density extrusion foaming techniques not particularly suitable for these polymer grades. Thus, the selection of the appropriate grade of PET for a specific end-use requires considerable care (Göschel, 2002). Normally the first consideration is the molecular weight of the polymer, which is generally reported as intrinsic viscosity (I.V.) or limiting viscosity number, $[\eta]$. The relationship between $[\eta]$ and molecular weight depends on the conditions of measurement. Thus, $[\eta]$ values should strictly be compared only when obtained by means of the same measurement method. To provide an approximate idea of I.V.-MW relationships, I.V. values of 0.43, 0.60, 0.72, and 1.00 dL/g correspond to number average molecular weights of 10000, 18000, 24000, and 40000 g/mol respectively (Gupta and Bashir, 2002). Table 1 summarizes the intrinsic viscosity range of available PET resins for three major application areas.

Table 1.1 Intrinsic Viscosity Range of PET

PET	$[\eta]$ (dL/g)
Fiber grade	
* Textile	0.40-0.70
* Technical	0.72-0.98
Film Grade	
* Biaxially oriented film	0.60-0.70
* Sheet grade for thermoforming	0.70-1.00
Bottle grade	
* Water Bottle	0.70-0.78
* Carbonated soft drink grade	0.78-0.85

There are certain rheological requirements for PET if it is to be used in application areas such as extrusion blow molding or extrusion foaming where melt strength is important (Xanthos, 2002). PET, as a linear condensation polymer, generally has low melt strength because of its linear chain structure and relatively low degree of polymerization. During the conventional film blowing and extrusion blow molding processes, where biaxial stretching is applied to the melt, the polymer cannot even support its own weight long enough for controlled biaxial stretching to take place. Thus, some PET bottles are produced via a different technology called injection-stretch-blow molding developed by Du Pont (Wyeth, 1973) or using an extrusion blow molding grade PET. Such grades have been melt modified by introducing long chain branching and/or widening its molecular weight distribution (MWD) resulting in higher melt strength (Xanthos, 2002).

Polymeric foams have several advantages over base polymers such as excellent insulating and cushioning properties and very good strength to weight ratio (Frisch, 1991). The favorable cost/performance characteristics of solid PET have also been extended to low density foams produced by single-layer extrusion or coextrusion for thermoforming and lamination. Compared to polyolefins and polystyrene foams, PET foams have several potential applications taking advantage of the combination of good mechanical properties, dimensional stability of the semi-crystalline resin at temperatures up to 200°C, and recyclability (Xanthos, 1998). Extrusion foaming of most plastic resins has been carried out successfully for some time, especially for polymers such as polystyrene and polyethylene characterized by notable strain hardening behavior, which is identified as a critical property for foamability (Gendron, 1998). However, most PET resins, since they are rheologically characterized by low values of melt viscosity, poor shear sensitivity, approaching Newtonian behavior and low melt elasticity, usually expressed as melt strength and extrudate swell, have poor foamability; they can not sustain the elongational deformations during the cell growth phase of extrusion foaming, thus allowing uncontrolled cell expansion and unstable growth of bubbles. Some other difficulties are related to the required high processing temperatures (260-290°C), the absence of a broad extrusion foaming window as compared to amorphous resins, the slow rate of crystallization and limited process stability, and possible interference of crystal nucleation with bubble nucleation. In addition, the sensitivity of PET to thermal, hydrolytic or thermooxidative degradation may lead to further reduction in MW and the formation of various by-products that could affect the foaming process (Xanthos, 1998).

1.1.2 Chemical Modification

In order to meet the above specific cost/performance/processability requirements, chemical modification or blending with a second component are effective ways to improve PET's properties and extend its use in applications which might otherwise have been unattainable. Reactive modification of PET alone may be accomplished with various reagents in the molten or solid state. Blending PET with a second polymeric component such as a polyolefin normally results in an immiscible blend due to the structural differences of the components. Thus, further modification is always needed and usually accomplished by means of reactive compatibilizers that are either by added separately or formed *in situ* during the compounding step (Xanthos, 2002).

Reactive modification of PET itself to increase MW and reduce the end-group carboxyl and hydroxyl contents is desirable for improving mechanical, chemical and rheological properties. Solid-state polycondensation is an applicable technique to complete the polymerization of PET and increase its MW. By 'solid stating' is meant that the polymer pellets remain in the solid state, below their melting temperature, during additional chain extension (Aharoni, 2002). The process may be divided into two separate stages. In the first stage PET pellets are fed into crystallizers to achieve a highly crystalline surface; after pre-dried at about 160°C under vacuum, they are transferred into preheaters and purge vessels under conditions set for promoting the continuing crystallization and polymer chain extension to increase MW. The disadvantages are slow reaction rate and special equipment requirements for large-scale operations. For these reasons, the use of the so-called chain extenders appears to be more attractive. These chain extenders are generally bi- or multi-functional compounds which react very easily with end groups such as -COOH, -OH and NH_2 of macromolecules including polyesters and polyamides. When these poly-functional compounds react directly with polyester end groups, they form bridges between the chains and increase viscosity and MW significantly (Xanthos, 2002). This coupling effect can take place during the last stage of the polymerization reaction, during solid stating (Al Ghatta, 1994), or even in an extruder where fast reactions with polymer chain ends in a nearly irreversibly manner with no volatile products are possible. The chain extended/branched PET has rheological characteristics that are suitable for applications such as extrusion of low density foams.

Blending PET with a second component, and, in particular, polyolefins, is another effective modification way to provide an attractive balance of mechanical, rheological and barrier properties and processability. Often, these polymers are found in the post-consumer municipal commingled plastic waste. The possibility of recycling these mixtures without any separation could be beneficial for the economics of recycling. The incompatibility of these two classes of polymers gives rise to coarse blend morphology and poor mechanical properties. Compatibilization is then a necessary step to obtain blends of PET and polyolefins with good properties from both virgin and recycled materials. In order to achieve compatibility, a functionalized third component, as for example, PP-*g*-MA (polypropylene-graft-maleic anhydride), PE-g-MA (polyethylene-graft-maleic anhydride), PE-g-AA (polyethylene-graft-acrylic anhydride), SEBS-g-MA (styrene-ethylene-butadiene elastomer-graft-maleic anhydride) and EVA (ethylene vinyl acetate copolymer) based graft-copolymers are added. An extensive literature search on those compatibilization methods is included in the following Chapter 3.

1.2 Unsaturated Polyesters (UP)

Unsaturated polyesters (UP) resins are among the four most important thermosetting resins besides phenolic, amino and epoxy resins and they represent about 20% of the total volume of thermosets. They are prepared in two steps. The first step is to synthesize a linear polyester of low MW of about 700-4000, containing carbon-carbon double bonds distributed in the chain. The polycondensation reaction results in an oligomer containing a significant content of terminal –COOH and –OH groups that may be available for further reaction (Figure1.2). This oligomer is then dissolved in a vinyl monomer (usually styrene) containing polymerization inhibitors. This composition can be stored for months. The polymer solution known as "unsaturated polyester resin" is then mixed with a free radical initiator such as a peroxide, often in the presence of promoters, compounded with fillers, reinforced with glass fibers and crosslinked by the copolymerization of unsaturated double bonds in the polyester with the vinyl monomer used as solvent. Glass fiber reinforced laminates for large structures such as boat hulls can be prepared by hand lay-up techniques. Reinforced structures for car bodies and other applications can be prepared by matched-die molding of bulk molding compounds (BMC) and sheet molding compounds (SMC) (Kia, 1993). The fillers and chemical thickeners such as metal oxides serve to modify rheological properties and improve processability. The major markets for UP resins include transportation, marine, construction, electrical and corrosion. Other applications include such diverse items as decorative furniture casting, simulated ornamental stone, buttons, trays, bowling ball, skis, surfboards, safety helmets, chemical processing equipments, missile shells, rocket motor cases.

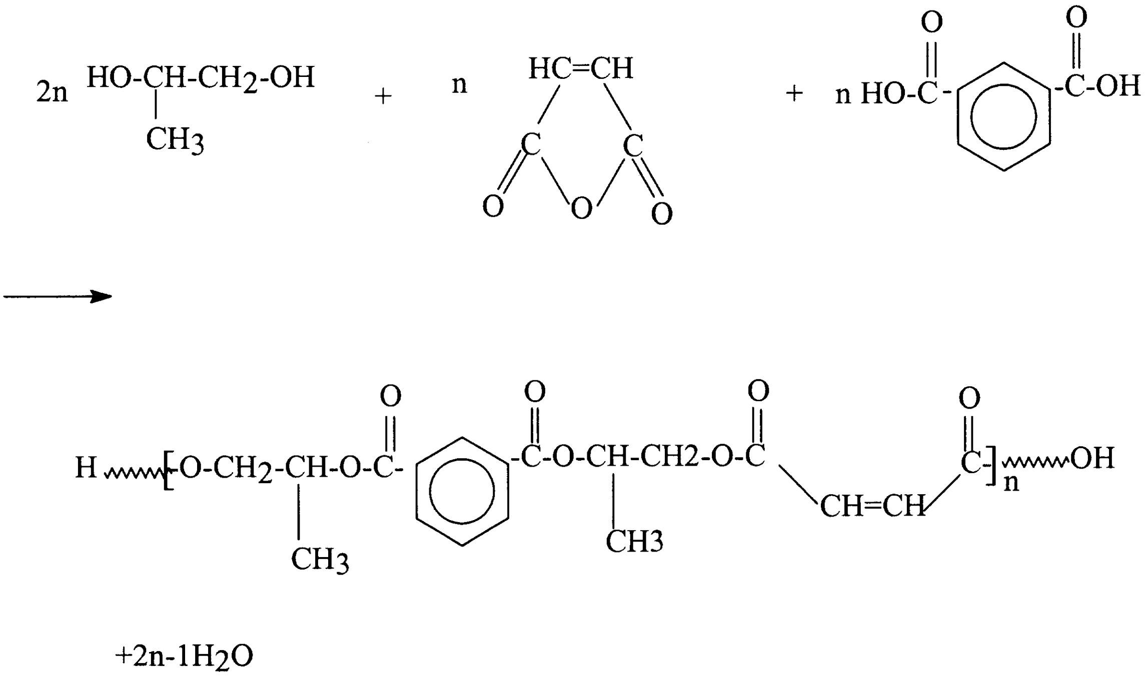

Figure 1.2 Unsaturated polyester synthesis from propylene glycol, maleic anhydride and isophthalic acid.

Unsaturated polyester resins are based on several components that may be combined in different ratios. Those components are: (a), glycols; (b), unsaturated acids and anhydrides; (c), saturated modifying acids and anhydrides; and (d), crosslinking monomers. The most widely used glycol is 1, 2-propylene glycol since it has no tendency to crystallize, is compatible with styrene (the most frequently used crosslinking monomer) and is available at low cost. For unsaturated acids, maleic acid and its anhydride or fumaric acid are mostly used for economic reasons. Saturated modifying acids are used in order to increase the distance between the double bonds along the polymer chain and control crosslink density and flexibility. The most widely used modifying saturated compound is phthalic anhydride due to its good compatibility with styrene and reasonably low price. Often, isophthalic anhydride is used where higher heat distortion temperatures and better alkali resistance are required. In summary, the choice of components is dictated by the properties needed for a particular application (Burns, 1982).

Many varieties of UP resins are now commercially available as they can be formulated to produce cured plastics ranging from hard and brittle to soft and flexible. The crosslink density, which deeply affects mechanical properties of UP resins, also can be controlled by the ratio of maleic anhydride to saturated acid whereas the rigidity/flexibility depends on the structure of the employed glycol and saturated acid.

CHAPTER 2

OBJECTIVES

There are two major objectives in this research: one is to develop a procedure to chemically modify a high MW saturated polyester, PET, and optimize its compatibility with PP by the introduction of various additives. Such modified PET based components having modified structural and rheological characteristics may be suitable in different applications such as low density extrusion foaming. The second objective is to modify a low MW unsaturated polyester, UP, and improve its compatibility with PP by introducing various additives such as peroxide and other reagents such as N,N'-1,3-phenylenedimaleimide (PDMI) and MgO. Such PP or UP based compositions with modified structural and rheological characteristics may be suitable as compatibilizers in PP/high MW polyester conventional blends and could also offer advantages in extrusion foaming.

2.1 Reactive Modification of Saturated Polyester (PET) and its Blends

Extrusion foaming of PET and its blends with PP to low densities is difficult due to its low melt viscosity, poor melt strength and melt elasticity and incompatibility with polyolefins. This section of the study focuses on understanding the structural modification of PET and its blends with PP during the extrusion process by using low MW multifunctional epoxides and the effects of the modification on the rheological properties. The objectives here are to understand the relationship between structure, properties and processing and eventually improve the processability, particularly the foamability of PET and its blends with PP, by reactive modification through melt processing.

2.2 Reactive Modification of Unsaturated Polyester (UP) and its Blends

Melt blending of the oligomeric UP with PP in order to functionalize the PP or form a composition with characteristics similar to those of thermoplastic elastomers is investigated in this work as a route to novel compositions. PP and UP are totally immiscible due to their different structural characteristics. Both have high reactivity in free radical reactions but respond in opposite ways to peroxide: PP degrades due to β-chain scission while UP crosslinks due to macroradical recombination. During these competing reactions within PP/UP blends, there are some possibilities to form PP-UP copolymers with graft or block copolymer structures, in the presence of coagents. The final products could have properties that make them suitable as compatibilizers in blends of high MW thermoplastic polyesters with polyolefins, or as rheological modifiers during extrusion foaming. Specific objectives are as follows:

1. Investigate the effect of peroxide and other reagents on the viscoelastic properties of the blend components at various concentrations and develop kinetic data for the simultaneous reactions;
2. Investigate the compatibilizing role of an organic peroxide in the reacted PP-UP blends in the presence of other reagents such as PDMI and MgO;
3. Develop optimal "reaction-mixing" process protocols;
4. Investigate the thermal, morphological, rheological and other properties of unreacted and reacted PP-UP blends;
5. Develop a functionalized PP with desirable properties to be used as compatibilizer in PP/high MW polyester blends;
6. Optimize the reactive blending process developed in batch mixers and extend in continuous modification by reactive extrusion.

CHAPTER 3

LITERATURE REVIEW

This chapter consists of two parts referring to the two different polyesters, respectively. The first part of this review on the chemical modification of PET presents previous work reported by various authors. The second part illustrates with some examples the vast possibilities offered by the chemical modification of UP and its blends with thermoplastics. Considering the limited information available for UP/thermoplastics blends, the review will concentrate on some systems with similar modification routes.

3.1 Reactive Modification of High MW Polyester (PET)

The concept of reactive modification is defined here not only as an application of traditional reactions of organic chemistry to macromolecules, but also as an application of reactive blending of two or more components through reactive compatibilization. Thus, modification of PET may involve not only PET homopolymer but also a mixture of two or more polymers. Reactive modification of PET itself can be accomplished through a variety of reagents in the melt state, solution, or on the surface of pellets. The modification of PET in the melt state can be implemented in continuous extruders, in the complete absence of solvents. Modification of PET blends is usually accomplished through reactive compatibilizers that may be added separately or formed *in situ* during the compounding step.

Four categories of melt reactions during the reactive modification of PET are classified in terms of their applications: (i) controlled degradation, used to adjust molecular weight or to produce monomers/oligomers (solvolytic tertiary recycling); (ii) capping of carboxylic end groups, especially in fiber-forming polyesters; (iii) chain extension/branching of the otherwise low MW and narrow MWD polyesters in order to produce materials with increased melt viscosity and melt strength for applications such as extrusion blow molding or low density extrusion foaming; and (iv) production of compatibilized blends with fine microstructure and enhanced properties by the addition of elastomers (for impact modification) or other thermoplastics (Xanthos, 2002). The latter two categories are focused in this study.

3.1.1 Chain Extension/Branching of PET

Chain extension/branching reactions of polyesters with polyfunctional coupling agents have been used to increase their viscosity and molecular weight, and improve their mechanical properties or rheological characteristics. The modified products also have a much lower carboxyl content, resulting in improved thermal and/or hydrolytic stability.

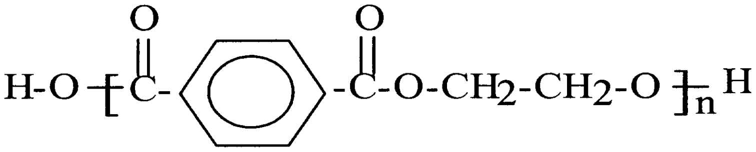

Figure 3.1 General chemical structure of PET.

Figure 3.1 shows the typical macromolecular formula of PET made from equimolar quantities of diacid and glycol. It can be seen that PET normally has two different functionalities as end groups. These two terminal nucleophilic groups, carboxyl and hydroxyl, have high tendency to form covalent bonds with suitable electrophilic functionality, such as cyclic anhydride, epoxide, oxazoline, isocyanate, or carbodiimide (Brown, 1992). Multifunctional coupling agents with the above functionalities react with two or more PET chains and are incorporated into the final chain-extended or branched polymer, thus, building molecular weight. Figure 3.2 lists some specific reactions between the carboxylic acid end groups with the above electrophilic functionalities.

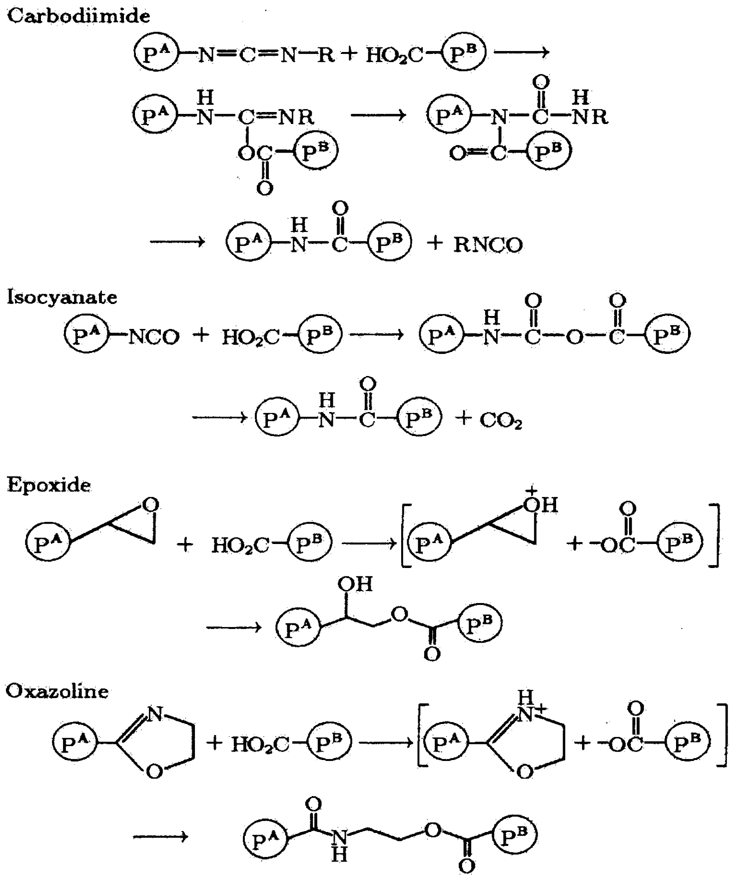

Figure 3.2 Schematic reactions between the carboxylic acid end groups with some electrophilic functionalities.

Various authors have discussed the processing details of some of the above chain extenders for PET in numerous papers. Inata and Matsummura (1985) have described polyoxazolines as chain extenders. For example, PET was chain extended with 0.5% 2,2'-bis(2-oxazoline) in a 30 mm extruder at 290°C and 3 mins residence time to increase its intrinsic viscosity from 0.78 dl/g to 1.07 dl/g. Karayannidis and Psalida (2000) used the 2,2'-(1,4-phenylene)bis(2-oxazoline), synthesized by the authors, to chain extend post-consumer bottle PET in a 250 ml three-necked round bottom flask equipped with a mechanical stainless steel stirrer under argon at 290°C. The I. V. of the reacted PET is increased from the original 0.78 dl/g to 0.85 dl/g. The extent of the viscosity increase after the chain extension reaction also depends on the efficiency of mixing and the type of catalyst. In all experiments large reduction in the carboxylic acid group content was observed.

Dijkstra et al. (1971) reported that using methylenebis(p-phenyl isocyanate) (MDI), the intrinsic viscosity of PET can be increases from 0.68 dl/g to 0.88 dl/g upon extrusion with only 0.8 wt% MDI in a 45 mm extruder at 260°C. When 1.5 wt% MDI was used, the intrinsic viscosity increased to >1.1dl/g. Kolouch and Michel (1983) also used MDI to build viscosity of PET with I.V. around 0.70-0.74 dl/g, in a 28mm corotating twin screw extruder. The temperature profile along the six zones was set as 160-250-280-320-280-265°C. The final product was free of gas bubbles, generated from the reaction and removed in the devolatilization zone, and had I.V around 1.02-1.08 dl/g.

Using polycarbodiimides as chain extenders for PET is reported by Thomas (1978). The polycarbodiimides used in this example were derived from oligomerization of aromatic diisocyanates such as toluene diisocyanate and were melt mixed with PET in a 28 mm W&P ZSK TSE at 254°C. The product was characterized by measuring unnotched Izod impact strength, which showed an increase from 14.1 ft-lb/in to 19.8 ft-lb/in by using 1-2 phr polycarbodiimide.

In addition to these chain extenders, polyepoxides and polyanhydrides appear to be the most suitable reactive modifiers for the chain extension of PET. This is because of their great availability, good thermal stability and low volatility at PET processing temperatures, absence of generation of by-products during the reaction and ease of mixing with PET. Particularly, materials with the epoxide functionality may react to form covalent bonds with both the carboxylic acid and hydroxyl end groups present in polyesters. The strong polarization of the hydroxyl group of carboxylic acids ensures fast reaction between epoxy/carboxyl groups, (the weak hydroxyl nucleophile functionality may also react with the epoxy ring under certain conditions), as shown in Figure 3.3a (Xanthos, 2000). By contrast, the polyanhydrides will react with the hydroxyl groups present in the polyester through the carboxyl groups formed by ring opening. Figure 3.3 b shows the possible reactions between pyromellitic dianhydride (PDMA) and PET (Khemani, 1997 and 1998). Those reactions have been reported to take place not only in a homogeneous medium, but also at the interface between immiscible components, catalyzed by a variety of compounds including Lewis acids and quaternary ammonium salts, and other inorganic salts (Brown, 1992).

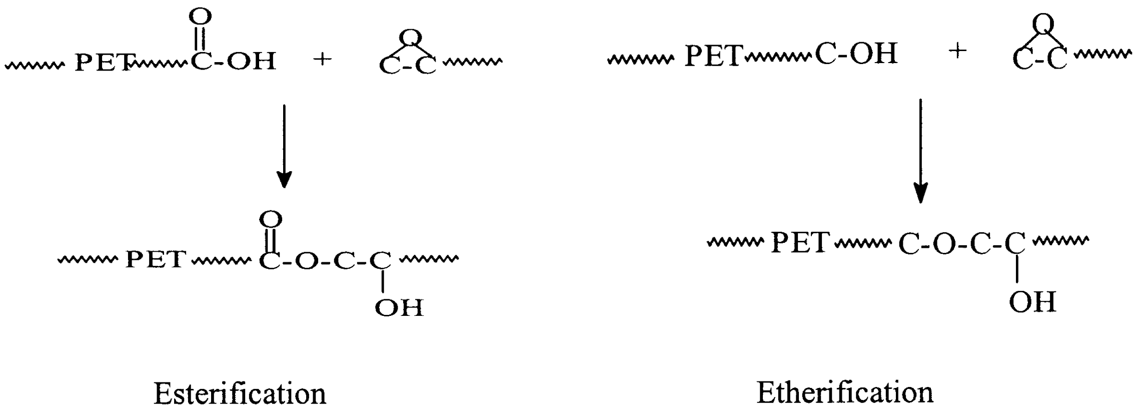

Figure 3.3a Schematic of PET end group reactions with epoxides.

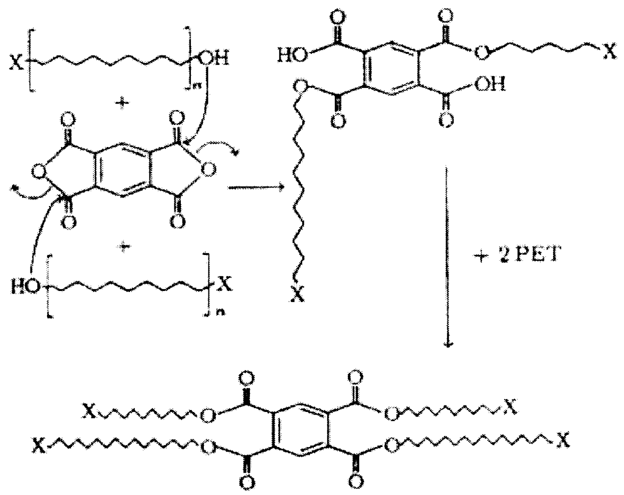

Figure 3.3b Schematic of reaction of PET with PMDA.

From a rheologicial point of view, the chain extension or branching may not only increase the MW of PET, but also increase its melt strength. That eventually improves the processability of PET for certain applications, especially low density extrusion foaming. The term of melt strength, although not well defined but qualitatively related to extensional viscosity, is widely used in certain polymer processing areas and serves as an indication of the "spinnability", ”foamability” or "blowability" of the polymer melts. The chain extended or branched PET with high melt strength is characterized by low MFI, high extrudate/die swell, high viscosity, high storage modulus and pronounced non-Newtonian behavior with high shear sensitivity (Yilmazer et al. 2000, Incarnato et al., 2000).

The production of extrusion foamable chain extended/branched PET has been reported by several authors. Xanthos et al. reported that extrusion modification of post consumer PET with PDMA in a concentrate form resulted in significant increase in melt strength and die swell. (Xanthos, 1999) The melt flow index (MFI) at 260°C/2.16 kg decreased from 26.6 g/10min to 4.38 g/10min and the nominal I. V. increased from 0.7 to

0.98 dl/g after modification with small amounts of PMDA. The most important improvement is in foamability. After reactive processing with PDMA, the modified PET can be extruded with CO_2 to give a good and uniform foam with density around 0.12 g/cc with average cell size of about 150 μm. Japon et al. also reported the increased foamability of recycled PET by reacting with tetraglycidyl diamino diphenyl methane (TGDDM) and the increase of the transient elongational viscosity around 17 and 39-fold. (Japon et al.,2000).

3.1.2 Reactive Blending of PET With Polyolefins

The reason for blending and alloying thermoplastic polyesters with other polymers is to tailor new materials with beneficial performance-cost profiles that meet actual application needs (Nadkarni and Rath, 2002). This tailoring approach, which also opens up new markets and other potential end-applications, needs much less investment or short development time compared to the development and manufacture of new, high value added chemical modified copolymers. Another compelling reason for blending of polyesters with other polymers is to facilitate the recycling of polyesters.

Miscibility or compatibility of the blend components is one of the basic requirements, for the development of polyester blends with useful properties (Krause, 1978). In the majority of cases, polyesters blends are immiscible with dissimilar polymers, resulting in separation of the blend phases and the formation of undesirable coarse morphologies in the absence of further modification; thus, the issue of compatibilization and enhancement of interfacial adhesion becomes all the more important. There are two compatibilization methods finding practical application: one is the incorporation of a separate chemical compatibilizer (reactive or non-reactive) into the immiscible polymer blends during melt compounding and the second is the formation of *in situ* compatibilizers during reactive compounding. In either type, the control of the compatibility at the interface between the constituent polymer phases is the key to optimization of the desirable property profile and to the stability of the blend morphology.

The combination of PET with polyolefins represents an important group of blends that may offer an attractive balance of mechanical and barrier properties, and processability (Nadkarni and Rath, 2002). Moreover, the use of recycled scrap from polyesters and polyolefins for ecological reasons is among the reasons for the development of such blends. However, the incompatibility of these two polymers, results in a "bad" morphology with gross phase separation and lack of adhesion between the phases, resulting in poor mechanical and barrier properties. Compatibilization is then a necessary step to obtain blends of PET and polyolefins with good properties from both virgin and recycled materials.

Both physical and reactive compatibilizers have been used in PET/polyolefins blends. The majority of the published data on the use of compatibilization refers to the follllowing two approaches: (i) addition of suitable block or graft olefinic copolymer containing reactive functionalities such as maleic anhydride (MA), glycidyl mathacrylate (GMA), or an epoxy group, or (ii) blending PET with suitably functionalized polyolefins. In the first approach that is usually preferred, graft copolymers formed *in situ* by the reactions between the functionalities of the copolymer and end-groups of PET assist in blend compatibilization (Xanthos, 2002).

As mentioned in the previous section, on the basis of its structure, PET is capable both of chemical reaction with polar polymer and of specific polar interactions, like H-bonding. The effectiveness of compatibilizers for PET/polyolefins blends has also been reported in terms of morphological and mechanical properties (Kalfoglou et al.,1995, Cartè and Moet, 1993). Attempts have been made to form compatible blends of PET with non-polar polyolefins by using rubber type elastomers such as ethylene/vinyl acetate copolymer (EVA) (Chen and Lai, 1994), ethylene/vinyl alcohol copolymer (EVOH) (Dimitrova et al.,2000) or a functionalized third component such as polypropylene-graft-acrylic acid (PP-g-AA) (Xanthos et al.,1990), polyethylene-graft-maleic anhydride (PE-g-MA) (Cartè, et al ,1993) and poly (styrene-b-(ethylene-co-butylene)-b-styrene—graft-maleic anhydride (SEBS-g-MA) (La Mantia, 1993). Improved morphology and better mechanical properties have been observed by using some of the above components.

Cartè (1993) published their findings on the morphology and impact properties of PET/high density polyethylene (HDPE) compatibilized with SEBS, SEBS-g-MA and PE-g-MA with modified SEBS giving the best results. Kalfoglou et al (1995) compared four different compatibilizers for PET/HDPE blend by reactive extrusion. The compatibilizers studied were an ethylene-glycidyl methacrylate copolymer (E-GMA), an ethylene ethylacrylate glycidyl methacrylate terpolymer (E-EA-GMA), a hydrogenated SEBS-g-MA and a MA-modified ethylene-methyl acrylate copolymer (E-MeA-g-MA). On the basis of morphological evidence and tensile testing, which proved most discriminating, they found that the compatibilizing effectiveness decreased in the order, E-GMA>E-EA-GMA>SEBS-g-MA>E-MeA-g-MA. These results are due to the different reactivities of the GMA vs. the MA functionality contained in these compatibilizers. GMA may react with both carboxyl and hydroxyl terminal groups of the PET and demonstrate higher reactivity compared to MA. In the latter case, MA may only react with the hydroxyl moieties and partly so because of the possibility of the reversibility of the esterification reaction at high mixing temperature.

There are several published studies examining the effects of the processing parameters such as screw speed, temperature, feed rate and sequence, and mixing time on morphology and compatibilization of blends (Plochocki et al., 1990, Wu, 1987, Willis and Favis, 1988, Cimmino et al.,1986 and Dagli and Kamdar, 1994). Cimmino et al found that when a compatibilizer is compounded with the minor phase first, the resulting blend has finer morphology, which appears to be true for blends of non-polar components. Willis and Favis (1988) concluded that when either the major or the minor components was polar (and hence capable of interaction with the compatibilizer), pre-compounding the compatibilizer with the non-polar component resulted in a finer morphology. Dagli and Kamdar (1994) studied the effects of the different sequences and modes of component addition on the compatibilization process of PET/HDPE blend with E-GMA. It was found that initial closer contact of E-GMA (polar) with non-polar HDPE resulted in better compatibilization. During the co-melting of HDPE and E-GMA, the E-GMA molecules appear to orient themselves in a way that favors the copolymer formation right at the interface. Initial closer contact of E-GMA with PET (polar) resulted in a coarser morphology and inferior mechanical properties. Such a sequence would result in E-GMA-PET copolymer molecules remaining in the PET phase and not being able to emerge at the interface. Their conclusions are that when a blend is undergoing compatibilization *in situ*, not only is the formation of compatibilizer molecules is very important but also their positioning at the interface. Grouping functionalized polymer with non-polar blend components appears to achieve both the formation of compatibilizer molecules and their positioning at the interface.

In general, two reactive blending processes are conceivable for the compatibilzation of immiscible blends: (1) the chemically inert polymer is functionalized in a separate extrusion step, and is then blended with the functional polymer in a second extrusion step; (2) both the functionalization and the reactive blending steps are executed in the same extrusion process. As an example, functionalization can be carried out in the first section of the extruder, followed by subsequent interfacial reaction between the functional and functionalized polymers. Process (1) is called a two-step reactive extrusion, while process (2) is called a one-step reactive extrusion. To some extent, the two-step reactive extrusion is easier to control but perhaps less economic due to the additional passage of materials through the extruder. Therefore, increasing efforts have been directed towards the *in situ* compatibilization of immiscible blends by one-step reactive extrusion. Sun et al have reported the effects of the process parameters on the *in situ* compatibilization of PP and poly (butylene terephthalate) (PBT) blends, a similar system to the PET/PP blend, by one-step reactive extrusion (Sun et al.,1996, Hu et al.,1996). In their one-step reactive extrusion process, PP pellets were premixed with a functional monomer such as MA, GMA or acrylic acid (AA) together with POX and fed from the first hopper, while the PBT pellets were fed from a second hopper further downstream into a co-rotating twin screw extruder. In that way, the functionalization of the PP occurred almost exclusively in the first zone between the first and second hopper, after which the interfacial reaction started between the functionalized PP and PBT.

Compatibilized PBT/PP blends were also made by two-step reactive extrusion process under similar conditions for comparison. Although the mechanical properties (i.e. elongation at break and impact strength) of the PBT/PP blends obtained by one-step reactive extrusion are not better than those of the blends obtained by a two-step process, the comparable data still demonstrated the feasibility and certain advantages of the one-step reactive extrusion process.

3.2 Reactive Modification of Low MW Unsaturated Polyester (UP)

As mentioned in Chapter 1, UP resins are among the four most important thermosetting resins and they represent about 20% of the total volume of thermosets. Wide applications have been found for UP resins including transportation, construction, electrical, furniture, casting and so on. However, due to their unique chemical structure, UP resins are continuously finding more application in many areas.

3.2.1 Chemical Crosslinking of UP

As shown in Figure 3.4, typically, UP has more than one functionalities, which can be involved in different chemical reactions. The crosslinking process can start in two different locations. Normally, the unsaturated double bonds within the polymer chains undergo a free-radical crosslinking in the presence of a comonomer. This is also called curing and it is a highly exothermic reaction. A three-dimensional structure can be produced by this curing process through the unsaturated acid component, usually maleic anhydride and with a vinyl monomer, the most common being styrene (Rojas et al.,1981, Fan and Lee, 1989, and Huang et al.,1990). For UP containing free carboxyl end groups, an ionic crosslinking process can also take place with and alkaline earth metal oxides such as MgO, ZnO and CaO or hydroxides, under suitable conditions. This is also known as "chemical thickening" (Saito et al.,1996, Rao and Gandhi, 1985, Vancsó-Szmercsányi et al.,1980).

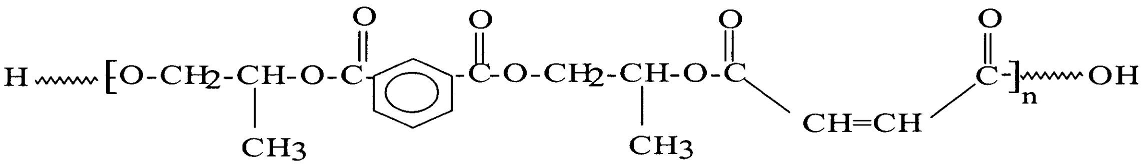

Figure 3.4 Typical chemical structure of UP made from propylene glycol, isophthalic acid and maleic anhydride.

Curing the UP resin is a delicate balance between the effects of the initiator, inhibitor and accelerator (promoter). Curing the UP resins is a free radical copolymerization reaction initiated by peroxides which decompose to free radicals. Curing may be effected in two ways: at elevated temperature (140-160°C) for molded products or at ambient temperature for large hand lay-up structures. Various monomers and a wide range of catalyst-accelerator-inhibitor systems are available (Sakaguchi 1974 and Cook et al., 1978).

In order to provide insights into the mechanism and kinetics of crosslinking of UP chains, a systematic study of UP crosslinking in the absence of vinyl monomer or other crosslinking agents was carried out by Martin et al. (Martin et al.,2001). Several UPs with different structure (i.e., different double bond concentration) have been selected and the gel fraction as a function of reaction time is monitored. They found that crosslinking of UP without the presence of vinyl monomers as crosslinking agents is not only possible but can produce significant and controlled amounts of gel. Their results also correspond to a series of patents assigned to Xerox Corporation (Mahabadi et al., 1995) describing UP crosslinking in the absence of vinyl monomer by a continuous reactive extrusion process for toner applications.

Chemical thickening of UP resins through its free carboxyl end groups with metal oxide is widely used in sheet molding compound (SMC) and bulk molding compound (BMC) technology to control viscosity at room temperature and during curing (Saito et al.,1996). Compared to other thickening reactions such as those of the UP resins with diisocyanates, thickening with MgO or ZnO is reversible to a large extent (Atkin, 1982). This means there will be a greatly reduction in compound viscosity upon heating due to the interionic forces between the ionic crosslinked chains. Other advantages of thickening UP with MgO or ZnO are the resultant tack-free, easily handled compounds that are still able to undergo free radical curing.

The important parameters of the thickening process were shown to be: (1) the molar ratio of metal oxide to carboxyl end groups (Alvey, 1971); (2) the water content of the medium (Vancsó-Szmercsányi et al., 1974), and (3) the MW of the resin (Burns et al., 1975). Regarding the reaction mechanism itself, two theories have been proposed (Judas et al., 1984 and Rao and Gandhi, 1985). Burns and Gandhi (Burns et al., 1975 and Gandhi and Burns, 1976) described the thickening reaction as the formation of a polymeric neutral salt. Vancsó-Szmercsányi et al. proposed a mechanism involving a two-step reaction between carboxyl end groups and metal oxide, with initial formation of basic or neutral salts, followed by the complexation of these salts by the ester groups in the chains and/or the hydroxyl end groups (Vancsó-Szmercsányi et al., 1974). There are evidences in favor of both mechanisms. However, both mechanisms have a common starting point, which is the formation of basic or neutral salts.

3.2.2 Reactive Blending of UP With Polyolefins

There are very few studies on the reactive modification of UP with other thermoplastic polymers such as polyolefins. However, the chemical structure of UP is similar to those monomers and macromonomers with a reactive double bond which is susceptible to radical addition. Typically those monomers include various 1-subsituted (e.g. acrylate esters, vinyl silanes, styrene) and 1,2-disubsituted monomers (e.g. MAH, maleate esters, maleimide derivatives) which have been successfully grafted to polyolefin substrates (Moad, 1998). The inherent reactivity of the UP double bond towards radicals may resemble that of the analogous monomers. However, due mainly to steric factors, UP will generally show a lesser tendency to undergo homopolymerization.

The melt phase grafting of various functional monomers such as maleates, fumarates and GMA onto polyolefins have been studied by many authors (Benedetti et al.,1986, Konar et al.,1993, Liu et al.,1993, Sun et al.,1995, Chen et al.,1996). The major application of these polymers has been as *in situ* compatibilizers in blends of polyolefins with polyamides or high MW polyesters. Most of the grafting reactions are promoted by peroxide and the grafting efficiency depends on the nature of the functionality of the selected monomer and other aspects of the polyolefin structure. Other factors such as processing conditions, removal of monomer residues, half life of POX and its decomposition temperature also play an important role.

Blending of PP/PE or PE/polystyrene (PS) is studied by several authors (Yu et al., 1990 and Sun et al.,1997 and 1998). Morphology and mechanical properties of the immiscible blend are improved by adding peroxide in a process of *in situ* compatibilization. In the PP/PE system, PP and PE respond to peroxide attack in two opposite ways: PP degrades, while PE crosslinks. There are possibilities for the formation of PP-g-PE copolymer due to the macroradicals recombination, although the probability of that happening without additional coagents may be very limited in a melt blending process. PP and UP are expect to respond to POX in a similar way as PP/PE system. By optimizing the processing conditions and addition of coagents to stabilize the macroradicals of PP and/or UP and localize the free radical reactions at the PP/UP interface, the possibility of *in situ* compatibilization process will be increased. This will be covered in detail in Chapter 5.

CHAPTER 4

EXPERIMENTAL

4.1 Materials

4.1.1 Materials in Reactive Modification/Blending of Low MW Unsaturated Polyester (UP)

The components used for the reactive modification/blending of UP include polypropylenes (PP) and coagents. Two types of PPs with different viscosities were employed: PP1 (Achieve 3825, Exxonmobil) and PP2 (Profax 6524, Bassel). The UP used in this study is propylene glycol based, 1:1 isophthalic acid and maleic anhydride from Interplastic Corporation. The coagents used in the study include peroxide (POX) [2,5-dimethyl-2,5-di(t-butylperoxy) hexane, Luperco 101XL, Atofina], N,N'-1,3-phenylenedimaleimide (PDMI) (Aldrich), maleated PP (PB3200) (Polybond 3200, Crompton Corporation) and magnesium oxide (MgO) (Aldrich). Their characteristics are listed on Table 4.1 and Table 4.2, respectively, whereas Figure 4.1 contains their chemical structures. During melt processing, PPs and UP were mixed at various weight ratios with or without coagents to prepare samples for subsequent characterization.

Table 4.1 Information on Major PP-UP Blend Components

	PP1	PP2	UP
Grade	Achieve 3825	Profax 6524	COR75-187-686
Manufacturer	EXXONMOBIL	Bassel	Interplastic Corporation
MI (230°C, 2.16kg)	32	4	~1500*
M_n (aver)	Not available	Not available	~2000
T_m or T_g (°C)	157.6#		44#
Comments	Pellets	Pellets	Brittle solid (Acid number is 18**)

* Estimated experimentally according to ASTM D1238 at 230°C

\# Measured by DSC at 20°C/min heating rate

** Determined experimentally

Table 4.2 Information on Coagents Used in PP-UP Blends

	Magnesium oxide	Peroxide	PB3200	PDMI
Grade	-325 mesh, 99+% pure	Luperco 101XL	Polybond 3200	97%
Manufacturer	Aldrich	ATOFINA Chemicals	Crompton Corporation	Aldrich
MI (230°C, 2.16kg)	N/A	N/A	110	N/A
MW	40.31	316	Not available	268.2
T_m (°C)	2800	-	160-170	198-201
Comments	Fine powder	10- hour half-life temp., 120 °C, (powder, 45% active)	Pellets	Yellow powder

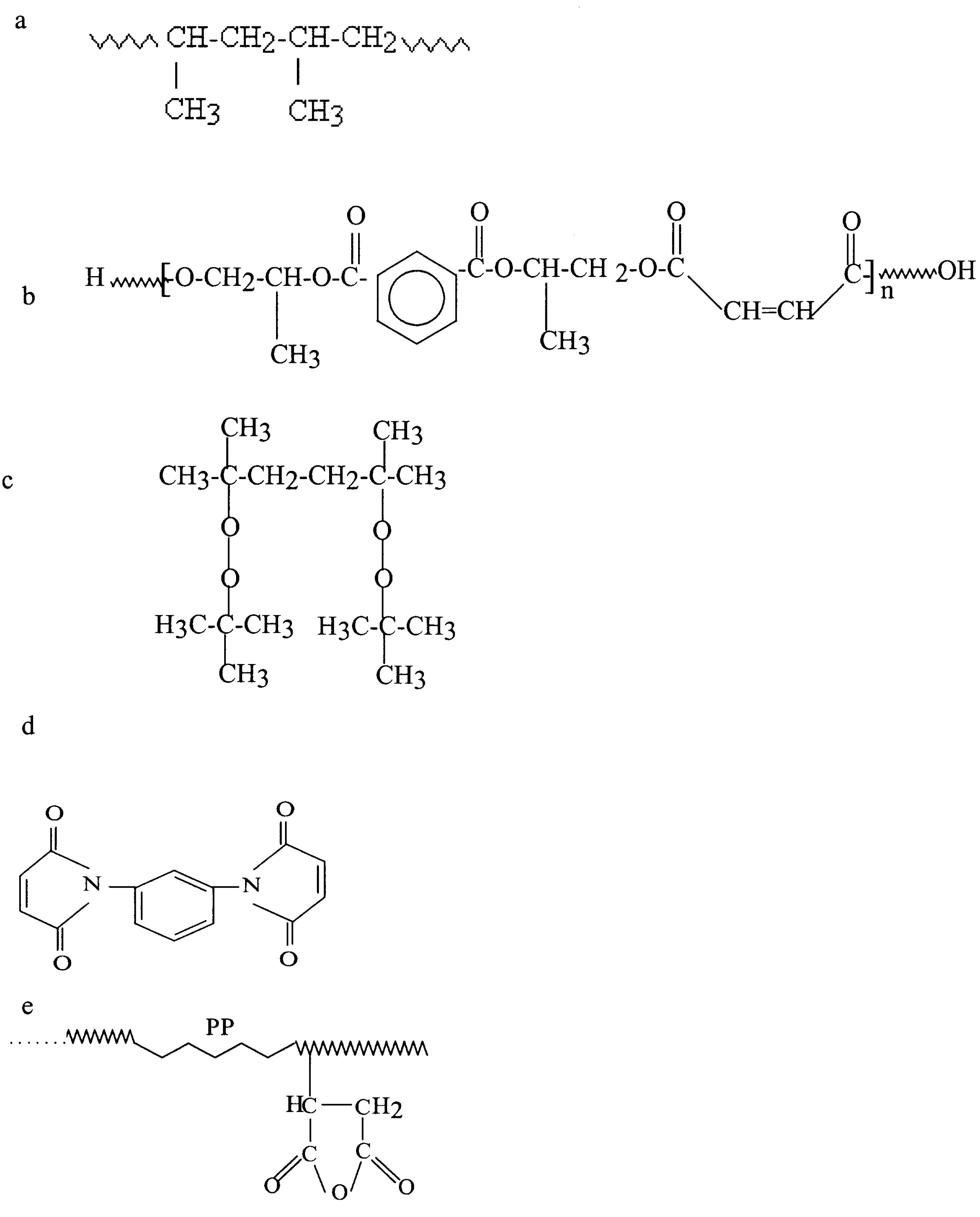

Figure 4.1 Structure of blend components (a-PP; b-UP;) and coagents (c-POX; d-PDMI; e-PB3200).

4.1.2 Materials in Reactive Modification/Foaming of High MW Saturated Polyester (PET)

Poly(ethylene terephthalate) was a post-consumer bottle grade pelletized resin of 0.71 nominal IV (Wellman) with carboxyl content (CC_p) = 27.9 eq/10^6g and hydroxyl content (HC_p) = 89 eq/10^6g based on an earlier end group analysis (Xanthos et al, 2001). The following five modifiers were evaluated:

- Dianhydride: Pyromellitic dianhydride (PMDA) - (Sigma-Aldrich)
- Dianhydride: 3,3', 4,4' Benzophenone tetracarboxylic anhydride (BTDA) - (Sigma-Aldrich).
- Diepoxide: N, N'-bis [3(carbo-2', 3'epoxypropoxy) phenyl] pyromellitimide (BGPM) – (laboratory synthesized,).
- Triepoxide: Triglycidyl isocyanurate (TGIC) - (Sigma-Aldrich)
- Tetraepoxide: Tetraglycidyl diamino diphenyl methane (TGDDM) – (Araldite® MY 721 Ciba-Geigy)

Chemical structures and important physical properties of the modifiers are given in Figure 4.2 and Table 3, respectively. With the exception of the diepoxide, all other modifiers were commercially available materials.

Isobutane gas was used as a physical-blowing agent during extrusion foaming experiments. (CAS No. 75-28-5, boiling point =-12°C, (S. O. S. Gases, Kearny, NJ)

Table 4.3 Characteristics of Modifiers

Modifier	*Molecular weight, MW*	*Form*	*Functionality*	*Reported M.P/B.P (°C)*	*Isothermal TGA thermal stability*§
PMDA (dianhydride)	218	White powder	Tetra-	283-286 (397-400)*	31.34
BTDA (dianhydride)	322	Beige powder	Tetra-	215-217*	97.39
BGPM (diepoxide)	569	Yellow powder	Bi-	270**	99.61
TGIC (triepoxide)	297	White powder	Tri-	100**	84.76
TGDDM (tetraepoxide)	423	Clear brown viscous liquid	Tetra-	Not available	99.02

* Suppliers data

** Measured

§ (Wt.% residual following heating at 300°C and holding for 300s under nitrogen)

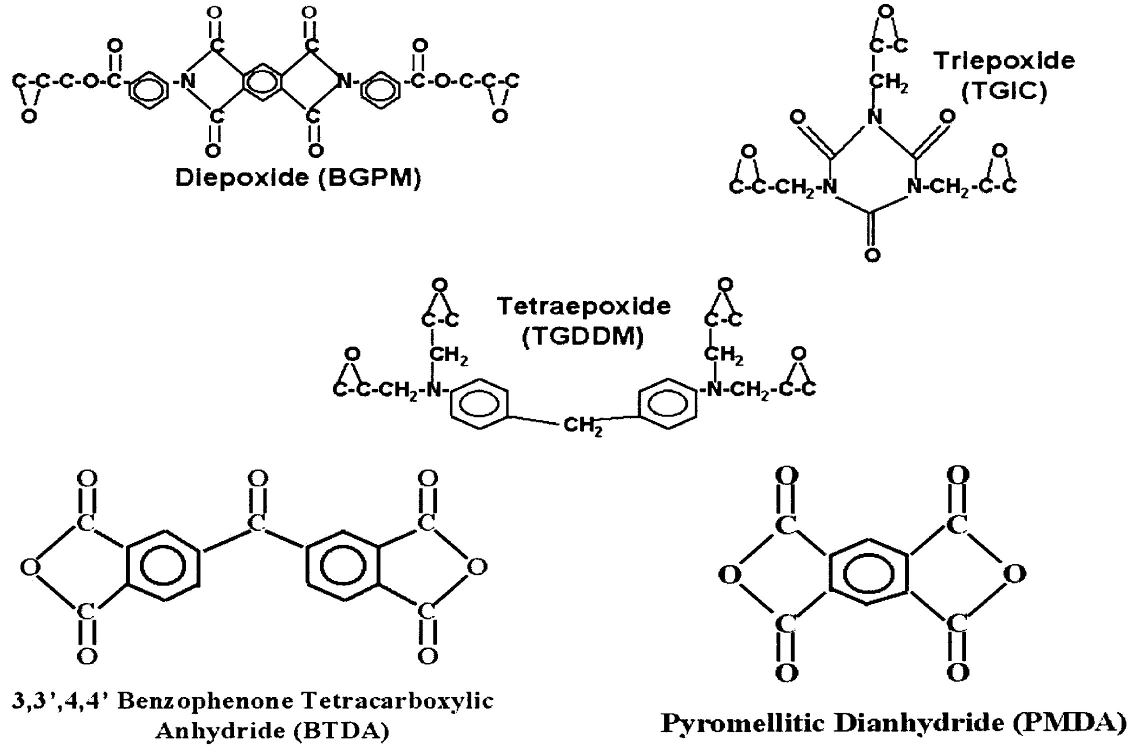

Figure 4.2 Chemical structures of modifiers.

4.1.3 Materials in reactive blending/foaming of high MW saturated polyester (PET)

Resins used in these experiments were pre-dried PET (Shell Traytuf 9506, 0.96 IV) and Polypropylene PP (EXXON Escorene PD 9374 MED). A commercially available polyolefin based copolymer containing around 1~2% acrylic acid (Primacor 3460) was used as potential compatibilizer, in some cases in the presence of a multifunctional coagent around 1~2% (triepoxide, TGIC) that was expected to react with the compatibilizer and the PET end groups, thus, acting as a bridging agent.

Carbon dioxide was used as a physical-blowing agent during these extrusion foaming experiments. (Matheson, Bond dry)

4.2 Processing

4.2.1 Reactive Processing of Unsaturated Polyester (UP)

4.2.1.1 Internal Batch Reactive Mixing. The PP/UP blends were prepared in an internal batch mixer (Brabender PlastiCorder Model PL2000) at 60 rpm and controlled temperature under a nitrogen blanket. The UP was pre-dried under vacuum for about 20 hrs at room temperature. In order to determine the effect of coagents on the individual blend components, PP or UP was first introduced into the batch mixer and coagents were added after 3min. For blends, the PP with or without POX was introduced into the batch mixer and processed for 3 mins, followed by the addition of the UP and the coagents. The changes of torque and temperature were monitored during processing. The samples were removed from the mixer after 15 mins processing time and dried before further characterization.

4.2.1.2 Continuous Reactive Extrusion. Two intermeshing co-rotating twin-screw extruders (Coperion) were used to melt blend PP/UP with or without POX or PDMI coagents during the reactive extrusion process. One is a 30mm diameter with length to diameter ratio of 16:1 (Extruder 1), the other is a 30mm diameter with length to diameter ratio of 40:1 (Extruder 2). The screws of the extruder were assembled from individual conveying and mixing elements and kneading blocks, as shown in Figs. 3a and 3b. PP and UP (pre-dried) were dry blended with or without coagents and introduced into the hopper of the extruder via a volumetric feeder at 3-3.5 kg/h feeding rate. The temperature profile from feed zone to die for both extruders ranged from 170°C to 210°C. The blends were melt extruded, pelletized and collected for further characterization.

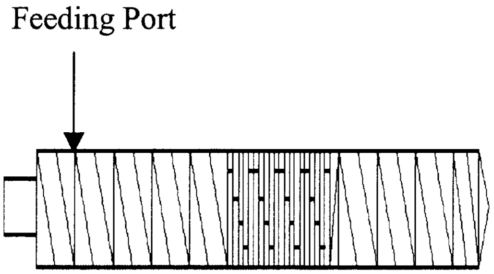

Figure 4.3a Screw configuration for extrusion compounding of PP/UP blends (extruder 1). Screw Configuration for Extruder 1: 5×42/42(convey) + KB45/5/28(kneading block) +20/10(reverse) + 3×42/42(convey) + 28/28(convey)

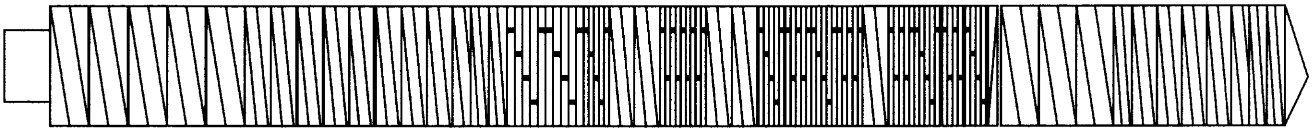

Figure 4.3b Screw configuration for extrusion compounding of PP/UP blends (extruder 2). 5*42/42 + 9*28/28 + 2*20/20 + 2*KB45/5/42 + KB45/5/28 + 2*28/28 + 2*KB90/5/28 + 2*28/28 + KB45/5/28 + KB90/5/28 + KB45/5/28 + KB90/5/28 + 28/28 + KB90/5/28 + KB45/5/28 + KB90/5/28 + KB45/5/28 +20/10(R) +3*42/42 + 42/21 + 5*28/28 + 2* 20/20

4.2.1.3. Reactive Processing in the Rheometer. A Rheometrics mechanical Spectrometer RMS-800 was used for the real time monitoring of the reactive processing of PP, UP and their reactive blends. During the sample preparation, PP and UP were ground into fine powders in the presence of liquid nitrogen and thoroughly mixed with coagents such as POX and PDMI at different concentrations. Steady shear measurements were used since the very low viscosity of the UP presented difficulties in generating sufficient torque for the regular dynamic tests at low frequency. The reactions leading to degradation of PP and crosslinking of UP were monitored by performing steady shear experiments at $2s^{-1}$ shear rate and 180°C, where the tested samples were in their Newtonian region.

4.2.2 Reactive Processing/Foaming of Saturated Polyester (PET)

4.2.2.1 Chain Extension. Initial experiments to develop kinetic data that could be applicable to continuous extrusion runs involved the use of a Brabender batch intensive mixer where torque changes at constant rpm and bowl set temperature were recorded as function of time. In the extrusion runs, solid modifiers (section 3.1.2) were dry blended at appropriate amounts (Table 4.4) with PET pellets pre-dried overnight at 120°C and fed through a volumetric feeder at 1.45kg/hr in the hopper of a 40:1 L: D, 32 mm segmented Killion extruder operating at a screw speed of 15 rpm and equipped with a 2.2 mm rod die. The liquid tetraepoxide was deposited on the pellets surface and fed in the same manner. Screw configuration involved conveying sections separated by mixing elements. Temperature settings along the barrel were 204–290-260°C. Actual die temperature, die pressure, and extrudate appearance and dimensions varied depending on the particular formulation. The maximum diameter (D_{max}) of free falling extrudates was measured as they exited the die of diameter D_d, and also at a distance of 15 cm from the die exit (D_{15}) in order to calculate: a) extrudate swell (die swell) as (D_{max} / D_d) and, b) sag expressed as diameter ratio (D_{max} / D_{15}).

Table 4.4 Extrusion Characteristics with Different Modifiers

Modifier	*Concentration, phr (1.5X stoichiometric amount)*	*Die Pressure (MPa)*	*Die Temperature (°C)*
None	-	0.96	270.6
Anhydrides			
PMDA	0.7	12.8	269.3
BTDA	1.1	3.38	274.1
Epoxides			
BGPM	1.1	4.68	275.6
TGIC	0.4	15.2	279.6
TGDDM	0.45	11.5	270.3

4.2.2.2 One-Step Chain Extension/Foaming. The same 32 mm diameter, 40 L/D Killion segmented single screw extruder equipped with gas injection port was used to produce foamed rods from unmodified PET and hopper fed mixtures of PET/modifier at the same feeding rate (1.45 kg/hr), and the same temperature profile as before. In a typical experiment with 1.1 phr BTDA modifier, isobutane was injected at 19D length at 2-3 phr concentrations and mixed into the PET melt. At steady state foaming conditions, die pressure was 3.8 MPa and die temperature about 270°C.

4.2.2.3 One Step Reactive Blending/Foaming. A 34 mm diameter 40 L/D (Leistritz) co-rotating intermeshing twin-screw extruder was used to process the blends described in section 3.1.3. Dry blended material with no additional nucleating agent was meter fed into the hopper. The screw of the extruder was designed to achieve melting within 10 L/D length with the carbon dioxide injection section immediately after. The rest of the length of the screw was used for mixing the blowing agent with the melt, pressurizing and cooling the gas laden melt to levels of pressure (around 400 psi) and temperature (around 250°C), that were considered as optimal. The melt was extruded through a 3 mm diameter rod die, expansion taking place thereafter.

4.3 Characterization

4.3.1 Characterization of Modified Unsaturated Polyester (UP)

The products of the PP/UP/POX reaction are multi-phase, multi-component systems and are expected to contain unreacted and reacted (degraded) PP, unreacted and reacted (crosslinked) UP and "block" and/or "graft" PP-UP copolymers at different concentrations.

Selective dissolution and FTIR Characterization. The follow procedure was designed to separate all the components and characterize them by means of FTIR. The samples were dissolved in hot xylene at around 120°C and the insoluble crosslinked UP was filtered at this high temperature using a Millipore stainless steel pressure filter unit (47 mm diameter) and Waterman #1 filter paper, preheated at 120°C in an oven. The remaining solution was cooled down to 40~50°C causing precipitation of PP and possibly formed PP-UP copolymer. The unreacted UP in the residue can be recovered by evaporating the solvent. FTIR spectra of samples were obtained using a Perkin-Elmer SpectrumOne FTIR spectrophotometer. The films for FTIR analysis were prepared by compression molding at 180°C and dried at room temperature under vacuum for 4 hours. Figure 4.4 shows the details.

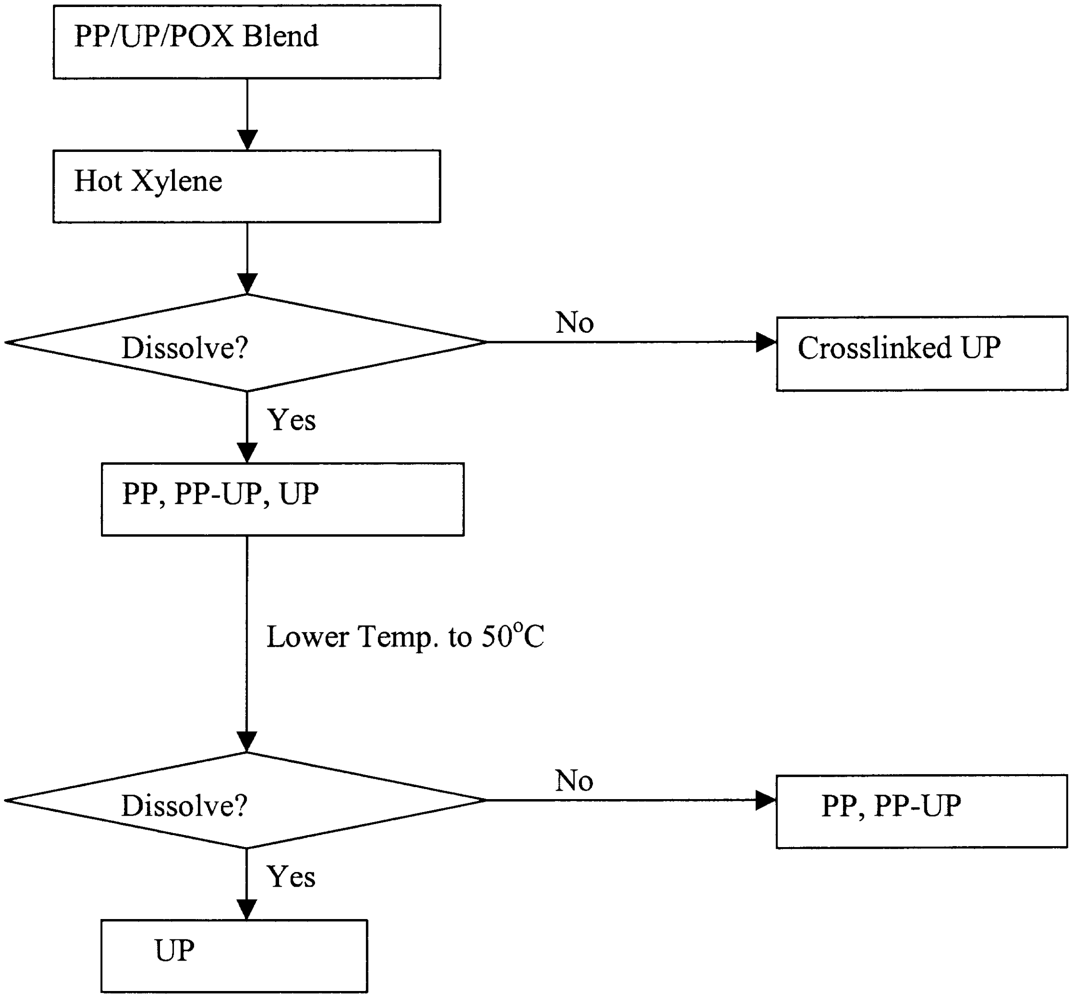

Figure 4.4 Schematic drawing of the fractionation of the components of the reacted PP/UP/POX system.

The thermal properties of the components and the reaction products were obtained using a Perkin-Elmer Differential Scanning Calorimeter (DSC-7). 5-10 milligrams of sample were first heated from 20°C to 200°C at a rate of 20°C/min. After cooling, the sample was reheated again at 20°C/min to obtain the PP melting endotherm and the UP transition temperature.

Thermogravimetric analysis (TGA) of the blend components was carried out in a non-pressurized system under nitrogen blanket using Model QA 50 (TA Instruments). For the isothermal test, an initial heating ramp within 2~3 min from room temperature to the set temperature was followed by isothermal heating for 15 min. For procedure heating test, the samples were heated at controlled heating rate from room temperature to the set temperature. The weight percentage losses were monitored during the heating process.

The solid dynamic mechanical properties were also measured with RMS-800 to investigate the relaxation peak point. In this temperature sweep mode, the experiments were carried out to determine the response to a material in linear temperature ramp zones at a fixed dynamic frequency. The material characteristics were determined at temperatures ranging from -80°C to 160°C at 10 rad/s using rectangular torsion fixtures. Specimens with rectangular geometry (7.5 cm × 1.25 cm, and 0.5 cm thickness) were prepared by compression molding (2 min melting/holding time, 5 min cooling time). Experiments were carried out under dry nitrogen.

Rheological properties of blends were determined by employing a RMS-800 with 25 mm diameter parallel plates at 180°C. The oscillatory shear experiments were carried out within the linear viscoelastic range of strain at frequencies from 0.1 to 100 rad/s.

While the melt flow index was measured in a Tinius-Olsen plastometer at 230°C and 2.16kg load for all blend components and the blends.

Morphology of the samples was observed by a scanning electron microscope (SEM) (LEO Field Emission Gun Digital SEM) at 1-3keV of working voltage. The samples were prepared in two different ways, either microtomed at –120°C, and the surface chemically etched in tetrahydrofunan (THF) to reveal subsurface detail, or fractured at liquid nitrogen temperature. Under the first conditions, unreacted UP would dissolve while PP and the crosslinked UP would not be affected. The size and the size distribution of the dispersed UP phase were analyzed by the Image-Pro Plus image analysis software (Media Cybernetics). About 300-500 domains were scanned with the image analyzer to obtain the average diameters and the size distribution. The data were interpreted using a number-average dispersed domain size, d_n, defined by:

$$d_n = \frac{\sum_{i=1}^{n} n_i d_i}{N} \tag{3.1}$$

Where, d_i is the diameter of the *i*th domain, n_i is the number of domain and N is the total number of the counted domains. The number-average diameter provides the most information about the domains on the low end of the distribution curve.

4.3.2 Characterization of Modified Saturated Polyesters (PET)

4.3.2.1 Solid Extrudates. Melt Rheology. The extrudates produced as in section 3.2.2.1 were characterized from industrially important parameters that are known to correlate with changes in MW and MWD and relate to processability. Melt flow index was measured in a Tinius-Olsen plastometer at 285°C and 2.16kg load. Melt strength was measured by an empirical/relative method by pulling a strand extruded from the die (25.4 mm long, 0.762 mm dia., entrance angle $\pi/2$) of a capillary rheometer operating at 285°C by a set of winding rolls. The transverse force at the largest draw ratio at which a given strand did not break was taken as melt strength.

Thermal analysis. Modifiers were examined for weight changes by isothermal thermogravimetric analysis (TGA), (QA 50, TA Instruments) at process temperatures (Table 3). Extrudates were analyzed by differential scanning calorimetry (Perkin-Elmer DSC7) at 20°C/min scan rate for glass transition temperature and melting/cooling transitions.

Solution rheology - End group analysis. Intrinsic viscosity (IV) was measured in phenol/tetrachloroethane 60/40 w/w solvent at a polymer concentration of 1% for all samples except for the ones modified with TGIC and TGDDM where IV was measured at 0.25% polymer concentration. IV was calculated by using the Solomon-Ciuta equation of a single point measurement. All IV solutions were prepared by heating the sample/solvent mixtures at 90°C for 20 min in a round bottom flask fitted with reflux condenser. The flask was then cooled to room temperature and the insoluble material (expressed as % gel content) was filtered through a sintered-glass filter G-3 without suction. TGIC and TGDDM modified samples were partly soluble in the solvent mixture and their filtration was very difficult. For these samples the new concentration of the solution after filtration was used for calculating IV.

Carboxyl content of the unreacted and reacted PET samples was measured according to Pohl's method by titrating a benzyl alcohol/chloroform polymer solution with standard NaOH in benzyl alcohol with phenol red as indicator by using a syringe immersed in the center of the solution. The PET samples were first dissolved at 215°C in benzyl alcohol and then mixed with chloroform, the latter acting as a liquefier and dispersant for the gel material present in some samples. For the high gel content TGIC and TGDDM samples, it is believed that the measured CC values correspond to a good approximation to their actual total carboxyl content. In attempts to provide an alternative to the more accurate but also more tedious and time consuming wet chemistry methods to determine hydroxyl content a mid -IR spectroscopic method was used with variable results.

4.3.2.2 Foam Extrudates. Average Cell Size Determination. The Cell Size Determination closely resembled ASTM 3576. Small rods were cut off the extruded samples, producing L/D close to 1. Ink was used to color the area to be investigated to clarify the cell walls. The specimen was then put under a microscope and the number of cell walls in 10 mm range was counted. Then, using the equation in ASTM 3576 section 9, (equation 3.2) the cell size was determined. This procedure was done in the X, Y, and machine direction.

$$d=t/0.616 \tag{3.2}$$

where d is the cell size in cm and t is the average cell chord length in cm.

Densities of the foams were determined using standard water displacement method.

Thermal properties of the foam products were obtained using a Perkin-Elmer Differential Scanning Calorimeter (DSC-7) at heating rate of 20°C/min from 20°C to 290°C. Crystallinity of PET and PP were calculated by dividing the enthalpy during the heating by the reference number for a 100% crystalline polymer.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Reaction Characteristics of Blend Components

5.1.1 Reaction between PP or UP With POX With or Without Coagents

Both PP and UP have high reactivity in free radical reactions but respond in opposite ways to peroxide: PP degrades due to β-chain scission while UP crosslinks due to macroradical recombination, as shown in Figure 5.1. The primary free radicals from the POX decomposition would preferentially abstract hydrogen atoms from the PP chain backbone and/or react with an internal double bond within the polyester chain and produce a backbone radical. These backbone radicals may have different fates. In the absence of co-reagents, PP backbone radicals usually undergo β-scission rather than reacting to form crosslinks, while UP backbone radicals will enter into crosslinking reactions with each other. The reactions of the individual components carried out in the batch mixer and the dynamic analyzer confirmed the opposite mechanisms, as shown in Figures 5.2 and 5.3 where time corresponding to number of POX half-lives at the reaction temperature is also shown on the top. The change of the melt viscosity of PP and UP, measured as torque or shear viscosity versus time, in the presence of peroxide indicate rapid degradation and crosslinking of PP and UP chains, respectively.

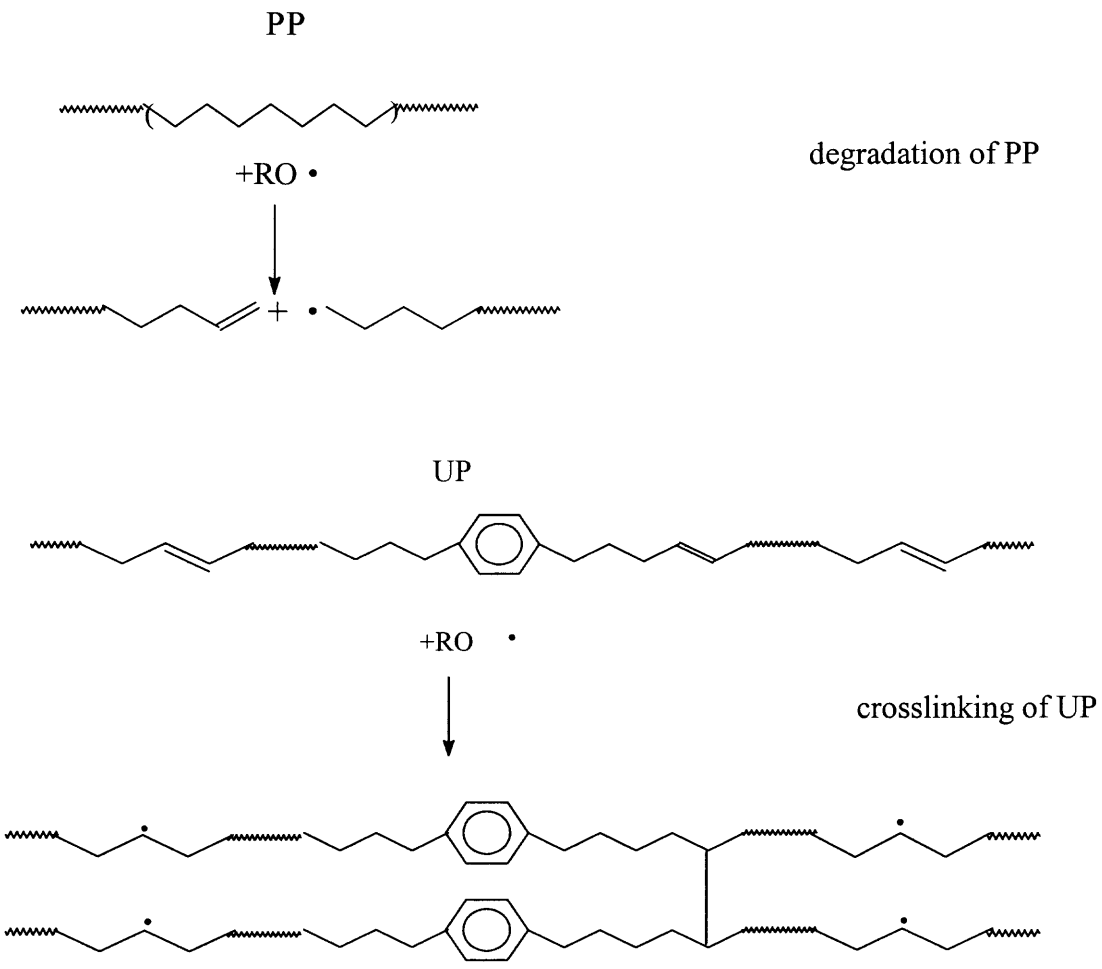

Figure 5.1 Schematic drawing of the reactions of UP and PP with POX.

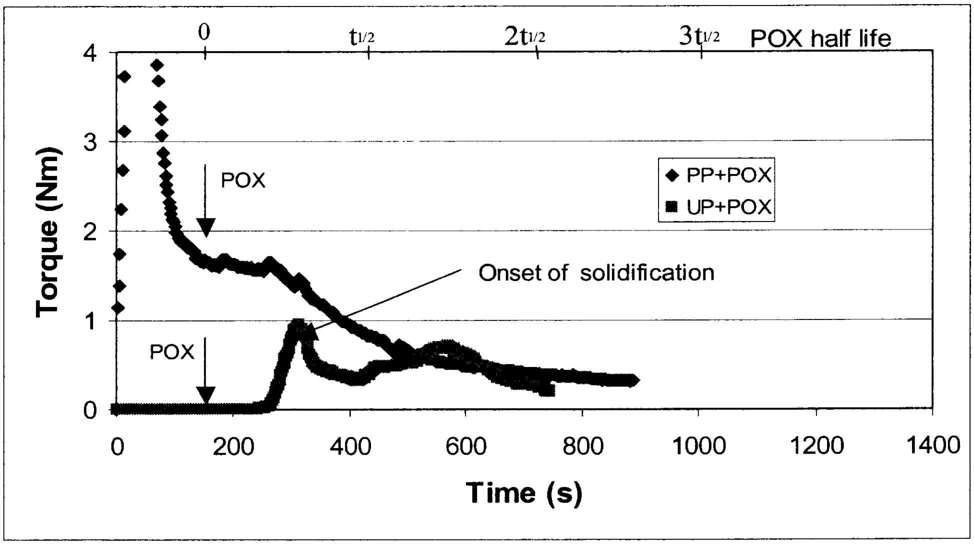

Figure 5.2 Changes in torque of PP and UP with POX (1 phr) in the batch mixer (160°C, 60rpm).

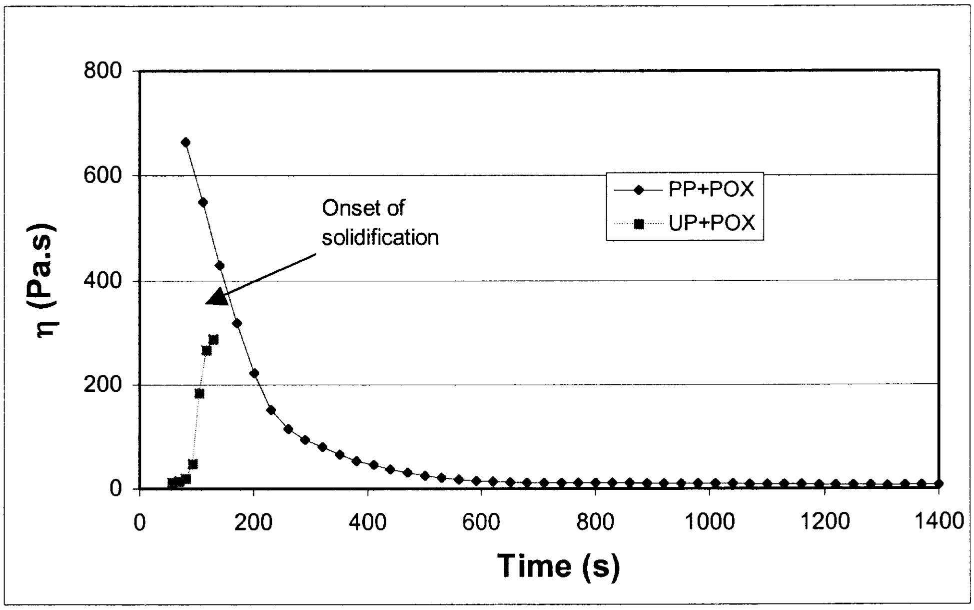

Figure 5.3 Changes in viscosity of PP and UP with POX (1 phr) in the RMS-800 (180°C, steady shear, $2s^{-1}$).

The kinetics of the reactions between POX and PP or UP are investigated by performing a series of steady shear experiments at different concentrations of POX and reaction temperatures, under nitrogen environment in the dynamic analyzer, RMS 800. The PP and UP were ground into fine powders and dry blended with POX at different concentrations. Figures 4a-4d show changes in the viscosity of PP and UP with POX in the RMS-800. It is obvious that the reaction rates strongly depend on the POX concentration and reaction temperature.

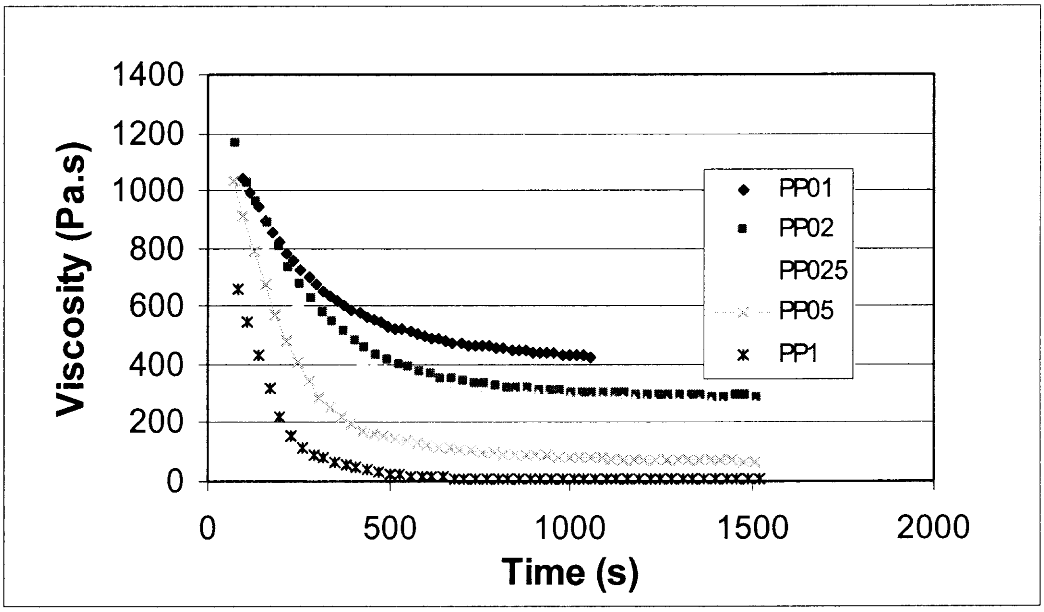

Figure 5.4a Changes in viscosity of PP with POX at different POX concentrations (0.01-1 phr) in the RMS-800 (180°C, steady shear, 2s^{-1}).

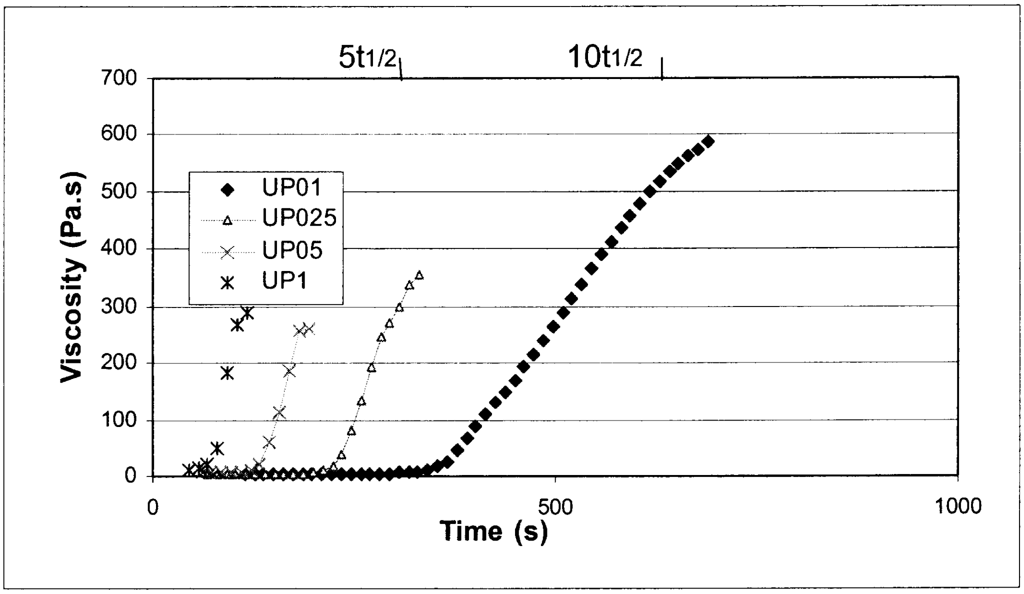

Figure 5.4b Changes in viscosity of UP with POX at different POX concentrations (0.01-1 phr) in the RMS-800 (180°C, steady shear, $2s^{-1}$).

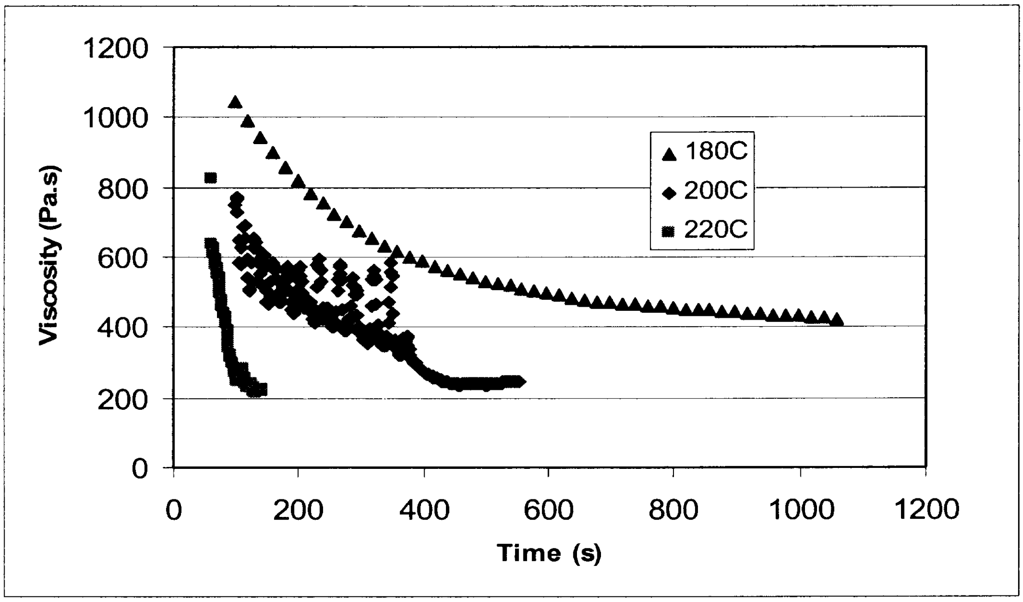

Figure 5.4c Changes in viscosity of PP with POX at different reaction temperatures in the RMS-800 (0.1 phr POX, steady shear, $2s^{-1}$).

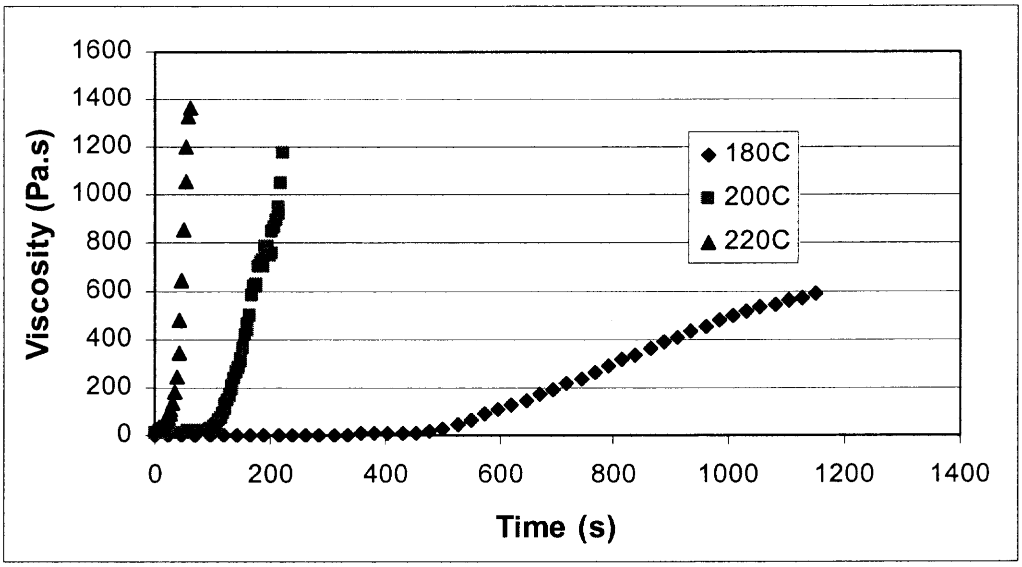

Figure 5.4d Changes in viscosity of UP with POX at different reaction temperatures in the RMS-800 (0.1 phr POX, steady shear, $2s^{-1}$).

In a general sense, the PP-POX and UP-POX reactive systems can be analyzed by treating the experimental viscosity versus time data with rate expressions analogous to those derived in chemical kinetics. The initial viscosity/time data (recorded during the onset of viscosity change) obtained at different concentrations of POX were found to follow the first order rate equation:

$$\frac{d\eta}{dt} = \pm k\eta \qquad (5.1)$$

where η is the viscosity (Pa.s), t is time (s) and k is the rate constant (s^{-1}), which is a function of POX concentration, processing temperature and, possibly, shear rate. The sign ± indicates the increase/decrease of the viscosity for UP/POX and PP/POX systems, respectively. The change of viscosities also corresponds to the changes of MW and MWD of PP and UP due to chain scission or crosslinking.

Table 5.1a Calculated First Order Rate Constants (*10^{-3} s^{-1}) and Half lives* (s) for PP/POX System in the RMS-800

Concentration of POX (phr)	Rate Constant, 10^{-3} s^{-1} (Half life, s)		
	180°C	200 °C	220 °C
0.1	2.2 (315)	3.6 (193)	25.6 (27)
0.2	2.8 (248)		
0.25	2.9 (238)		
0.5	5.2 (133)		
1	10.3 (67)		

* Half life values are shown in parentheses

Table 5.1b Calculated First Order Rate Constants (*10^{-3} s^{-1}) and Half Lives* (s) for UP/POX System in the RMS-800

Concentration of POX (phr)	Rate Constant, 10^{-3} s^{-1} (Half life, s)		
	180 °C	200 °C	220 °C
0.1	3.2 (217)	10.8(64)	42(17)
0.25	6.5 (105)	-	-
0.5	9.1 (76)	-	-
1	11.3 (61)	-	-

* Half life values are shown in parentheses

Table 5.2 Half Lives# (s) for POX

Temperature (°C)	180	200	220
Half life (s)	68.4	12	2.4

Data obtained from supplier's (Atofina) website

Tables 1a and 1b list the values of the calculated rate constants, k, and the half lives based on *k* by using equation (5.2). It is evident that the reaction rates, or the calculated rate constants, *k*, increase with increasing concentration of POX and reaction temperature. The values of the calculated half lives range between 60s and 300s. It is also of interest to note that at high concentrations of POX, the half lives of the reactions between PP or UP with POX are very close to the half lives of the POX at the same temperature, as shown in Table 5.2.

$$t_{1/2} = \frac{\ln 2}{k} \tag{5.2}$$

The activation energy, E_a, of the reactions can be estimated for 0.1phr POX concentration based on the values of *k* at different reaction temperatures by employing the Arrhenius expression, equation 5.3

$$k = k_0 e^{-\frac{E_a}{RT}} \tag{5.3}$$

where k_0 is referred to as the pre-exponential or the frequency factor and have a weak temperature dependence. The temperature T is in Kelvin. R is a constant and equals to 8.3145 J $\mathrm{mol^{-1}K^{-1}}$. The standard method for obtaining E_a is to graph experimental rate constant data on an Arrhenius plot, i.e., ln$k$ vs. $1/T$. The slope gives E_a/R. Table 5.3 shows the calculated activation energy of the reactions of PP or UP with POX.

Table 5.3 Calculated Activation Energy (E_a, kJ/mol) of the Reactions

	Activation energy (kJ/mol)
Chain scission of PP	127
Crosslinking of UP	158
Decomposition of POX*	155

* Data calculated through the above method. The value from the supplier's (Atofina) website is 163.8 kJ/mol

From the above Tables 5.1a and 5.1b, it is obvious that the reactions in this particular case are controlled by the concentration of POX. However, in order to determine the rate controlling step, the time required for a free radical, decomposed from POX, to diffuse to the center of the PP or UP particles could be estimated from Equation 5.4, by assuming a diffusivity coefficient D_{AB} around 10^{-6}cm^2/s (Steinfeld et al., 1989). The diameters, d, of PP and UP are taken as 0.130cm and 0.018cm, respectively. By calculation, t_{dif} is around 4000s for PP and 800s for UP.

$$t_{dif} = \frac{(d/2)^2}{D_{AB}} \tag{5.4}$$

Compared to the reaction time of PP degradation, which is around 400s, the diffusion time for POX into the PP domains is much larger. Therefore, it can be assumed that PP degradation is diffusion controlled. However, the crosslinking reaction of UP appears to be much more complicated.

Very unlike those studies of controlled PP degradation performed in extruders or static mixers (Tzoganakis, 1988), there is no adequate mixing during these experiments in RMS-800 at steady shear mode. It is very difficult for POX to diffuse into the polymer phase without any dispersive mixing; thus, the free radicals generated from the decomposition of the POX will mostly attack the adjacent polymer chains at higher reaction rate. For the low concentration of POX, the number of free radicals is much less and the diffusion path to reach unreacted polymer domains is longer compared to that at higher concentration of POX; thus, the time required for the polymer chains to collide with the active free radicals that will initiate chain scission or crosslinking is much longer and this will slow down the reaction rates accordingly. When POX concentration is increased, the availability of free radicals is easier, thus, promoting faster reactions. It can be expected that at a certain POX concentration where there are enough free radicals, the reaction rates may remain constant at a certain temperature and will be no longer a function of the POX concentration. Also, since temperature control is much better and shear rate ($2s^{-1}$) is low and constant, the possibility of generating free radicals due to temperature variation and/or shear is negligible compared to that due to POX.

Various modeling studies proposing mechanisms and kinetics for the degradation of PP using POX have been published but seldom such a task has been done for the crosslinking of UP in the presence of POX. In the present work, the overall kinetics of degradation of PP and crosslinking of UP can be expressed by the following equation (5.5), derived in Appendix A.

$$\frac{d\eta}{dt} = \pm 2 f C_5 k_d [I] \tag{5.5}$$

where, the sign ± indicates the increase/decrease of the viscosity for UP/POX and PP/POX systems, respectively. f is initiator efficiency (number of polymer chains broken after hydrogen abstraction through initiator radicals divided by the number of initiator radicals formed), which is usually a function of the peroxide concentration and reaction temperature. k_d is the rate coefficient for initiator dissociation. C_5 is a constant related to the molecular weight of PP or UP.

Tables 5.4a and 5.4b summarize some results obtained by implementation of the above kinetic model for the PP degradation and UP crosslinking. Although it is not linear, a discernible trend is observed on the dependency of the initiator efficiency on POX concentration and experimental temperature. At low POX concentration and low experimental temperature the efficiency is higher, since the free radicals generated from the decomposition of POX are more prone to attack the polymer backbone chains that surround them instead of disappearing due to side reactions. It is also of interest that at higher POX concentration and higher experimental temperature, the initiator efficiency for UP crosslinking is higher than that for PP degradation. This may due to the low viscosity of the UP matrix compared to PP, assuming that both reactions are diffusion controlled.

Table 5.4a Calculated Values of $f \times C_5$ Obtained from Experiments of PP Degradation

Temp. (^oC)	k_d ($\times 10^{-3}$ s^{-1})	POX Concenration (phr)	$f \times C_5$ ($\times 10^4$ Pa·s^2)
180	10.1	0.1	8.03
		0.2	5.26
		0.25	4.75
		0.5	3.28
		1	1.72
200	57.8	0.1	3.33
220	288.8	0.1	1.92

Table 5.4b Calculated Values of $f \times C_5$ Obtained from Experiments of UP Crosslinking

Temp. (°C)	k_d ($\times 10^{-3}$ s^{-1})	POX Concentration (phr)	$f \times C_5$ ($\times 10^4$ Pa·s^2)
180	10.1	0.1	9.05
		0.2	
		0.25	6.75
		0.5	4.93
		1	4.51
200	57.8	0.1	7.78
220	288.8	0.1	3.69

The reaction rates of PP degradation and UP crosslinking are not only affected by the above parameters, but can also be controlled through unsaturated bifunctional additives such as PDMI, which is able to form rapidly macroradicals and possibly delay the reaction between POX and PP or UP. PDMI, like other bis-maleimide derivatives, has been shown to promote crosslinking of PP and minimize degradation in the presence of peroxides (Romani, et al., 2001). Although it is unable to initialize macroadicals by chain scission, the PDMI can react with free radicals, especially with PP macroradicals through the double bond and prevent them from undergoing β-scission. The macroradicals so formed also can lead to intermolecular bonding through coupling with other non-terminal macroradicals. Figure 5.5a shows the viscosity changes of the PP/POX system with or without PDMI; in the PP/POX/PDMI system, the PDMI was ground into a fine powder and dry blended with the PP/POX mixture. Note that the initial part of this experiment may not be reliable since PP was not full melted at the very beginning. However, a large difference is observed over the entire experimental time, which may be attributed to the bridging effect of PDMI between PP and POX during the reaction.

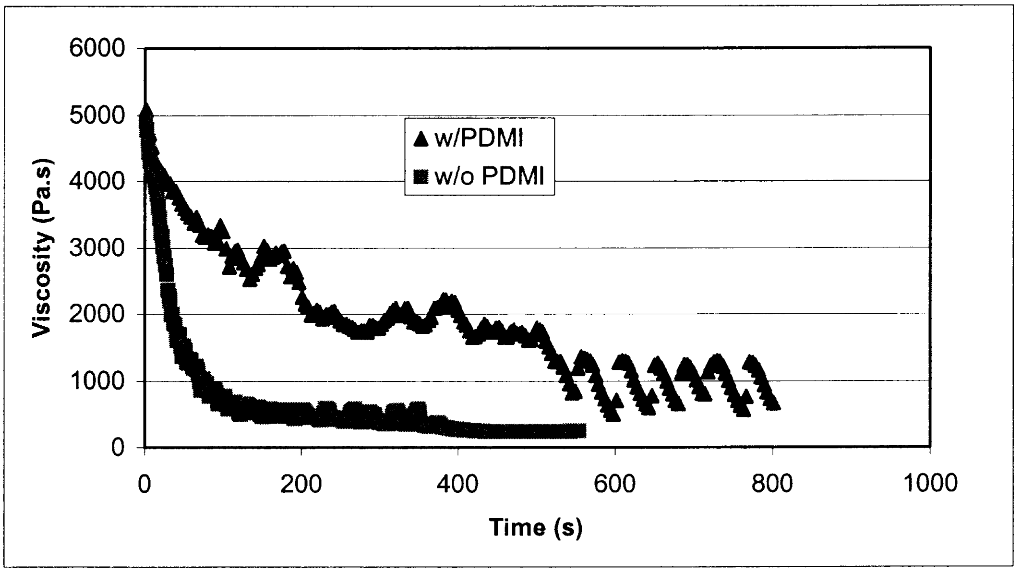

Figure 5.5a Comparison of viscosity changes of PP/POX system with or without PDMI (1phr) in the RMS-800 (0.1phr POX, 200°C, steady shear, $2s^{-1}$).

No work has been reported on the effect of PDMI on the UP/POX reaction system, to the best of our knowledge. Figure 5.5b shows that there is almost no viscosity change when adding PMDI into the UP/POX system. This may be possibly due to the higher reactivity of POX radicals towards PDMI, rather than towards UP.

5.1.2 Reaction between PP or UP With MgO With or Without Coagents

Unsaturated polyesters containing free terminal carboxyl groups can also interact with metal oxides and hydroxides such as MgO, ZnO, $Mg(OH)_2$ and form complex compounds (Vancsó-Szmercsányi et al., 1974). This behavior has been already applied to sheet molding compound (SMC) technology to increase the resin viscosity at room temperature and turn the compound from a viscous liquid to a tack-free solid, by what is also known as "chemical thickening".

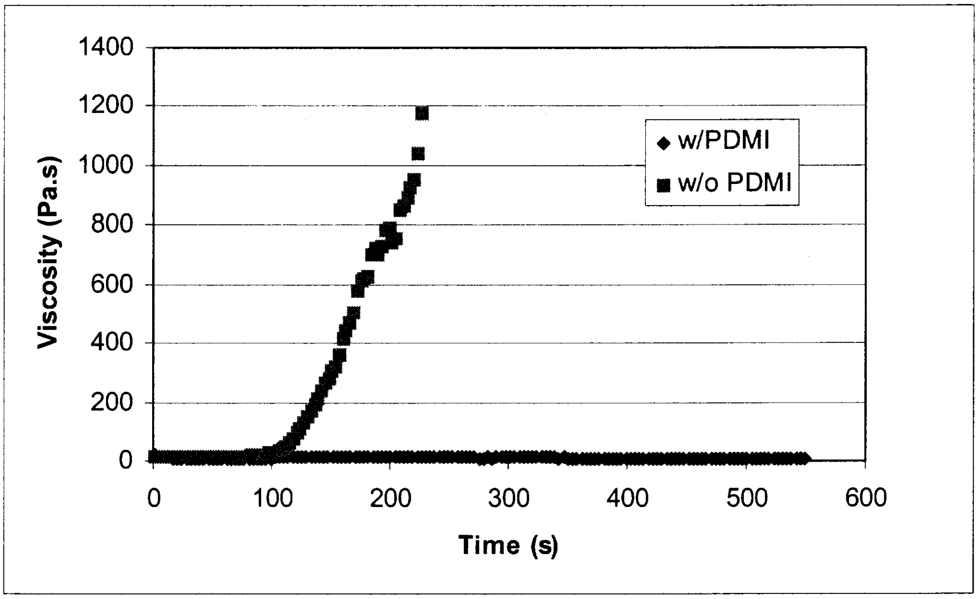

Figure 5.5b Comparison of viscosity changes of UP/POX system with or without PDMI (1phr) in the RMS-800 (0.1phr POX, 200°C, steady shear, $2s^{-1}$).

A Brabender batch mixer was used to prepare composites containing UP and magnesium oxide (MgO) at various temperatures and 60 rpm. As shown in Figures 5.6 and 5.7 UP has a strong interaction with MgO during melt processing at 220°C. Its viscosity can be increased 10-1000 fold within 15 mins processing time. It is also shown that, unlike results reported by several authors (Vancsó-Szmercsányi et al., 1974, Rao et al., 1985) on the room temperature reactions, the MgO moisture content at high processing temperatures seems to have no effect on the reaction between MgO and UP. TGA data show that there is around 1% weight loss when MgO is heated to 100 °C and an additional 1% weight loss when heating continues to 220 °C. This may indicate that there are some difficulties to remove all moisture around 100 °C and at 220 °C processing temperature residual water is rapidly removed without any catalytic effect. However, there is a large difference when performing the reaction under different atmosphere. The reaction rate under air although similar to that under nitrogen initially becomes much lower after about 500 seconds. The mechanism is not quite understood, although, it may due to the onset of degradation of UP at this high temperature in the presence of oxygen, which affects the formation of the coordination complex as suggested by some authors (Rao and Gandhi, 1985) .

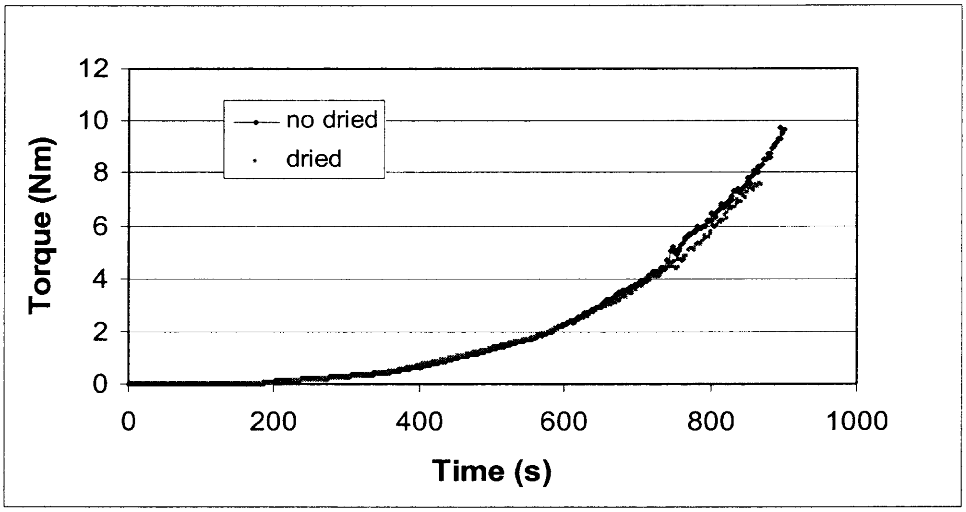

Figure 5.6 Comparison of the changes in torque of UP with 30wt% MgO processed at 220°C (MgO non-dried and pre-dried at 100°C).

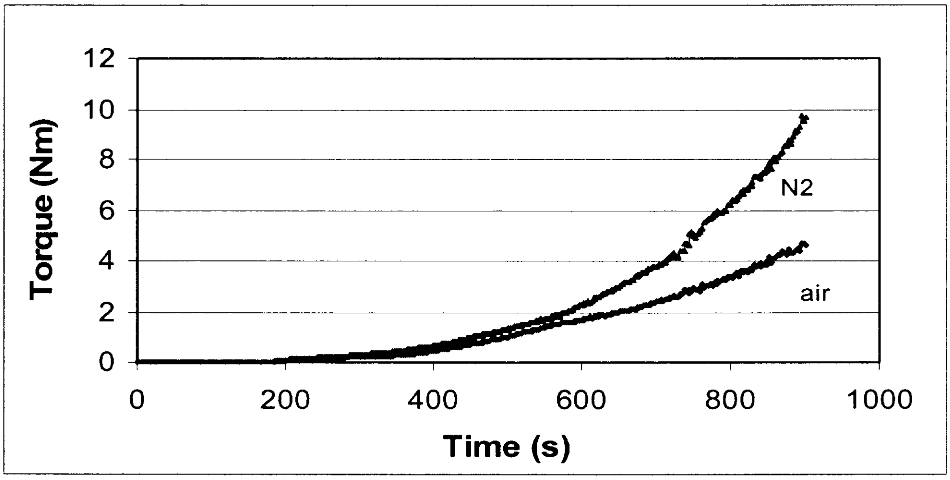

Figure 5.7 Changes in torque of UP with 30wt% MgO processed at 220°C under air or N_2, respectively.

Two mechanisms have been proposed in the literature to account for the interaction of polyester and magnesium oxide. One is a chain extension mechanism and the second is the formation of a coordinate complex, also known as two-stage thickening mechanism (Judas et al., 1984). The common starting point for these two mechanisms is the formation of basic and neutral salts with the polyester end groups as per the following reactions:

$\text{---COOH} + \text{MgO} \rightarrow \text{---COOMgOH}$

$\text{---COOH} + \text{HOMgOOC} \rightarrow \text{---COOMgOOC---} + H_2O$

In the chain extension mechanism, it is postulated that dicarboxylic acid groups on the UP chains react with MgO to produce a very high molecular weight (MW) species (via condensation polymerization) and thus give rise to a large increase in viscosity (shown in Figures 5.6 and 5.7). However, this theory only applies to those UP molecules terminated by carboxylic groups with structure HOOC~~~COOH. For other possible polyester structures such as HOOC~~~OH and HO~~~OH, the MW of the polyester will only increase two-fold or not at all if the chain extension mechanism is followed. Therefore, it is not possible to use this theory to explain the large increase of viscosity in thickening of UPs with structures having terminal OH functional groups, which have been reported in several publications (Vancsó-Szmercsányi et al., 1974).

$\sim\sim\text{UP}\sim\text{COO}^{-+}\text{Mg}^{+-}\text{OOC}\sim\text{UP}\sim\text{COO}^{-+}\text{Mg}^{+-}\text{OOC}\sim\text{UP}\sim\sim\sim$

In the two-stage mechanism, it is postulated that a high MW salt is first formed, then a complex is formed between the salt and carbonyl groups of the ester linkages, as shown in Figure 5.8. The second stage of this theory is considered to be responsible for the large increase in viscosity. A number of publications support this mechanism (Vancsó-Szmercsányi et al., 1974 and Rao and Gandhi, 1985).

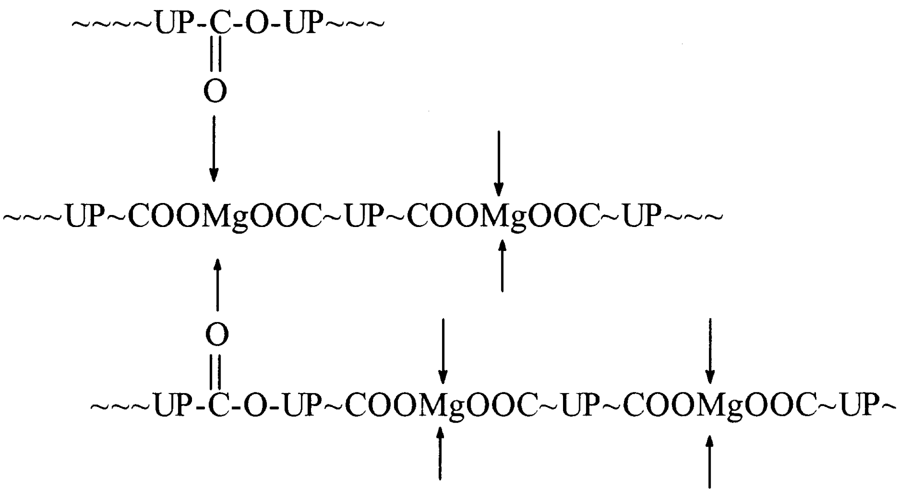

Figure 5.8 Schematic structure of UP-MgO complex.

Figures 5.9 and 5.10 show the effects of MgO concentration and processing temperature on the reaction between UP and MgO. It can be seen that the reaction rate increases significantly with increasing MgO concentration at 220°C. It is also shown that at a lower processing temperature, such as 100°C, the viscosity, in terms of torque value, increases rapidly from 0.5Nm to 2Nm presumably due to the dispersion effect of the filler and then increases very slowly, indicating a slow reaction rate between UP and MgO. At an intermediate temperature, such as 180°C, the reaction of UP and MgO is faster than before but still linear, although the final viscosity value is lower than at 100°C due to the less pronounced dispersion effect of MgO at this higher temperature. When processed at much higher temperature (200°C and 220°C), the reaction is much faster, resembling auto-acceleration.

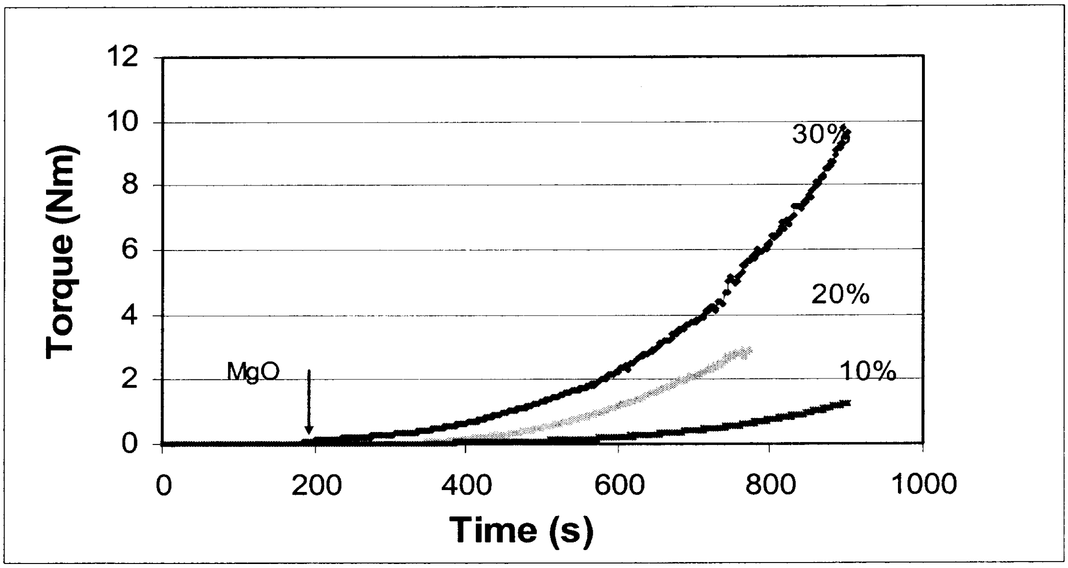

Figure 5.9 Changes in torque of UP with various amounts of MgO at 220 °C.

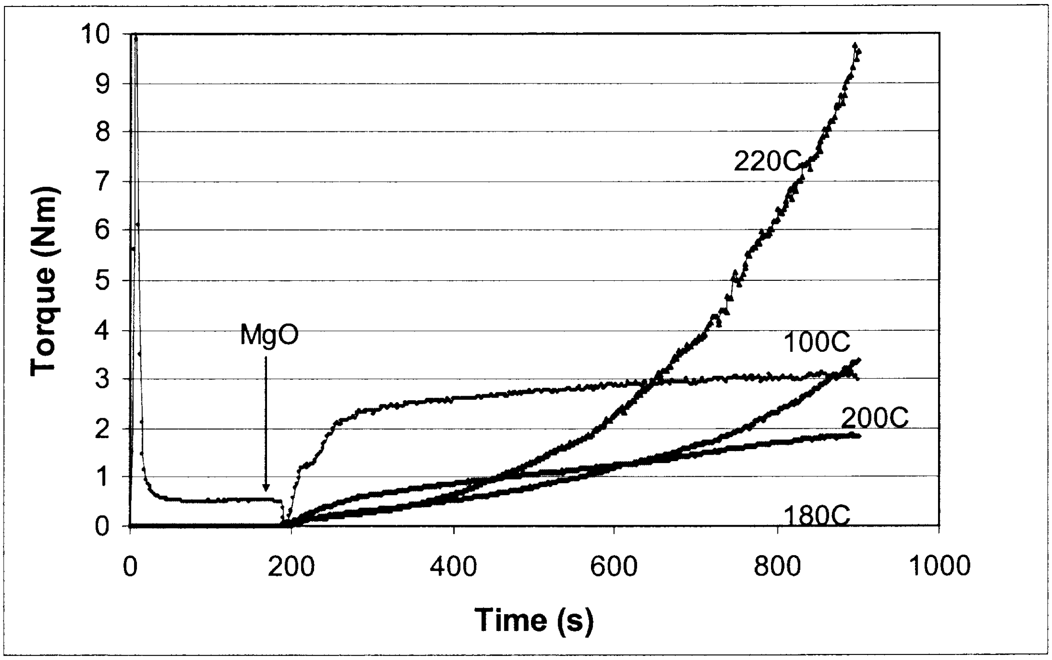

Figure 5.10 Changes in torque of UP with 30wt% MgO at 100, 180, 200 and 220 °C.

According to the two-stage mechanism, the formation of the coordination complex is considered to be responsible for the large increase in viscosity. It can be postulated that at low temperature the formation of MgO-UP salts is the kinetic controlling step during the reaction, while at high temperature the formation of MgO-UP salts and the coordination complex are almost simultaneous, resulting in the large increase in viscosity within 15 mins processing time. In the current study, it is very difficult to present a model to describe mechanism and kinetics of the crosslinking behavior of UP with MgO only by monitoring the concentration of MgO and the reaction temperature.

The T_gs of the reacted UP/MgO composites processed for about 15 mins were measured and analyzed by using DSC. It is shown in Tables 5.5a-5.5b and Figures 5.11a-5.11c that the T_g of the composites increase with increasing MgO concentration and processing temperature. This is expected since T_g is directly related to free volume that is decreasing with increasing crosslinking density. It is interesting that the magnitude of the thermal transition temperature is less pronounced during the second heating in the DSC experiment. This may correspond to structural changes during the heating/cooling/heating cycle.

Attempts were made to measure the total insolubles in hot THF over a period of 24 hrs; these would include UP gels and MgO and would serve as an indication of the magnitude of the crosslinking density of the UP/MgO composites. Overall, the gel content increases with processing temperature and concentration of MgO. The relationship between T_gs, obtained from the first heating, and percentage of insolubles is almost linear, as shown in Figures 5.12a and 5.12b.

From the data of the Table 5.5a, it appears that a high degree of crosslinking is obtained at 220 °C, where the percentages of insolubles include 30% MgO and 26.2% gel. At lower temperature, gel content is much lower although a certain amount of MgO could be found in suspended in the soluble polyester or would be present in soluble linearly chain-extended polyester molecules. The data in Table 5.5b confirm the formation of high gel content at 220 °C.

Table 5.5a Tg of UP/30%MgO Composites As A Function of Processing Temperature (15 mins processing time)

	UP resin	UP/30%MgO			
Processing temperature (°C)	N/A	100°C	180 °C	200 °C	220 °C
T_g at First heating (°C)	43.93	47.71	51.37	54.99	63.46
T_g at Second Heating (°C)	44.13	49.25	53.27	55.57	60.23
Total Insolubles (%)	0	24.4	27.8	30.9	56.2

Table 5.5b Tg of UP/MgO Composites As A Function of Concentration of MgO (15 mins processing time At 220°C)

	UP resin	UP/MgO at 220 °C			
MgO content (%)	0	1.3%	10%	20%	30%
T_g at First heating (°C)	43.93	50.97	55.98	57.86	63.46
T_g at Second Heating (°C)	44.13	51.56	52.76	55.04	60.23
Total Insolubles (%)	0	2.4	26.5	37.4	56.2

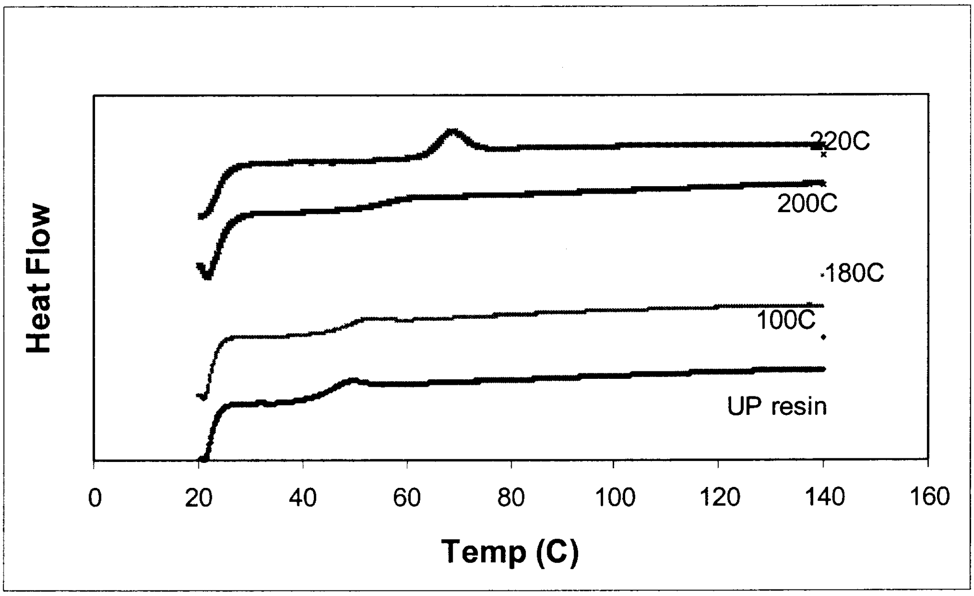

Figure 5.11a T_g values of the UP/30%MgO composites prepared at different processing temperatures (1st heating).

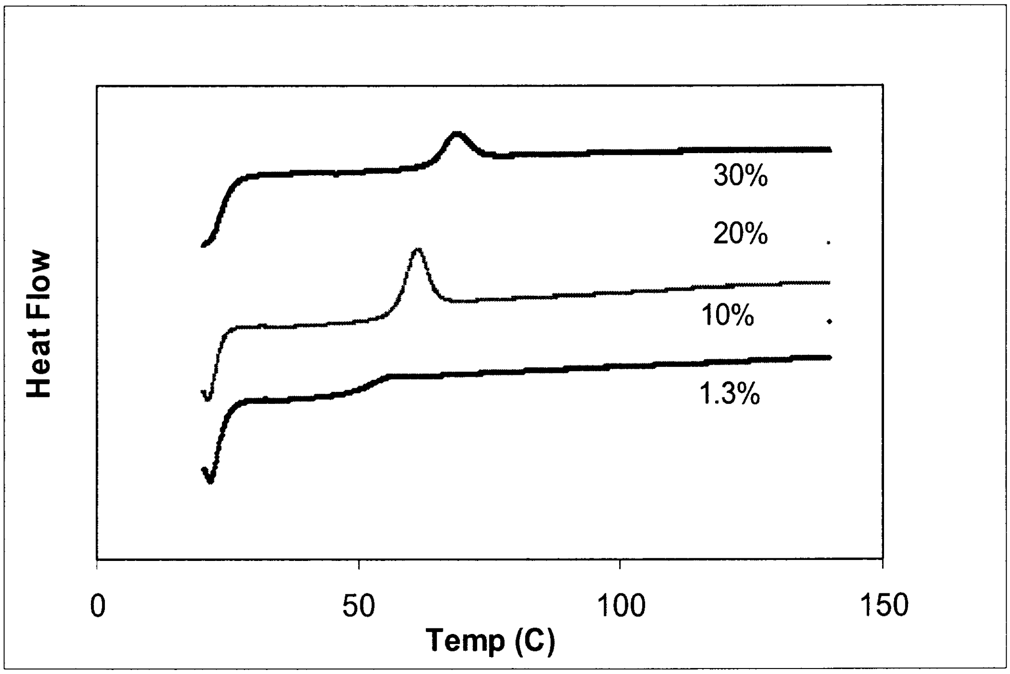

Figure 5.11b T_g values of the UP/MgO composites prepared at 220°C and different concentrations of MgO (1st heating).

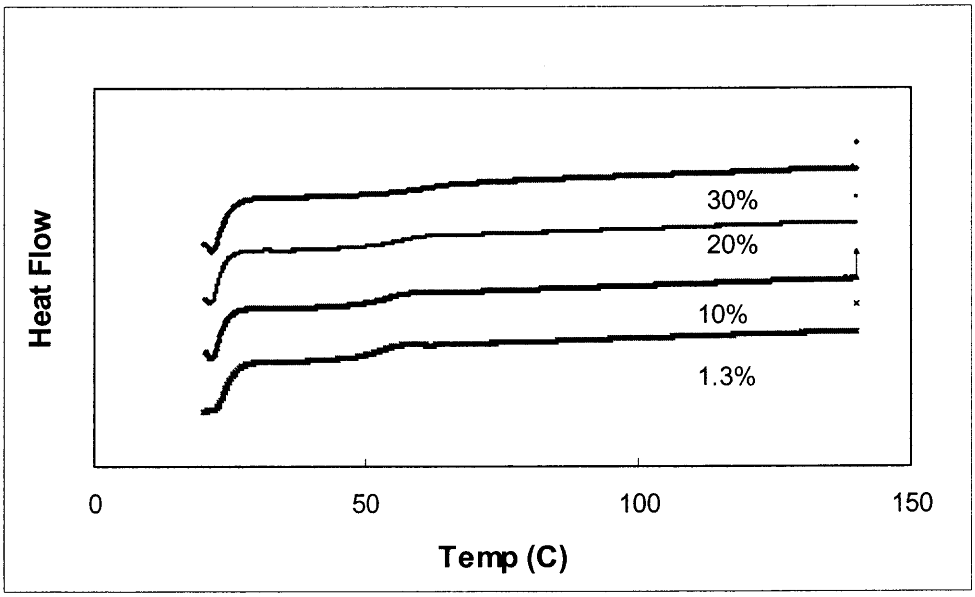

Figure 5.11c T_g values of the UP/MgO composites prepared at 220°C and different concentrations of MgO (2nd heating).

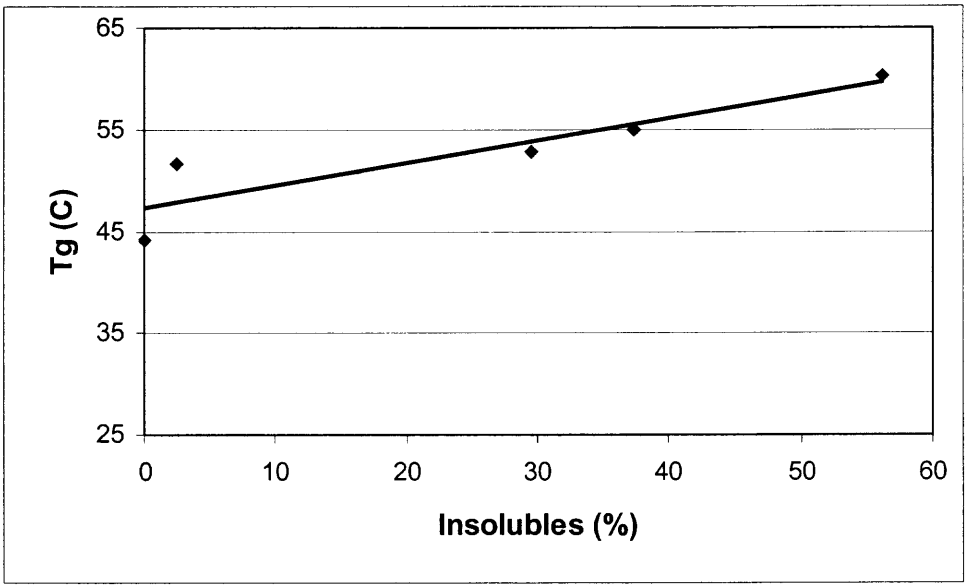

Figure 5.12a The relationship between the values of T_gs and the percentage of insolubles of UP/MgO samples prepared at 220°C and different concentrations of MgO.

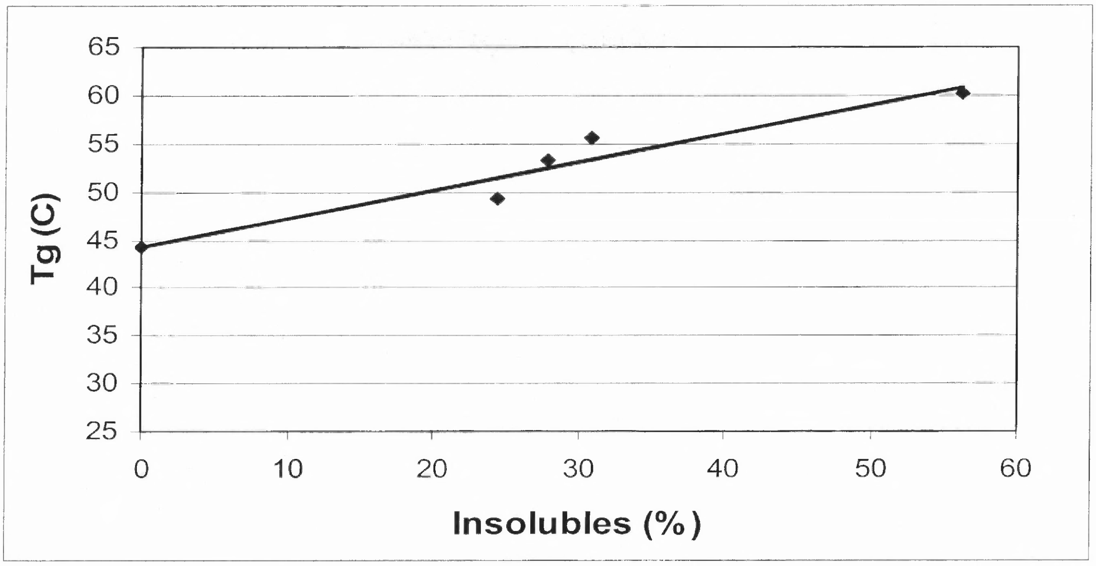

Figure 5.12b The relationship between the values of T_gs and the percentage of insolubles of UP/30%MgO samples prepared at different processing temperatures.

Figure 5.13 is an example of the morphology of the reacted UP/30%MgO composite prepared at 220°C in the batch mixer. Excess of MgO particles with an average size around 0.5 µm are well distributed within the reacted UP matrix.

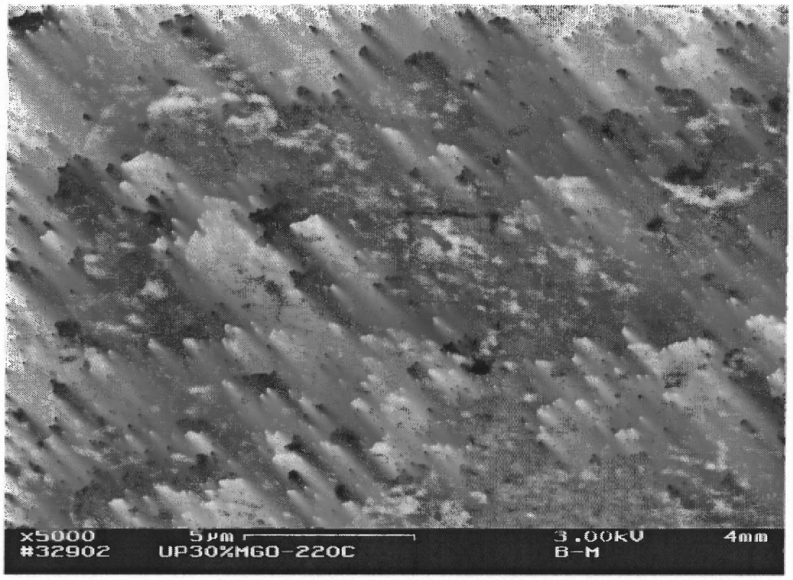

Figure 5.13 Morphology of UP/30%MgO blend prepared in batch mixer at 220°C (15 mins processing, x5000).

No reaction/interactions between MgO and PP have been reported in the literature and, therefore, interfacial adhesion is expected to be poor. In order to increase the affinity between these two components, PDMI, an organic coagent, was also introduced along with small amount of POX (0.2 phr) during melt mixing of the PP and MgO. As shown before, PDMI can react with PP in the presence of POX to form a graft or crosslinked structure (Romani et al., 2002). It can also react with MgO in the presence of a small amount of water to form a complex (Khunova et al., 1999 and Liauw et al., 2000). The formation of the complex involves change of color from yellow to pink, which was also observed in the present study in the absence of any water added. Figure 5.15 shows FTIR spectra of MgO, PDMI and the reacted MgO/PDMI mixture, respectively. The change around 1718 cm-1, which corresponds to the carboxyl vibration and the large reduction of the band at 3100 cm-1, corresponding to the C-H stretch at the five member ring of PDMI in the reacted MgO/PDMI mixture may be attributed to the formation of a MgO-PDMI complex. In that case, PDMI will serve as an interphase modifier for PP and MgO during the reactive mixing process. This may be significant during blending of PP/UP with MgO additives such as PDMI and POX, where the two immiscible components, PP and UP, will have a chance to interact with each other through these inorganic and organic coagents. Figure 5.14 shows a similar morphology of PP/30%MgO composite prepared in the batch mixer at 220°C in the presence of PDMI and POX, compared to that of UP/30% MgO composites (Figure 5.13). The compatibilizing effects of MgO during the blending of PP/UP blends will be covered in the following section.

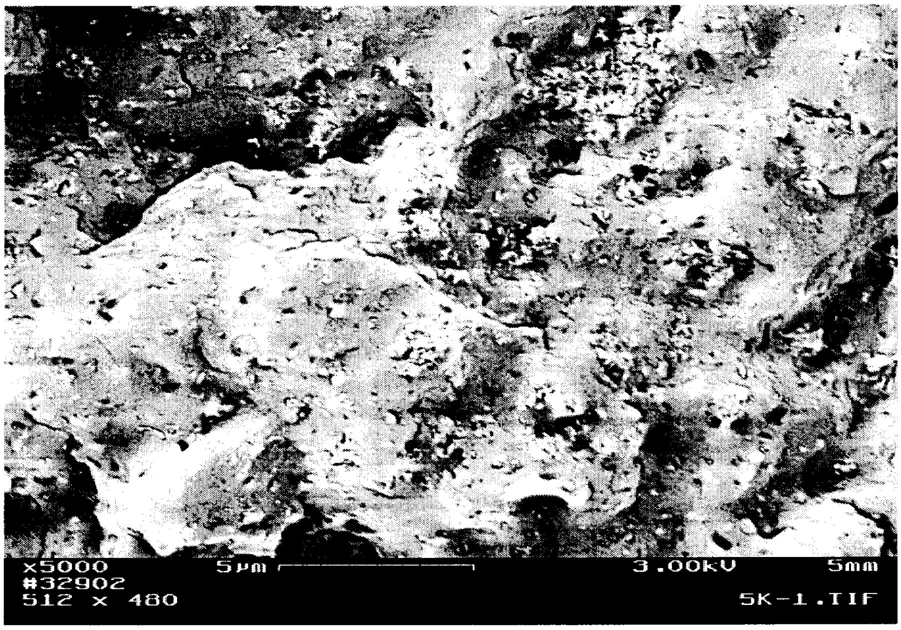

Figure 5.14 Morphology of PP/PDMI/MgO (with 0.2 phr POX) blend prepared in the batch mixer at 220°C.

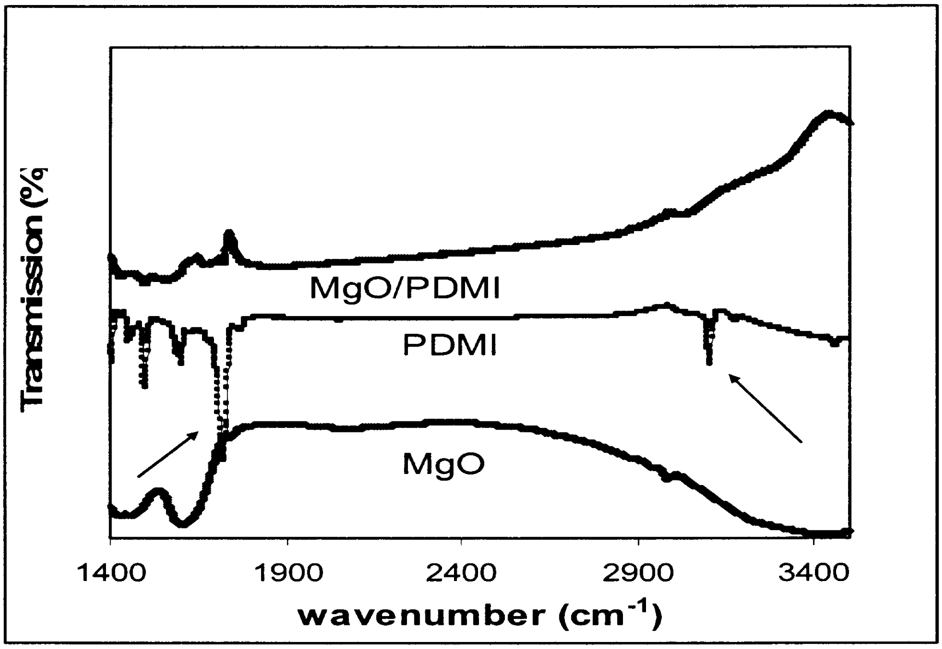

Figure 5.15 FT-IR spectra of MgO, PDMI and reacted MgO/PDMI.

5.2 Blends Prepared In A Batch Mixer

Polypropylene and UP are totally immiscible due to their difference in chemical structures and resulting different solubility parameters and properties. The initial viscosities of these two polymers are also very different. Thus, the initiator (POX) may not equally partition into these two separate polymer phases when blending them together, although in this particular study the reaction rates are shown to be of the same magnitude. A parameter defined as a partition coefficient K is defined by the following equation:

$$K = \frac{[I]_{PP}}{[I]_{UP}} \tag{5.6}$$

where $[I]_{PP}$ represents the instantaneous initiator concentration in the PP phase and $[I]_{UP}$ represents the instantaneous initiator concentration in the UP phase. However, since viscosity and miscibility of these two polymers are changing during the reactions, those two parameters, $[I]_{PP}$ and $[I]_{UP}$ may not be constants and keep changing with reaction time too. Thus, the value of K is also a function of time and not easy to estimate.

When the initiator (POX) is partitioned into each polymer phase, the reaction may take place independently due to the immiscibility of these two polymers. If there is no adequate mixing, the possibility that reactions will take place at the interphase is very low and can be neglected. However, in order to produce much more uniform PP/UP blends with a finer morphology and better rheological properties, intensive mixing is needed during processing. In the PP/UP system, the initial viscosity ratio of PP and UP is more than 1000 times. Thus, UP, although its viscosity and MW are continuously increasing, will still initially have significant mobility resulting in high possibility of interfacial reactions; this is one of the keys to make the “in situ” reactive compatibilization process possible.

5.2.1. Morphology Development as A Function of Reactive Mixing Time

Figures 5.16a-5.16b show the torque-time curves of the 5PP/3UP and 3PP/5UP blends in a batch mixer. The PP with or without POX was first added into the batch mixer for 3 mins in order to advance its degradation, since its initial viscosity is too high, compared to that of UP. Less mismatch in viscosity, not only at the time of addition of the UP, but also during the subsequent 500-1000 seconds when simultaneous competing reactions occur would result in more favorable instantaneous conditions for dispersive mixing of the immiscible components. It can be seen that melt blending of PP/UP blends without peroxide (referred to as unreacted blends, U) yields a much lower final torque value, compared with the peroxide containing blends (referred to as reacted blends, R) in spite of the high concentration of the degrading PP component. This suggests that among the competing degradation and crosslinking reactions, either the reaction of UP with peroxide is predominant or the grafting cross-reaction may have a chance to take place, suppressing the extend of degradation of PP and resulting in the formation of a “block” or “graft” PP-UP copolymer structure.

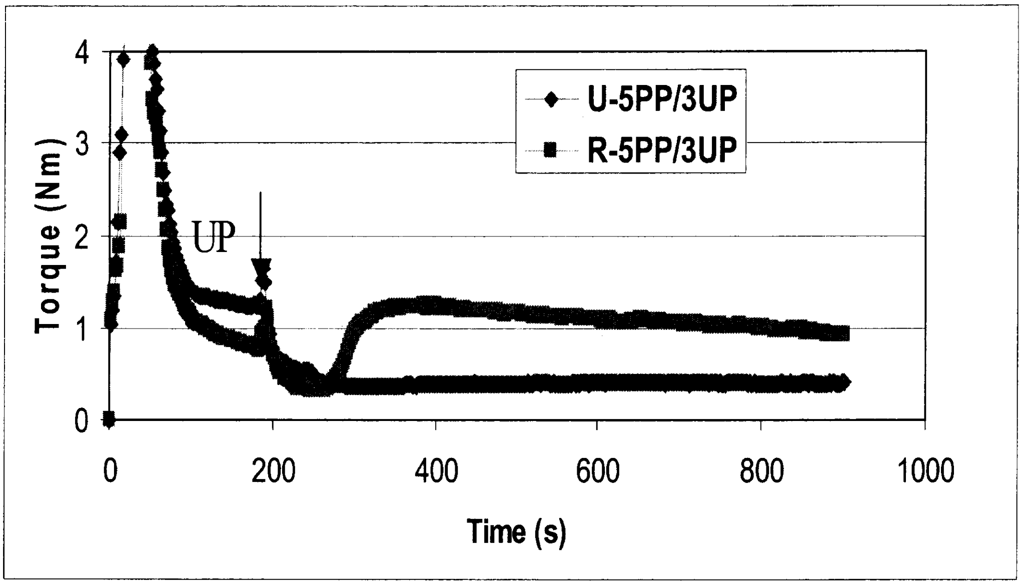

Figure 5.16a Changes in torque of 5PP/3UP with and without peroxide (1phr) in the batch mixer (160°C, 60rpm).

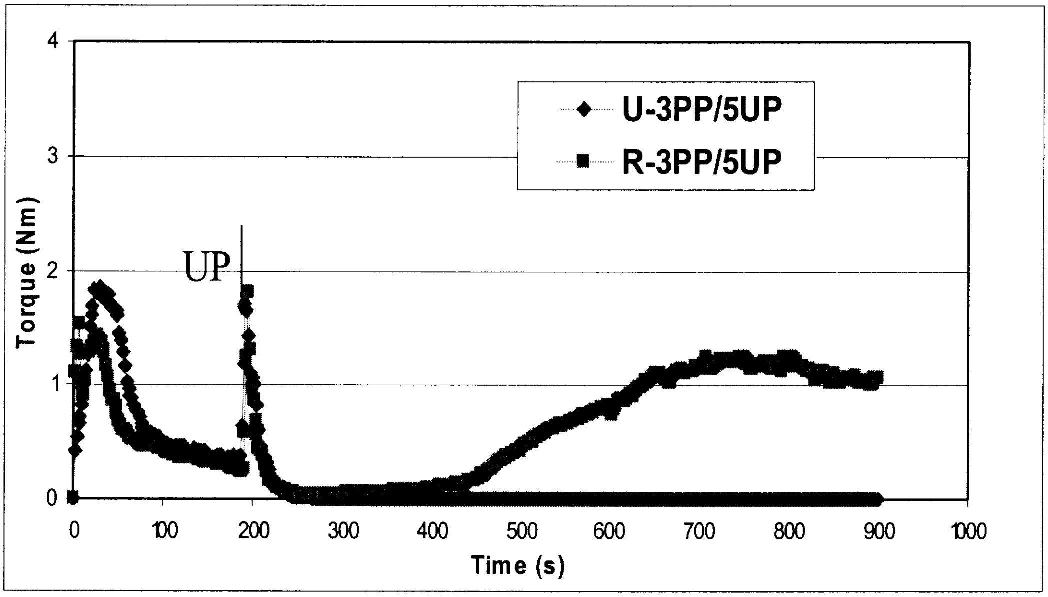

Figure 5.16b Changes in torque of 3PP/5UP with and without peroxide (1phr) in the batch mixer (160°C, 60rpm).

Morphology analysis of the blends as a function of mixing time reveals much more information of the effects of the POX concentration on the products. As mentioned earlier, PP and UP are totally immiscible due to their different molecular structures. The large differences in their initial viscosity values and polarities are expected to play a very important role in the morphology development of their blends (Favis, 2000). It is clear that in the absence of any additional compatibilizing species that can reduce the interfacial tension between PP and UP, the unreacted 5PP/3UP blends must have coarse morphologies. This is confirmed in Figure 17a, which shows a typical immiscible system. The adhesion between the blend components appears to be very poor, as expected. The dispersed domain sizes are ranging from 0.7 to 43μm resulting in a broad size distribution. By adding a small amount of POX during the melt blending, a continuous change of the dispersed domains sizes and their size distribution can be observed as a function of time. These morphological changes may be attributed to the continuous decrease of the PP/UP viscosity ratio during the reaction resulting over short time intervals in essentially equiviscous conditions, which are favoring dispersive mixing. Another important factor is the "*in situ*" formation of a graft copolymer PP-UP by macroradical recombination, which will act as a compatibilizer reducing interfacial tension, and promoting increased interfacial adhesion with concomitant effects on morphology (Hudson and Jamieson, 2000).

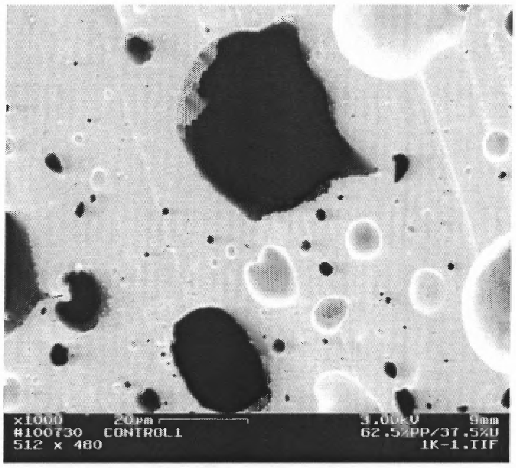

Figure 5.17 SEM of unreacted 5PP/3UP (blank, 15mins, processing).

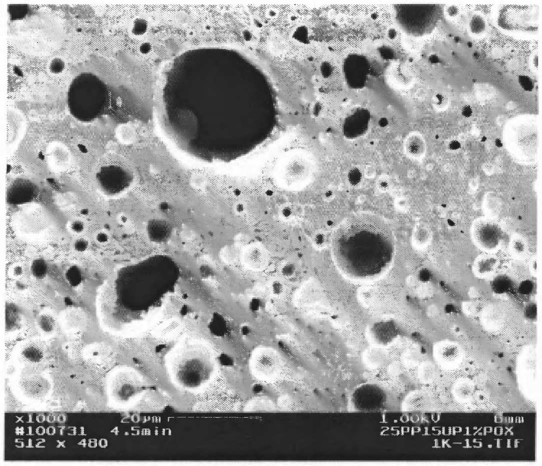

Figure 5.18a SEM of reacted 5PP/3UP (1phrPOX, 270s)

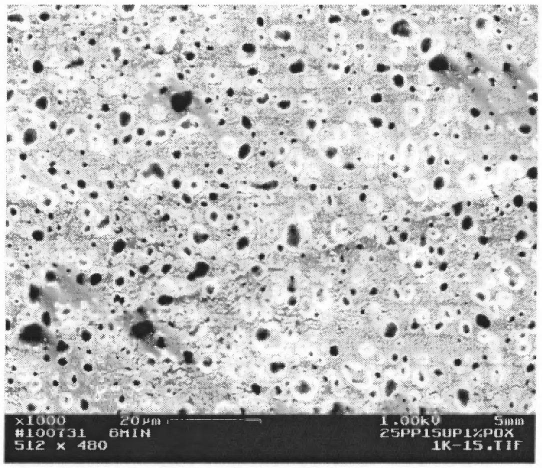

Figure 5.18b SEM of reacted 5PP/3UP (1phrPOX, 360s)

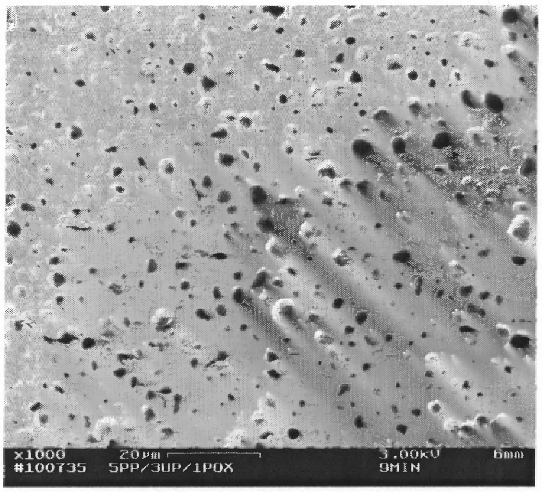

Figure 5.18c SEM of reacted 5PP/3UP (1phrPOX, 540s)

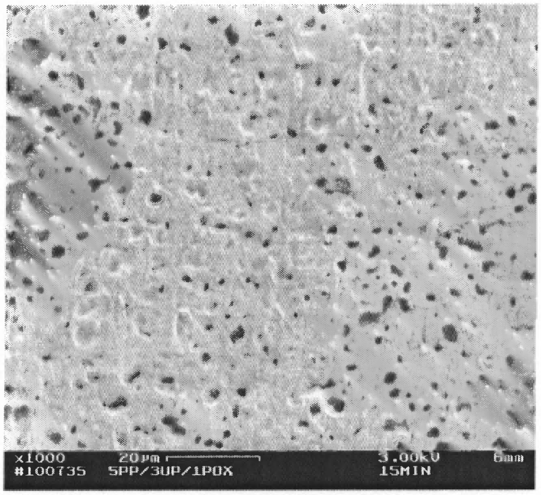

Figure 5.18d SEM of reacted 5PP/3UP (1phrPOX, 900s)

Table 5.6 Summarized Average Diameter and Diameter Range of Unreacted and Reacted 5PP/3UP Blends

	Unreated 5PP/3UP	Reacted 5PP/3UP (270s)	Reacted 5PP/3UP (360s)	Reacted 5PP/3UP (540s)	Reacted 5PP/3UP (900s)
Number-average diameter (µm)	4.89	3.89	1.56	1.48	1.36
Diameter range (µm)	0.68~42.65	0.61~28.67	0.36~9.18	0.2~4.8	0.3~3.1

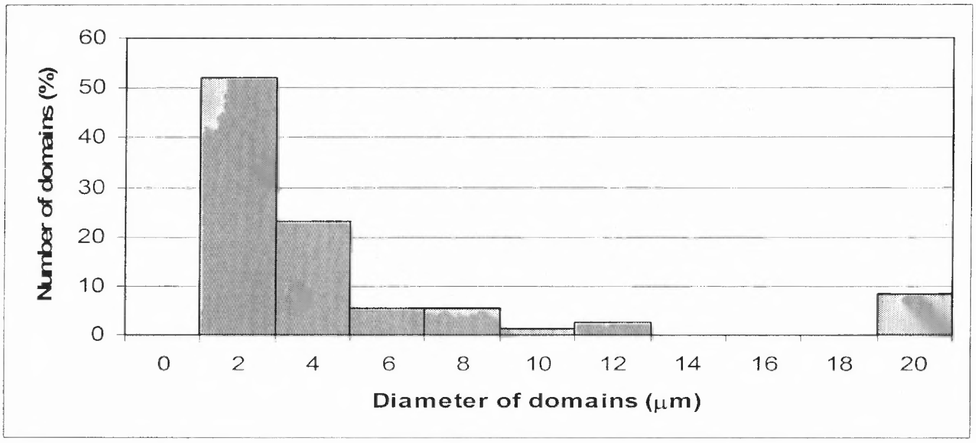

Figure 5.19a Domain size distribution of unreacted 5PP/3UP blend.

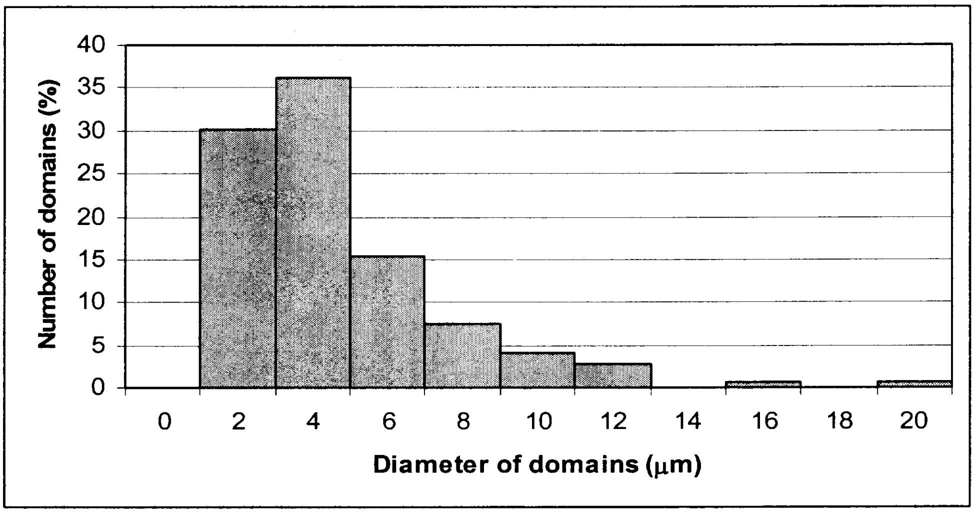

Figure 5.19b Domain size distribution of reacted 5PP/3UP blend (1 phr POX, 270 s).

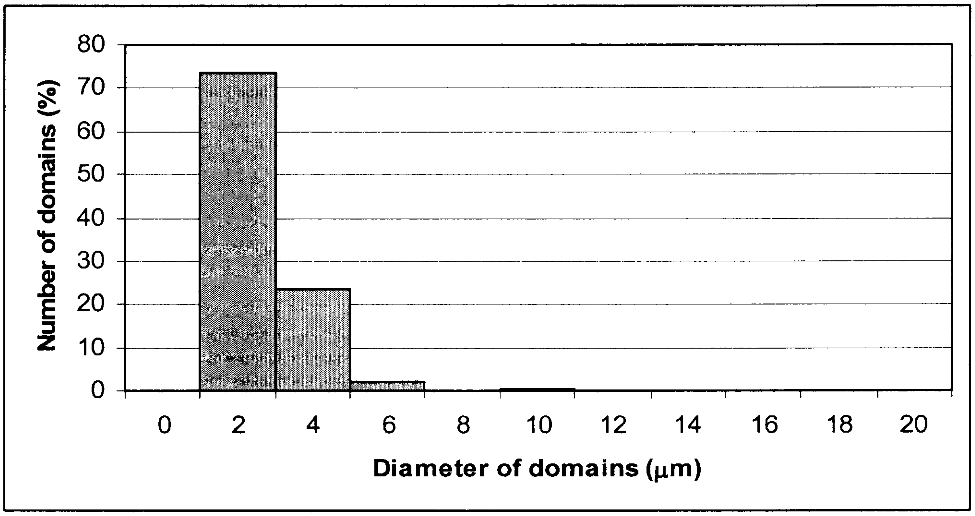

Figure 5.19c Domain size distribution of reacted 5PP/3UP blend (1 phr POX, 360 s).

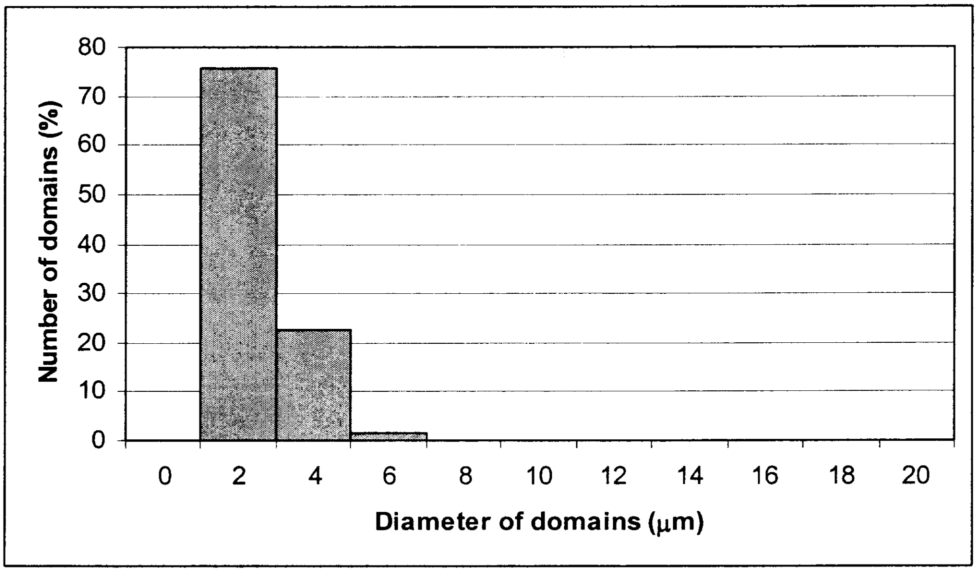

Figure 5.19d Domain size distribution of reacted 5PP/3UP blend (1 phr POX, 540 s).

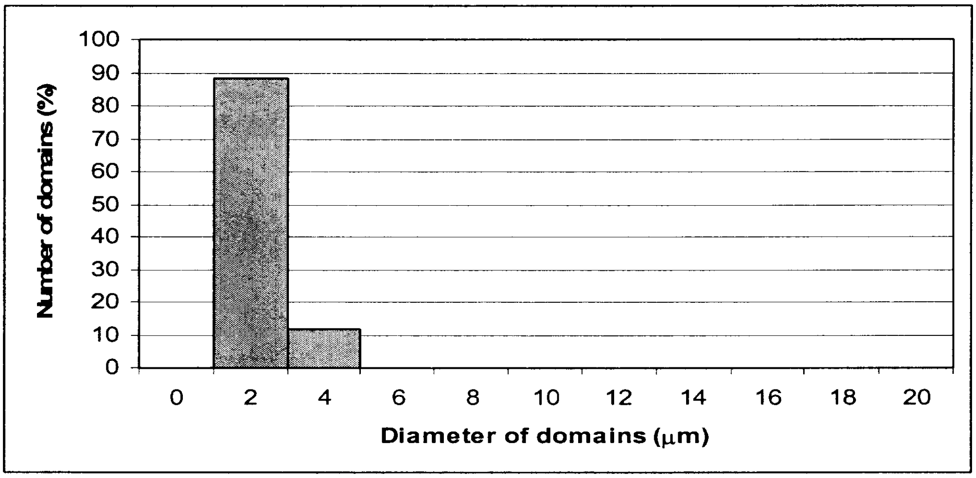

Figure 5.19e Domain size distribution of reacted 5PP/3UP blend (1 phr POX, 900 s).

Table 5.6 and Figures 5.19a-5.19e summarize the domain size and their size distribution. At the beginning of the reactive blending, the blend exhibits much broader polydispersity. After 15 mins processing, the average domains size is dramatically decreased to 1.4 and the size distribution is narrowed down to the range from 0.3 μm to

3.1μm. This indicates the reactions within the POX and blend components greatly reduce the coalescence and lead to, not only decreased average dispersed phase size, but also to narrower particle size distributions. The POX during the reactions not only brings the mismatched viscosity closer to the unity but also serves as a compatibilizing agent. It can be imagined that the reactive *in-situ* compatibilizing role of POX during the reaction be can be improved by increasing the intensive of mixing or adding some coupling coagent.

Taylor et al (1932) first studied the deformation and breakup of a single Newtonian liquid drop in a Newtonian liquid matrix in a simple steady shear flow. However, in the present study, both matrix and dispersed phase are not simple liquids and possess much more complicated viscoelastic properties that are changing with processing time. Furthermore, the strain field is a complex combination of non-uniform, transient shear and elongational field. Tayor's equations are not accurate enough to describe the system of interest and only provide a basis for analyzing the experimental results. An expression for determining the size of the largest drop that exits in a fluid undergoing a deformation at any steady shear rate can be written by the following equation:

$$d = \frac{4\Gamma(\eta_r + 1)}{\dot{\gamma}\,\eta_m(\frac{19}{4}\eta_r + 4)} \qquad (5.7)$$

where d is the diameter of the drop, Γ is the interfacial tension, $\dot{\gamma}$ is the shear rate, η_m is the matrix phase viscosity and η_r is the viscosity ratio

$$\eta_r = \frac{\eta_d}{\eta_m} \qquad (5.8)$$

A number of authors have investigation the morphology development of polymer blends in processing equipment (Wu et al., 1987, Utracki and Shi, 1992, Esseghir et al., 1995 and 1996). Generally speaking, the formation of the blend morphology depends on many factors, such as the composition of the blends and their viscosity ratio, the processing methods, interfacial modification and so on. In the present study, the most important parameter is the viscosity ratio, capillary number and *in-situ* compatibilzer, POX. Those two dimensionless parameters, viscosity ratio η_r and capillary number (*Ca*) are defined as below:

$$Ca = \frac{\dot{\gamma}\,\eta_m d}{2\Gamma} \tag{5.9}$$

where η_d is the viscosity of the dispersed phase and d is the characteristic diameter of the droplets. The capillary number, *Ca*, is the ratio of the flow stresses (matrix viscosity times shear rate, $\eta_m\,\dot{\gamma}$) to the droplet interfacial stresses ($2\Gamma/d$).

The break-up phenomena of Newtonian and non- Newtonian droplets in both simple shear and extensional flows have been studied by many researchers (Taylor et al., 1932, Karam et al., 1968, Favis, 2000). The governing factors for droplet break up are the viscosity ratio η_r and Capillary number. Droplet break-up occurs when a critical capillary number, Ca_{crit}, is reached. Ca_{crit} depends on the type of flow and the viscosity ratio. It is experimentally believed that the viscosity ratio should be approximately unity to achieve a fine morphology. Figure 5.20 shows Ca_{crit} for drop break-up as a function of η_r in simple shear and 2-D elongational flows. For a viscosity ratio of one, the critical capillary numbers are in the range of 0.1-1for both simple shear and extensional flows. As the viscosity ratio becomes larger than 4, simple shear flows cannot overcome the interfacial tension between the components and droplets cannot be broken up. However, extensional flows do not exhibit any limit for droplet breakup since they generate significantly higher stresses, which are more efficient in breaking up droplets. In the aforementioned morphology study, there are some abrupt changes in particle size from 4μm in Figure 5.18a to 1.5μm in Figure 5.18b corresponding to the significant torque changes from 0.2Nm to 1.2 Nm shown in Figure 5.16 at approximately 270 to 360 seconds reaction time. This is also a time when the ratio of the torque of dispersed phase (UP) to the torque of the matrix (PP) is reaching unity, as shown in Figure 5.2. The viscosity ratio was found to have a marked effect on the morphology of the dispersed phase, with the phase size reduction by a factor of three, from the torque ratio of above 500 to around 1~2. This dependence of the phase-size-to-viscosity ratio resembles that of Newtonian fluids in an elongational flow field. Other compatibilizing mechanisms such as the formation of in-*situ* compatibilizer may also be strongly favored within this time interval range.

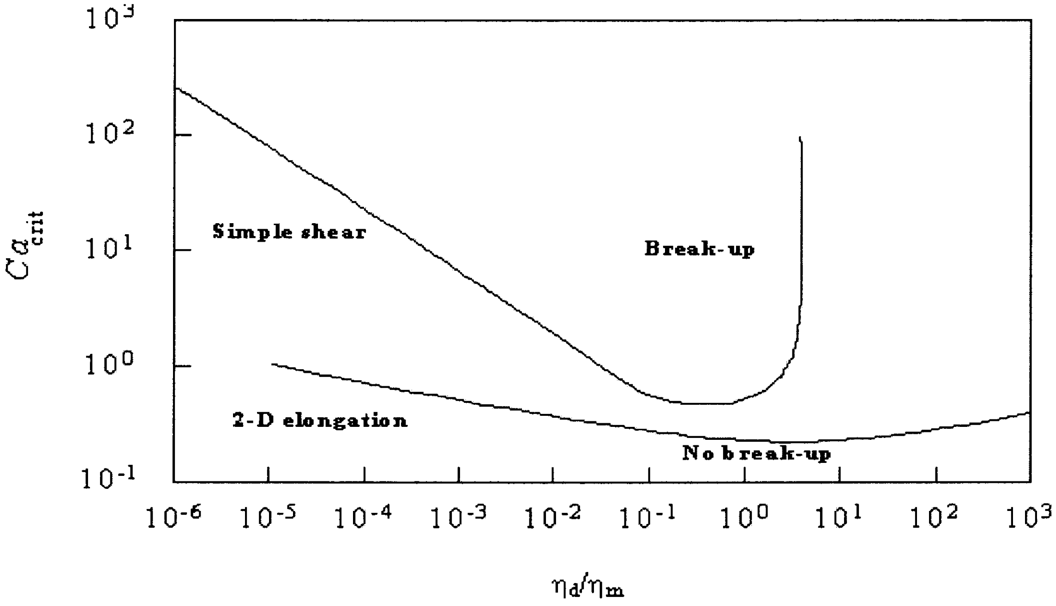

Figure 5.20 Critical capillary number for drop break-up as a function of viscosity ratio in simple shear and 2-D elongational flows (Grace, 1982).

5.2.2 The Effect of POX Concentration

The effects of the concentration of POX on both 5PP/3UP and 3PP/5UP were investigated in terms of torque-versus-time relations and their morphological and rheological properties. It has been already discussed in the previous section that the rate of the individual reactions between POX and PP or UP are controlled by the availability of POX, in the absence of adequate mixing. It is also expected, in the blend system, that the POX concentration will still affect the rate of those individual reactions. Figures 5.21a-5.21b show the effects of the POX concentration on the torque-time curves of the 5PP/3UP and 3PP/5UP blends, prepared by the same experimental procedure as that of the reacted blend components in the batch mixer. In Figure 21a, since the 5PP/3UP blends contain a lower amount of UP, whose presence predominantly affects the final torque value, the effect of POX concentration on the final torque values is also less pronounced. However, it can be observed that the higher POX concentration in the reacting system, the faster the torque will reach its maximum value, which indicates that the reaction rates between the blend components and POX are much faster at higher POX concentration. On the other hand, a large difference can be observed in the 3PP/5UP system (Figure 5.21b), where the final toque values seem to be a function of POX concentration. The higher the POX concentration in the system, the higher will be the torque value to be reached after 15mins processing in the batch mixer.

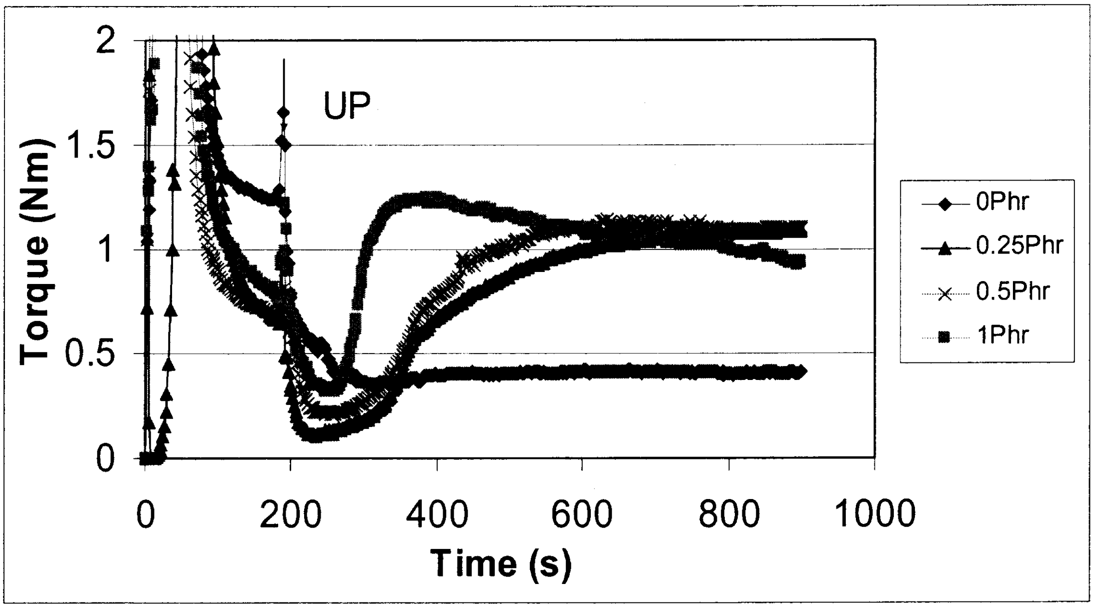

Figure 5.21a The effect of the POX concentration on the torque vs. time behavior of 5PP/3UP blends (160°C).

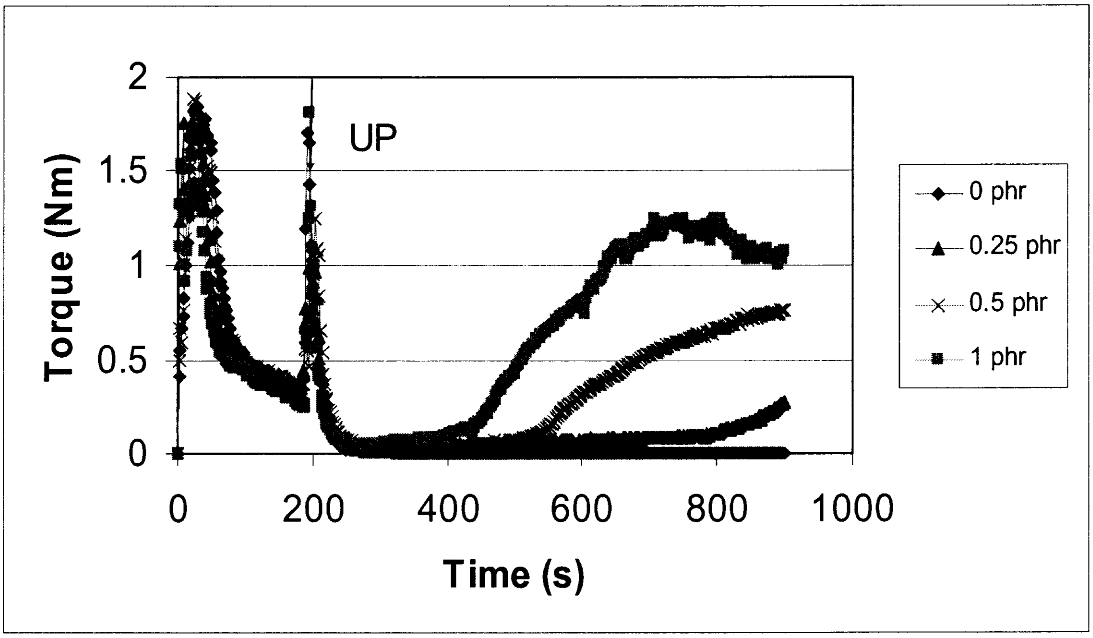

Figure 5.21b The effect of the POX concentration on the torque vs. time behavior of 3PP/5UP blends (160°C).

The morphological study reveals much more information of the effects of the POX concentration on the final products. In the aforementioned study, the unreacted 5PP/3UP blends have coarse morphologies due to the large differences in initial viscosity values and polarities of the blend components. In the reacted systems of Figures 5.22b-5.22d, the dispersed domain sizes narrow down to around 1µm and are more uniform compared to the unreacted system. However, an interesting feature is that regardless of the POX concentration, the morphologies of the reacted 5PP/3UP systems are more or less similar after 15 mins processing time, which suggests that the POX concentration does not play a major role in the formation of a finer morphology.

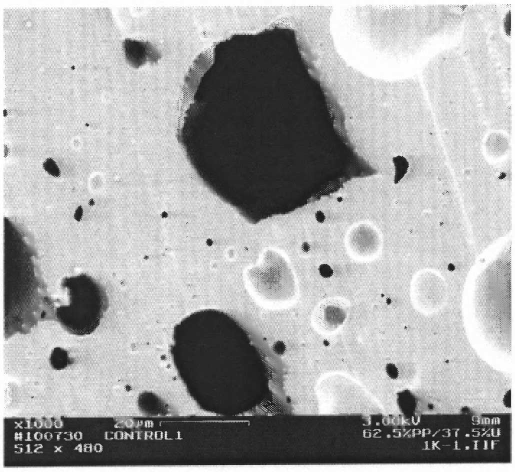

Figure 5.17 SEM of unreacted 5PP/3UP (blank, 15mins, processing).

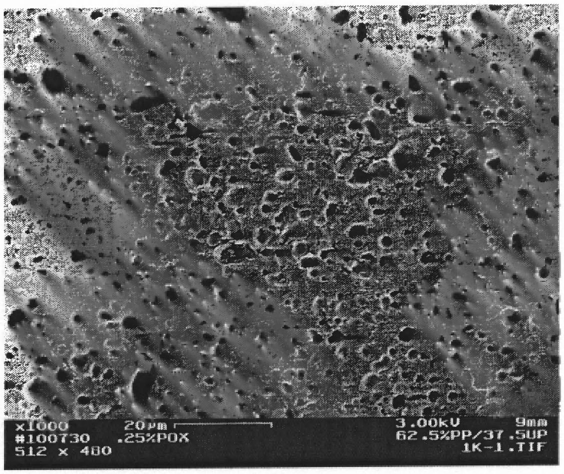

Figure 5.22b SEM of reacted 5PP/3UP (0.25phr POX, 15mins processing).

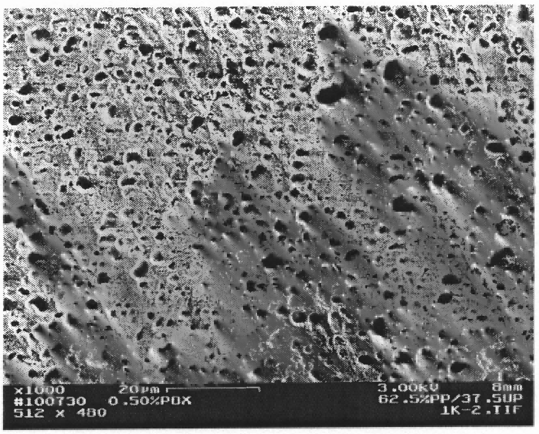

Figure 5.22c SEM of reacted 5PP/3UP (0.5phr POX, 15mins processing).

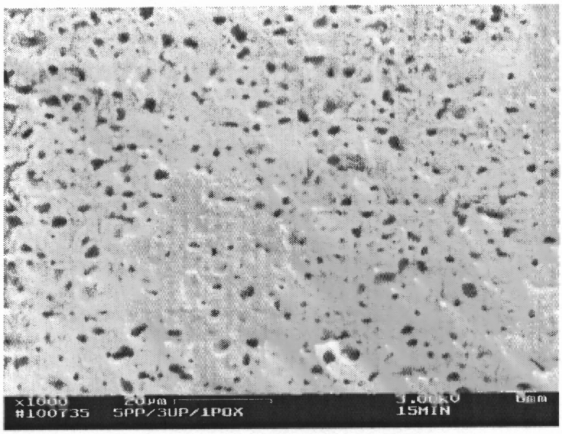

Figure 5.22d SEM of reacted 5PP/3UP (1phr POX, 15mins processing).

However, when it comes to the 3PP/5UP systems, large differences are clearly shown by the SEM pictures (Figures 5.23a-5.23b). In Figure 5.23a, the average domain size of the dispersed PP phase can still be estimated to be around 100µm in spite of the problem with sample preparation by etching the readily soluble unreacted UP phase. After reacting with POX, the viscosity of the matrix (UP) is becoming larger and UP is more difficult to be extracted off, thus, maintaining a more stable structure during the sample preparation. The higher the POX concentration in the system, the higher the viscosity of the blend and the finer and more uniform the morphology of the final products (Figures 5.23b-5.23d).

Figure 5.23a SEM of unreacted 3PP/5UP (blank, 15mins processing).

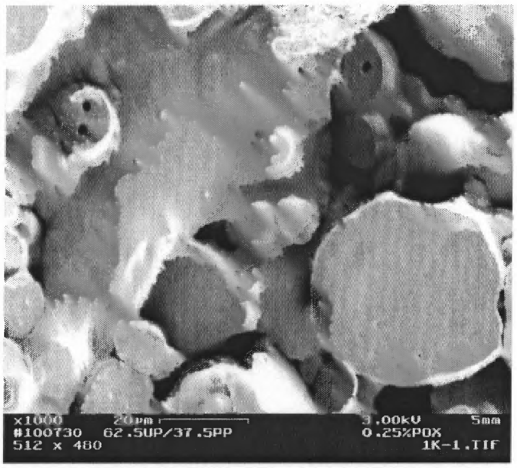

Figure 5.23b SEM of reacted 3PP/5UP (0.25phr POX, 15mins processing).

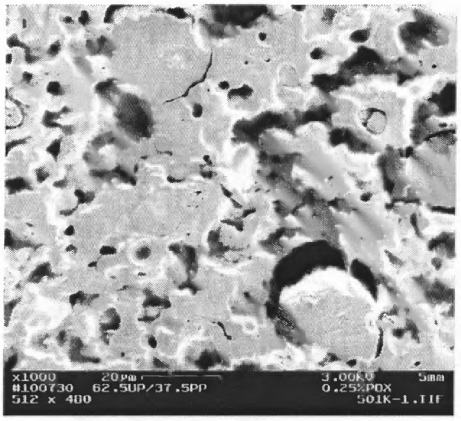

Figure 5.23c SEM of reacted 3PP/5UP (0.5phr POX, 15mins processing).

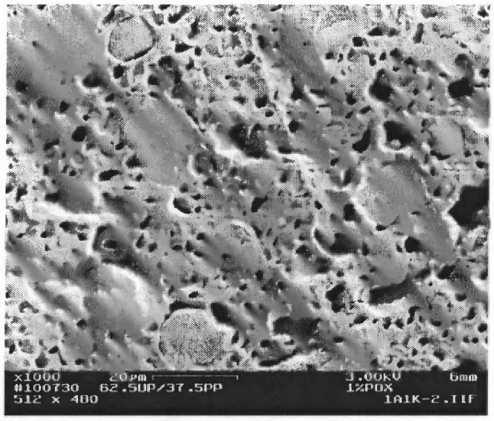

Figure 5.23d SEM of reacted 3PP/5UP (1phr POX, 15mins processing).

Figures 5.24a-5.25b reveal the fracture surfaces of 5PP/UP and 3UP/5PP blends. Better images are shown in Figures 5.25a and 5.25b compared to those prepared by solvent etching since the internal phases are poorly bonded. Both unreacted blend systems have a coarse morphology, although the 3PP/5UP blend seems to have a slightly finer dispersed domain size due to the lower matrix viscosity. The reacted blend systems (Figure 5.24b and 5.25b) show better adhesion and uniformity.

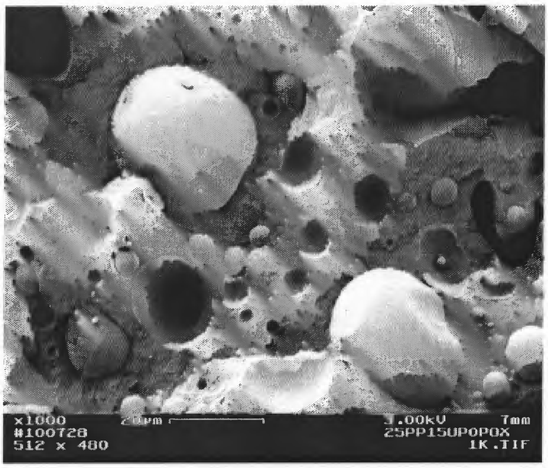

Figure 5.24a SEM of the fracture surface unreacted 5PP/3UP (blank, 15 mins processing).

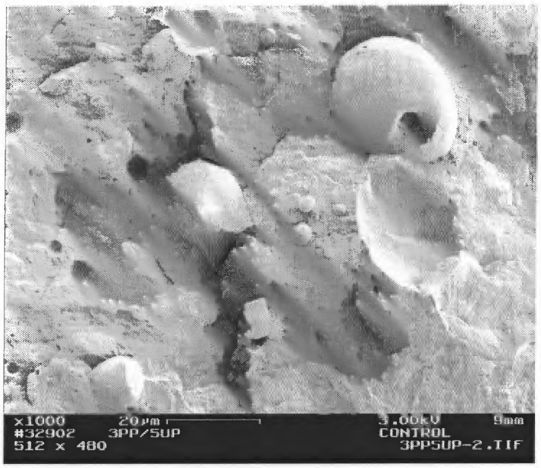

Figure 5.25a SEM of the fracture surface unreacted 3PP/5UP (blank, 15 mins processing).

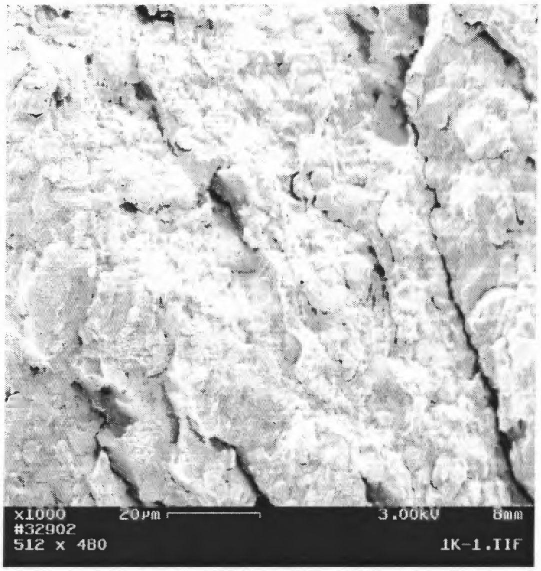

Figure 5.24b SEM of the fracture surface reacted 5PP/3UP (15 mins processing).

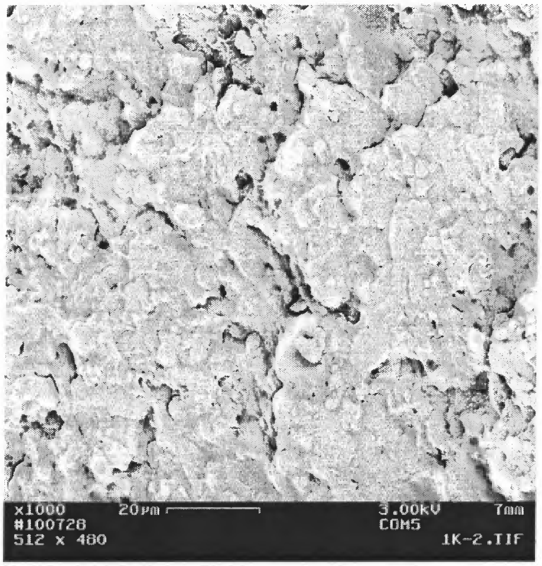

Figure 5.25b SEM of the fracture surface reacted 3PP/5UP (15 mins processing).

The viscoelastic properties of the blends can be obtained from small amplitude dynamic mechanical tests. The storage modulus, G', loss modulus, G", and the complex viscosities (η^*) of the blends with or without the addition of POX are shown in Figures 5.26a-5.27c. The systems are very complicated since there are two opposite effects: the degradation of PP with peroxide decreases the viscosity of PP and narrows its molecular weight distribution, while the crosslinking reaction of UP and peroxide increases the viscosity of UP and broadens its molecular weight distribution. In general, polymer blends exhibit solid-like behavior at high frequencies and this is directly related to molecular weight of the blend components with the complex modulus decreasing with decreased molecular weight of the matrix (Larson, 1999, and Souza, 2002). The storage modulus, G', is qualitatively equivalent to a transient shear relaxation modulus G(t) at $t=1/\omega$; thus, the shape of G(t) displays a mirror image of G'. When the UP becomes crosslinked, the relaxation modulus at equilibrium, G_e, is shifted to longer times, which corresponds to low frequencies. The characteristic feature of the equilibrium region in crosslinked systems is that the magnitude of G" is smaller than that of G' in that frequency region, i.e. the elastic properties prevail.

For 5PP/3UP blends, the addition of the POX decreases the values of the storage modulus, loss modulus and the complex viscosity almost over the entire frequency range, which is apparently due to the excessive degradation of the PP matrix. The difference is more pronounced at low frequencies, especially in the comparison of storage modulus. However, a well defined secondary plateau can be distinguished for the reacted 5PP/3UP blends at low frequencies, which is due to the influence of the dispersed, crosslinked UP domains. As the POX concentration increases, the concentration of the crosslinked UP will also increase and the secondary plateau becomes more obvious.

Different phenomena can be observed in the 3PP/5UP blends. The reacted blends give a higher storage modulus, loss modulus and viscosity over the entire frequency range. In this system, UP becomes the matrix and the crosslinking effect of UP is predominant. The secondary plateau is also well defined for all reacted blends. Figure 5.27c also shows a pronounced suspension behavior with a well defined yield stress for all reacted blends, which are apparently due to the presence of dispersed UP gel particles in the unreacted/reacted medium. Such rheological behavior is similar to that of thermoplastic elastomers and may be particularly desirable in extrusion foaming (Sahnoune, 2000 and 2001). However, the highest value is obtained when the POX concentration is 0.5 phr indicating 0.5 phr POX concentration may be a optimal condition to compromise degradation of PP and crosslinking of UP .

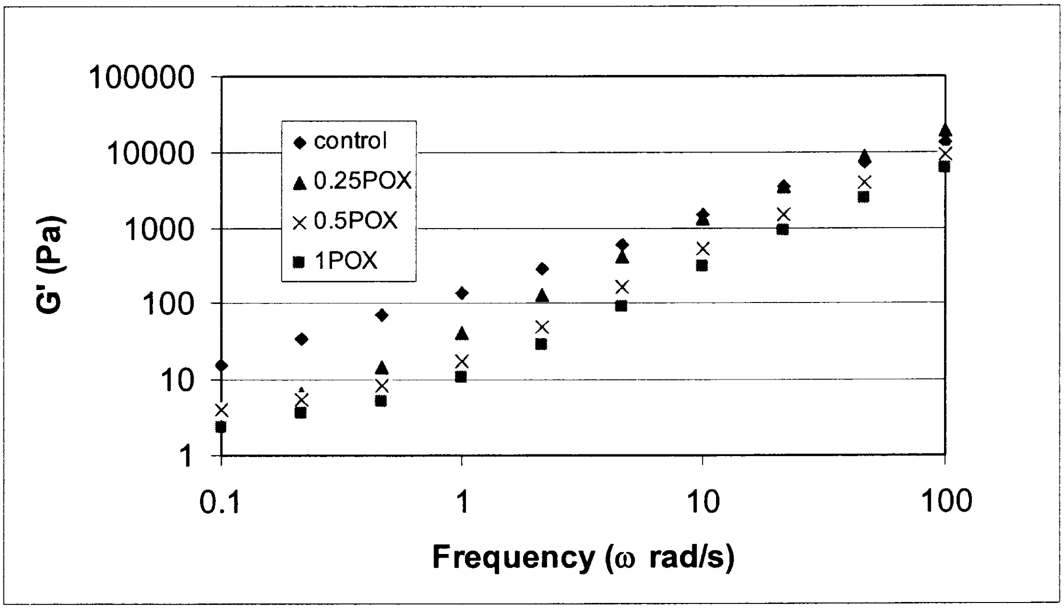

Figure 5.26a Storage modulus (G') vs. frequency (ω) of the unreacted and reacted 5PP/3UP blends at 180°C testing temperature.

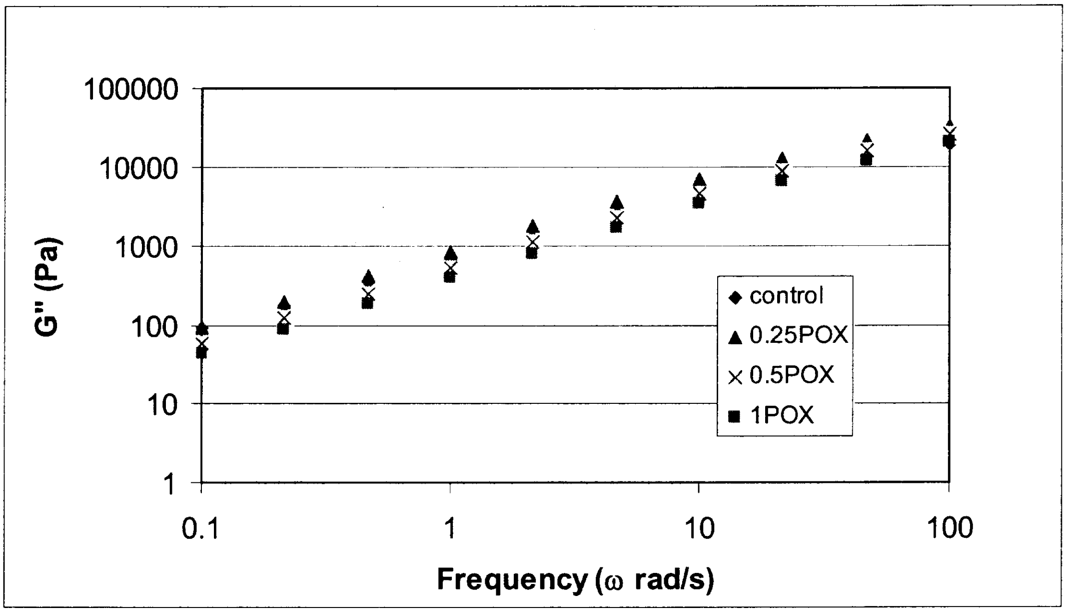

Figure 5.26b Loss modulus (G") vs. frequency (ω) of the unreacted and reacted 5PP/3UP blends at 180°C testing temperature.

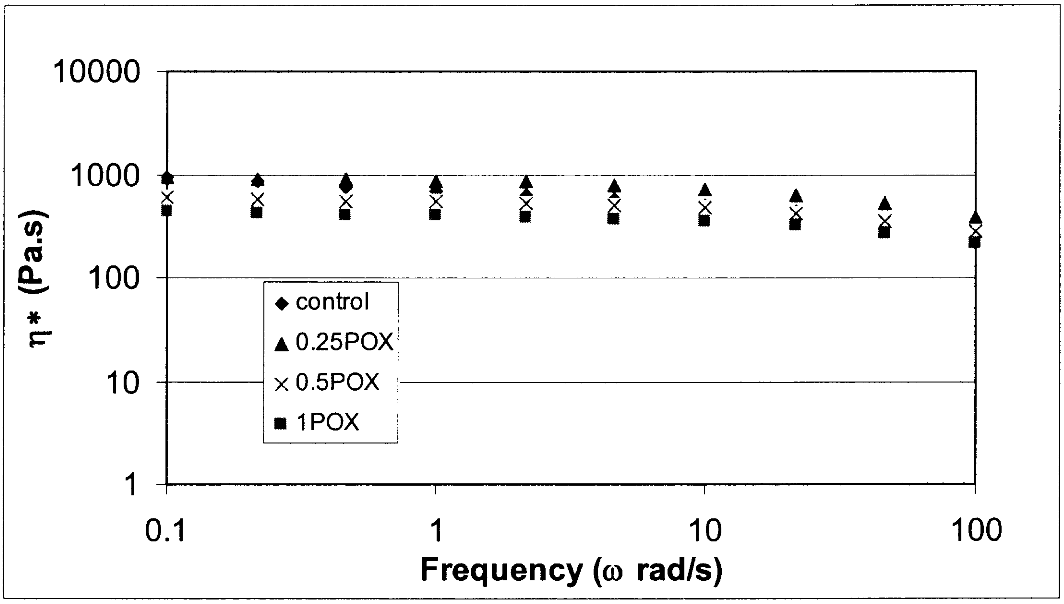

Figure 5.26c Complex viscosity (η^*) vs. frequency (ω) of the unreacted and reacted 5PP/3UP blends at 180°C testing temperature.

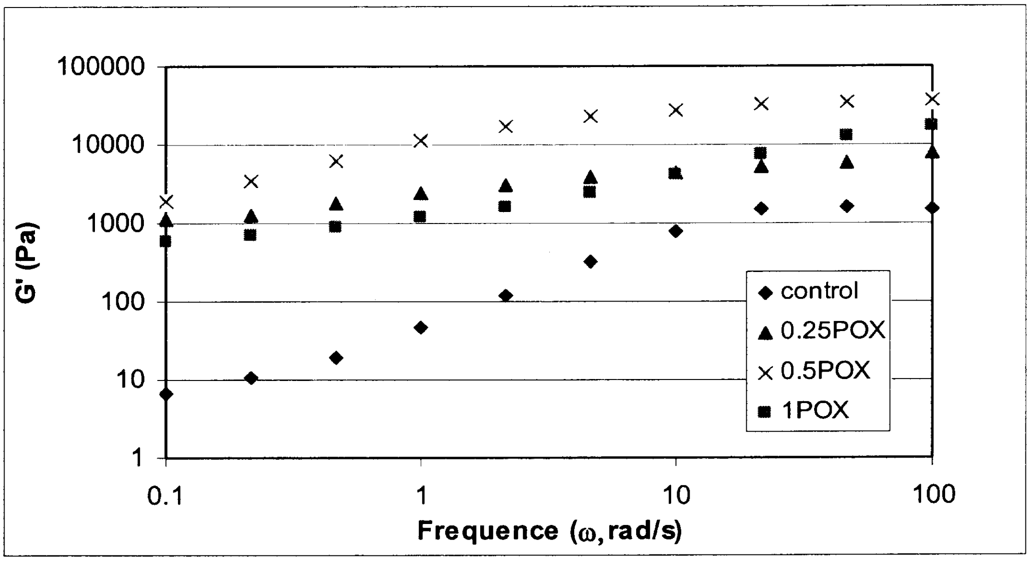

Figure 5.27a Storage modulus (G') vs. frequency (ω) of the unreacted and reacted 3PP/5UP blends at 180°C testing temperature.

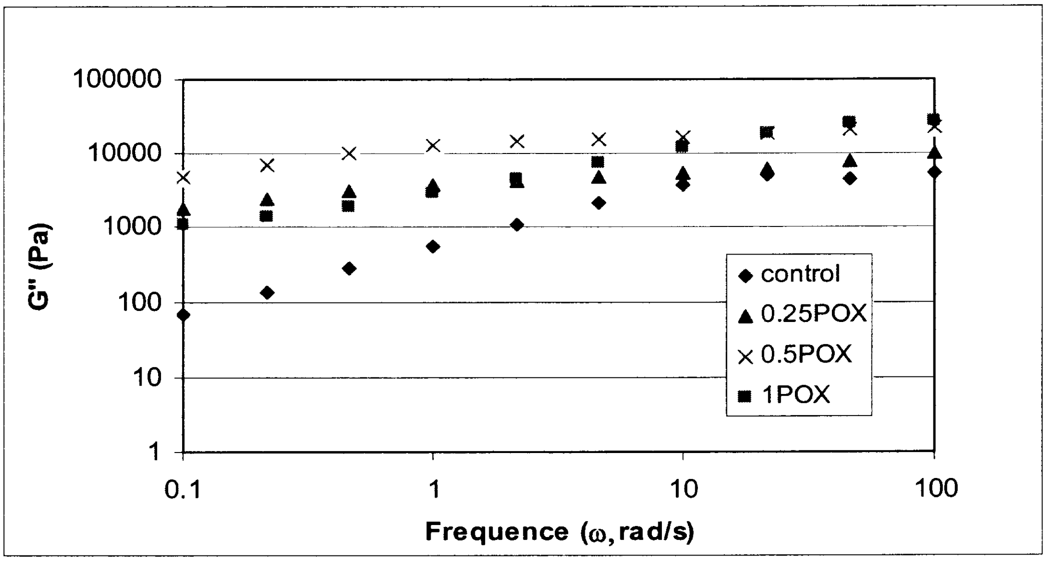

Figure 5.27b Loss modulus (G") vs. frequency (ω) of the unreacted and reacted 3PP/5UP blends at 180°C testing temperature.

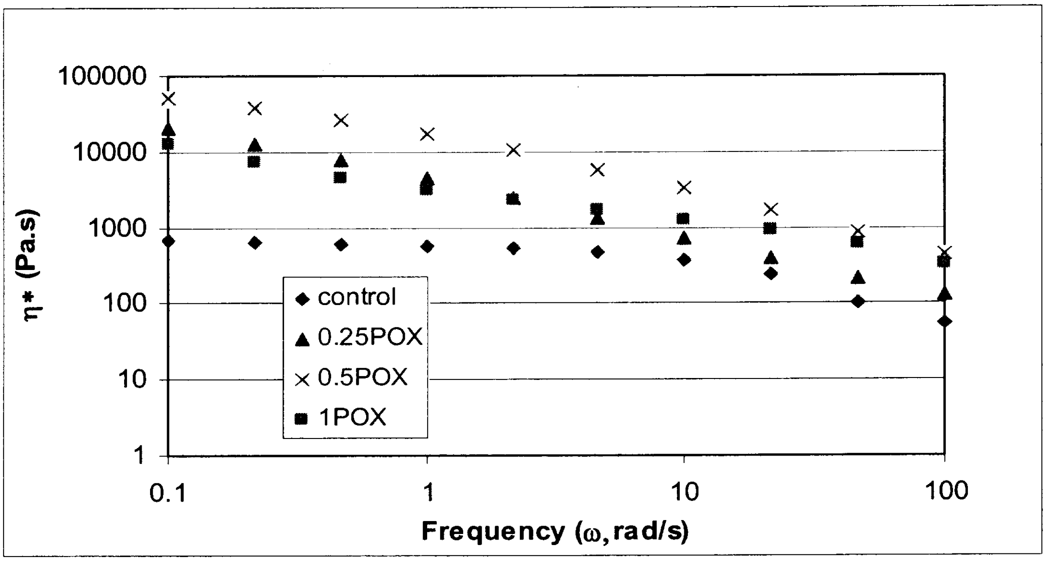

Figure 5.27c Complex viscosity (η*) vs. frequency (ω) of the unreacted and reacted 3PP/5UP blends at 180°C testing temperature.

5.2.3 The Effect of Additives

5.2.3.1 The Effect of the Organic Additive. As mentioned before, PDMI will react with PP and UP individually, promoted by POX. Figures 5.28a-5.28b show the morphologies of 5PP/3UP blends by adding the PDMI as coagent. The blends were prepared by a similar procedure as before except that the processing temperature is elevated to 190°C due to the high melting point of PDMI. Figure 5.28a shows a similar morphology as that of the unreacted 5PP/3UP blends (Figure 5.17a) since there is no POX to promote reaction between PDMI and blend components. However, the reacted 5PP/3UP systems show large differences. The reacted 5PP/3UP blend containing PDMI possess a much finer morphology, as shown in Figure 5.28b, which is directly comparable to Figure 5.18d. In that Figure, the UP phase is also finely dispersed but can be more easily extracted. This may be due to the combined effect of lower processing temperature and absence of PDMI. The effect of PDMI promoted by POX may decrease the interfacial energy between the two immiscible blend components and increase the possibilities of the interphase reactions to generate more PP-UP compatibilizing copolymer.

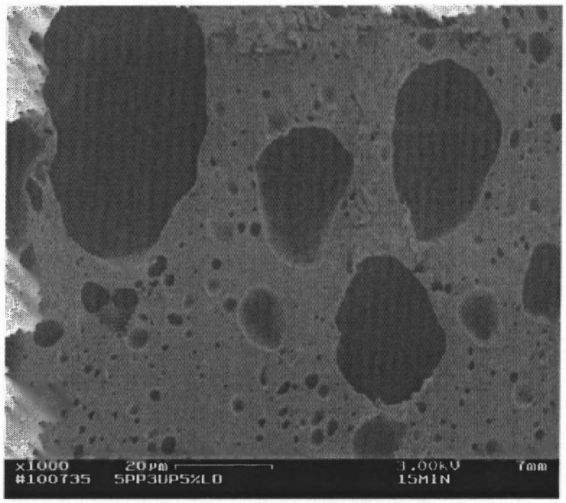

Figure 5.28a SEM of the solvent etched surface of unreacted 5PP/3UP (15mins processing, 190°C, 1 phr PDMI x1000)

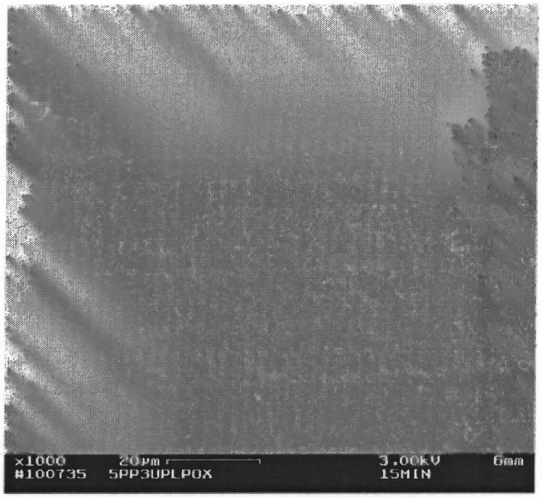

Figure 5.28b SEM of the solvent etched surface of reacted 5PP/3UP (15mins processing, 190°C, 1 phr PDMI/1 phr POX, x1000)

The viscoelastic properties of the reacted 5PP/3UP blend change upon the addition of PDMI. The storage modulus of the reacted blend with PDMI has a much higher value over almost the entire frequency region and a more pronounced secondary plateau. At low frequencies, enhancement of elasticity and longer relaxation times indicates a higher MW and MWD of the blend system containing PDMI. A more pronounced non-Newtonian behavior is also observed in the complex viscosity curve of the reacted 5PP/3UP blend containing PDMI. It is clear that the presence of PDMI suppresses the degradation of PP matrix and the crosslinking of UP domains, through formation of the PP-UP copolymer that increases the interaction of the blend components.

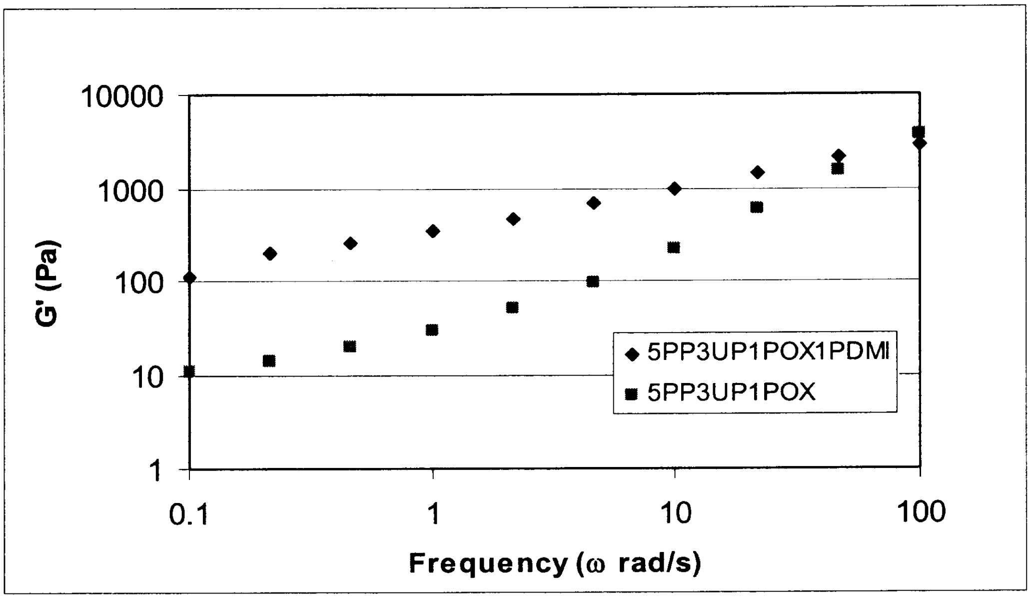

Figure 5.29a The effect of PDMI on the storage modulus (G') of the reacted 5PP/3UP blends at 180°C testing temperature.

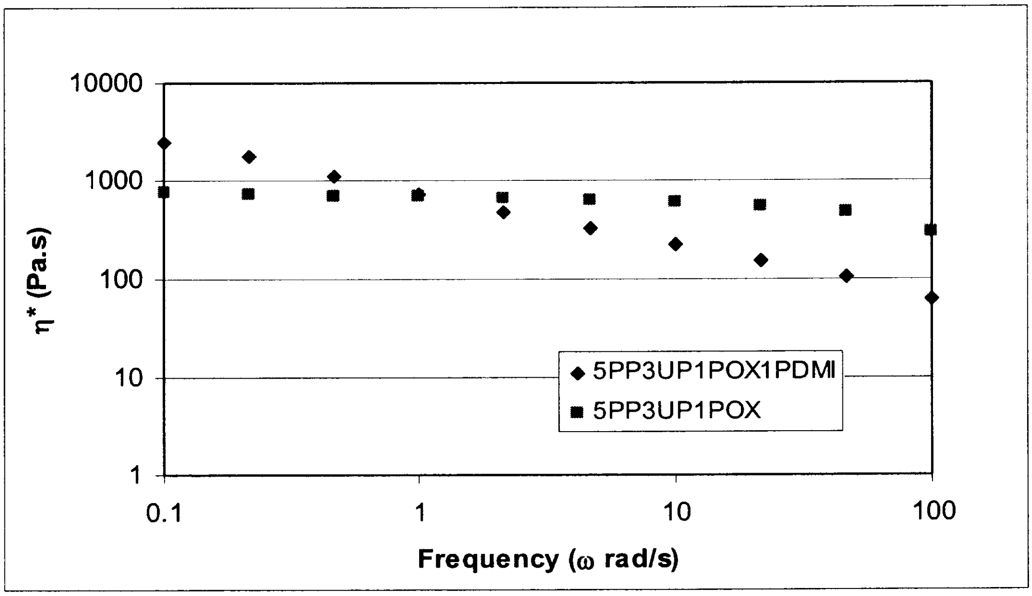

Figure 5.29b The effect of PDMI on the complex viscosity (η^*) of the reacted 5PP/3UP blends at 180°C testing temperature.

5.2.3.2 The Effect of the Inorganic Additive and Other Coagents. As shown before, UP has a strong interaction with MgO without any additives at high temperatures while PP only interacts with MgO through coagents such as PDMI (Vancsó-Szmercsányi et al., 1974 and Liauw et al., 2000). When blending PP/UP blends with MgO, it can be said that, without any additive, MgO will only react with UP phase. Similar coarse morphologies can be observed for those 5PP/3UP blends containing 14% MgO without other coagents. The blends were prepared at processing temperature at 220°C at procedure shown in Figure 5.30 except one more step for the addition of MgO after 6 mins processing. The ratio of UP and MgO is 100:30, which is a same ratio in the studies of reactions between UP and MgO. The SEM pictures shown in Figures 5.31a-5.31d not only confirm the formation of immiscible blend morphology, but also show the more complex composite-droplet morphologies, which also known as "sub-inclusion" and "salami-like" morphologies. The encapsulation of MgO in the minor UP phase, rather than formation of separately dispersed phases, is mainly due to the strong reactions between UP and MgO which was confirmed in the previous section. This kind of behavior could be predicted via Harkins's equation (Hobbs et al., 1988 and 2000).

$$\lambda_{31} = \Gamma_{12} - \Gamma_{32} - \Gamma_{13} \tag{5.10}$$

where λ_{31} is the spreading coefficient for component 3 to encapsulate component 1 and Γ_{12}, Γ_{32}, and Γ_{13} are the interfacial tensions between the respective polymer pairs in the blend. When λ_{31} is positive, encapsulation of component 3 around component 1 will occur. In the present study, components 1, 2 and 3 will be MgO, PP and UP, accordingly. Although there are no precise data on the interfacial tensions within these components, it can still be estimated, roughly, that the value of Γ_{13} will be negative and will be a great contribution to make a positive λ_{31}.

It is also very interesting to find some small PP particles within the dispersed UP domains. This could also be predicted via Harkins's equation. In this case, components 1, 2, and 3 would be PP, MgO and UP, accordingly. The value of Γ_{32} will be negative and will contribute to make a positive λ_{31}; thus, the encapsulation of PP into the UP phase becomes very possible. The increased viscosity of the dispersed phase, UP, through reaction with MgO also improves the retention of the subinclusions (Favis et al 1990).

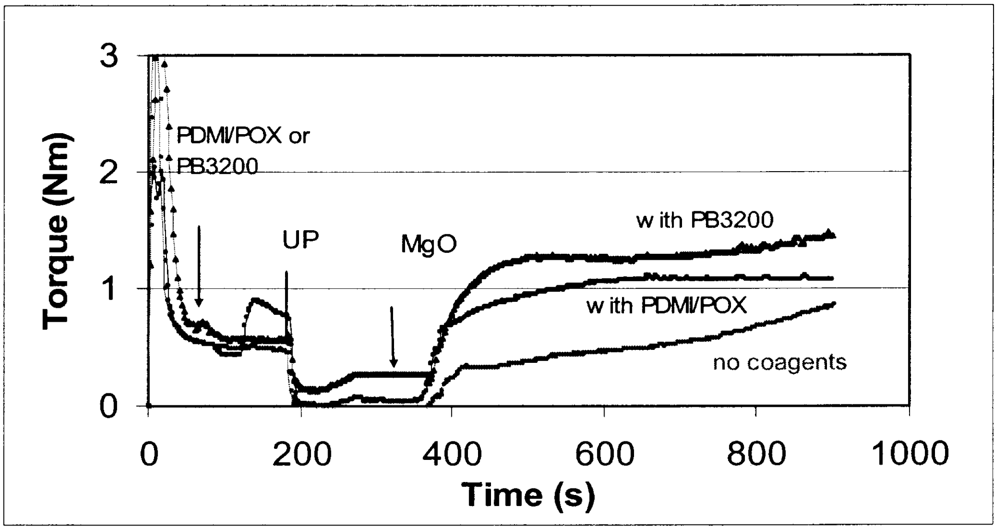

Figure 5.30 Changes in torque of 5PP/3UP with MgO and coagents in the batch mixer (220°C, 60rpm).

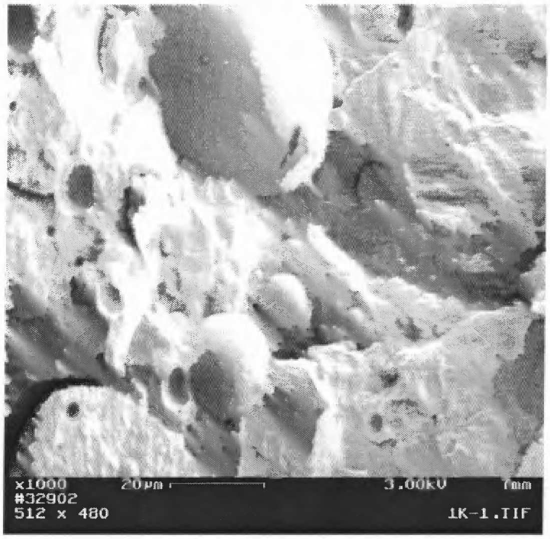

Figure 5.31a SEM of the fracture surface of unreacted 5PP/3UP containing MgO (15mins processing, 220°C, x1000).

Figure 5.31b SEM of the fracture surface of unreacted 5PP/3UP containing MgO (15mins processing, 220°C, x1000).

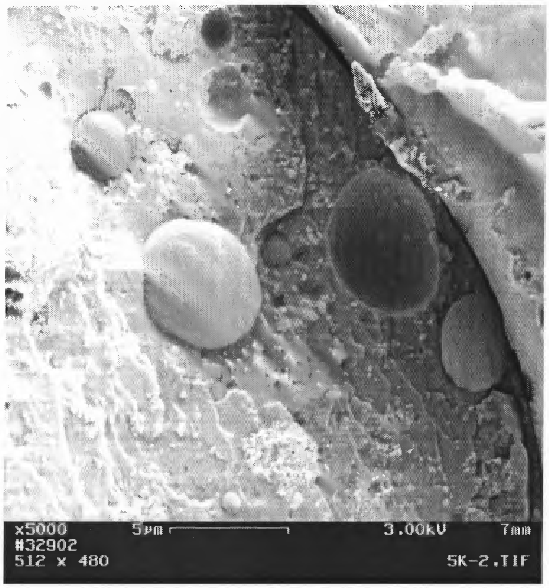

Figure 5.31c SEM of the fracture surface of unreacted 5PP/3UP containing MgO (15mins processing, 220°C, x5000).

Figure 5.31d SEM of the fracture surface of unreacted 5PP/3UP containing MgO (15mins processing, 220°C, x10000).

The effect of the addition of coagents (PDMI/POX or PB3200) was monitored during melt processing, as shown in the torque versus time curves of Figure 5.30. It can be seen that, without coagents, the 5PP/3UP blend responds somewhat slower to the introduction of MgO during the very beginning since MgO can only react with the UP phase and the reaction may be diffusion controlled. In the presence of coagents, the torque increased rapidly in a short period upon the addition of MgO since competing reactions took place between MgO and the UP phase, and MgO and the PP phase through PDMI or PB3200. The first two reactions have been studied in the previous section. The third reaction between the carboxylic group of PB3200 and MgO has also been reported in the literature (Brown, 1992). PB3200 is a commercial compatibilizer for most of polypropylene and polyester blends. Its compatibilizing effect is confirmed in Figures 5.32a and 5.32b. The smaller domain size and the elongated thread-like shapes in these two SEM pictures indicate a decreased interfacial tension between PP and UP. In this case, MgO can also serve as a bridging agent between UP and PDMI or PB3200, the latter having also interacted with PP; the final result is a higher torque after 15 mins. However, when PB3200 is selected as the coagent, there will be no POX induced degradation; thus the blend will give a highest torque value during processing.

Figures 5.33a-5.33d confirmed the compatibilizing effect of MgO through coagents. The capability of the chemical reactions of MgO with both UP and PP phases, directly or indirectly, decrease interfacial tension by binding the two components together; thus, resulting in the formation of much finer morphologies with reduced domain size and narrower size distribution.

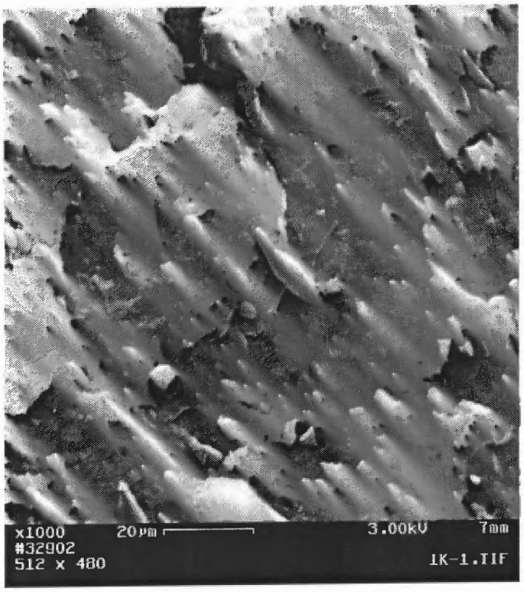

Figure 5.32a SEM of the fracture surface of 5PP/3UP/PB3200 blends (15mins processing, 220°C, x1000).

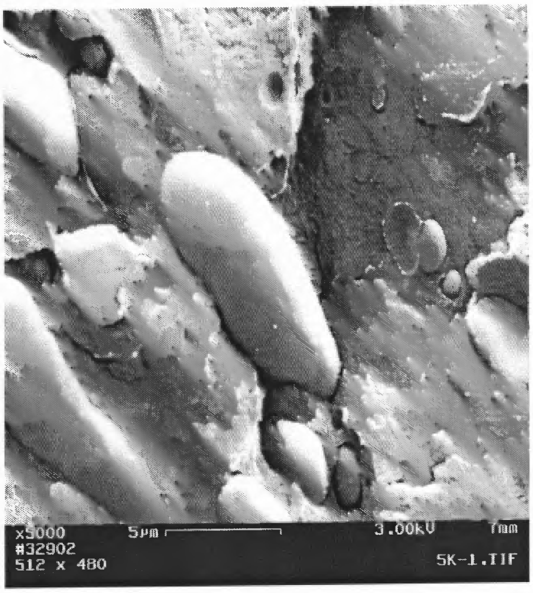

Figure 5.32b SEM of the fracture surface of 5PP/3UP/PB3200 blends (15mins processing, 220°C, x5000).

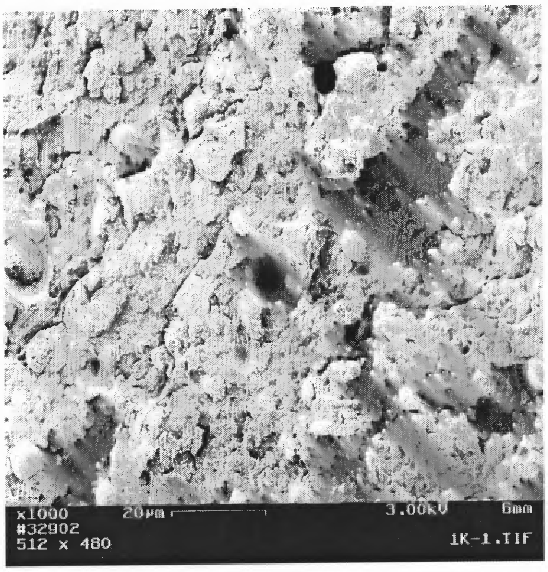

Figure 5.33a SEM of the fracture surface of 5PP/3UP/PDMI containing MgO (15mins processing, 220°C, x1000).

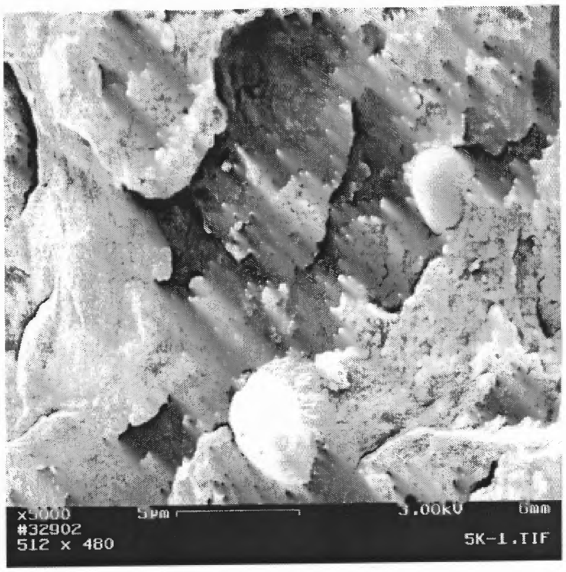

Figure 5.33b SEM of the fracture surface of 5PP/3UP/PDMI containing MgO (15mins processing, 220°C, x5000).

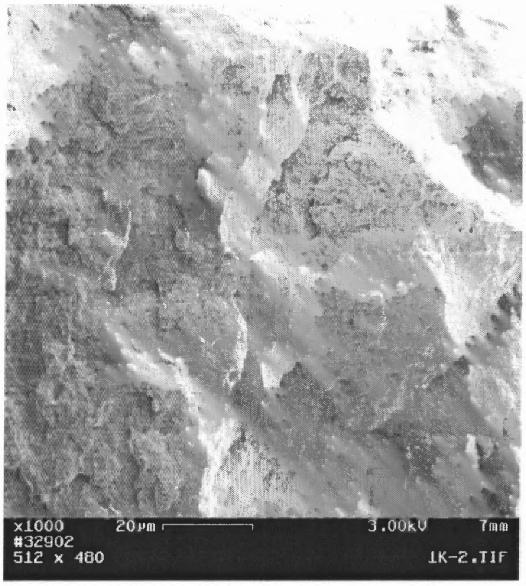

Figure 5.33c SEM of the fracture surface of 5PP/3UP/PB3200 blend containing MgO (15mins processing, 220°C, x1000).

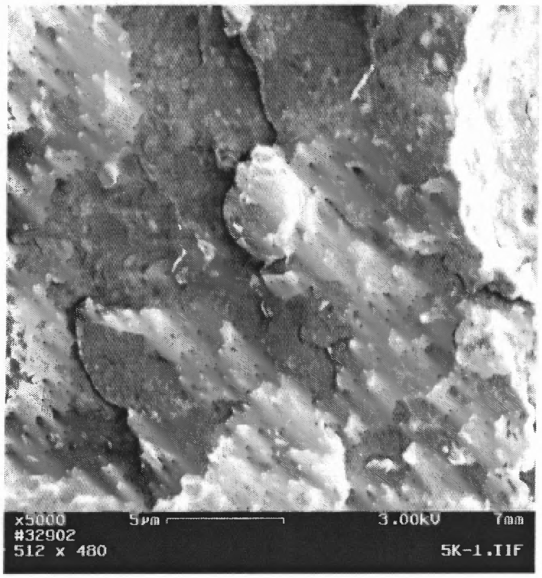

Figure 5.33d SEM of the fracture surface of 5PP/3UP/PB3200 blend containing MgO (15mins processing, 220°C, x5000).

The comparison of dynamic mechanical properties of the above 5PP/3UP blends is shown in Figures 5.34a-5.35b. As expected, the incorporation of the inorganic reactive additive, MgO, increased the modulus and complex viscosity of the blends, dramatically. In Figures 5.34a-5.34b, the curves of storage modulus and complex viscosity versus frequency of 5PP/3UP containing 14% MgO shift up vertically compared to the unreacted 5PP/3UP blends. The values of their storage modulus and complex viscosity increased up to 5 times over the entire frequency range in the presence of MgO. The addition of PDMI/POX as coagents has little effects on the viscoelastic properties of the 5PP/3UP blends, although the values of G' and η^* are slightly lower due to the POX induced degradation of PP matrix.

However, when PB3200 is used as a coagent, large differences appear at low frequencies, as shown in Figures 5.35a and 5.35b. A higher modulus than the 5PP/3UP-

MgO sample and a distinct secondary plateau can be observed. This behavior indicates not only the large increase in viscosity of the dispersed UP domains but also the stronger interaction between dispersed UP gel particles and the PP matrix (Larson, 1999 and Souza, 1995), resulting from more pronounced compatibilizing effect of PB3200.

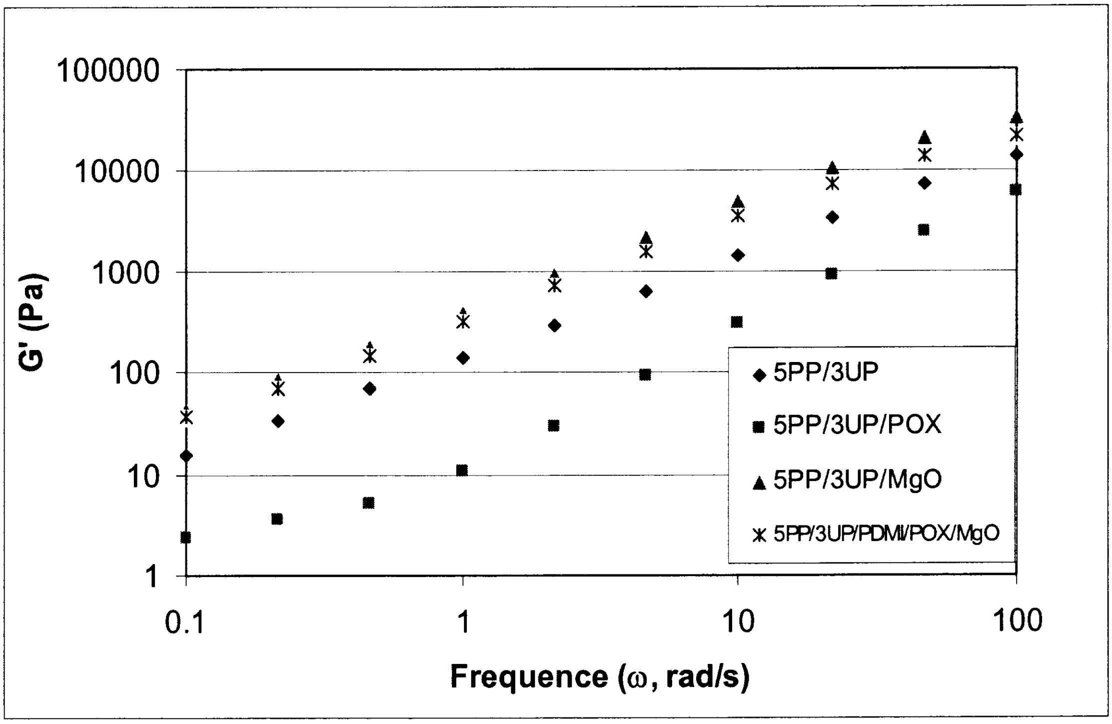

Figure 5.34a The effect of the addition of MgO and PDMI on the storage modulus of the 5PP/3UP blends at 180°C testing temperature.

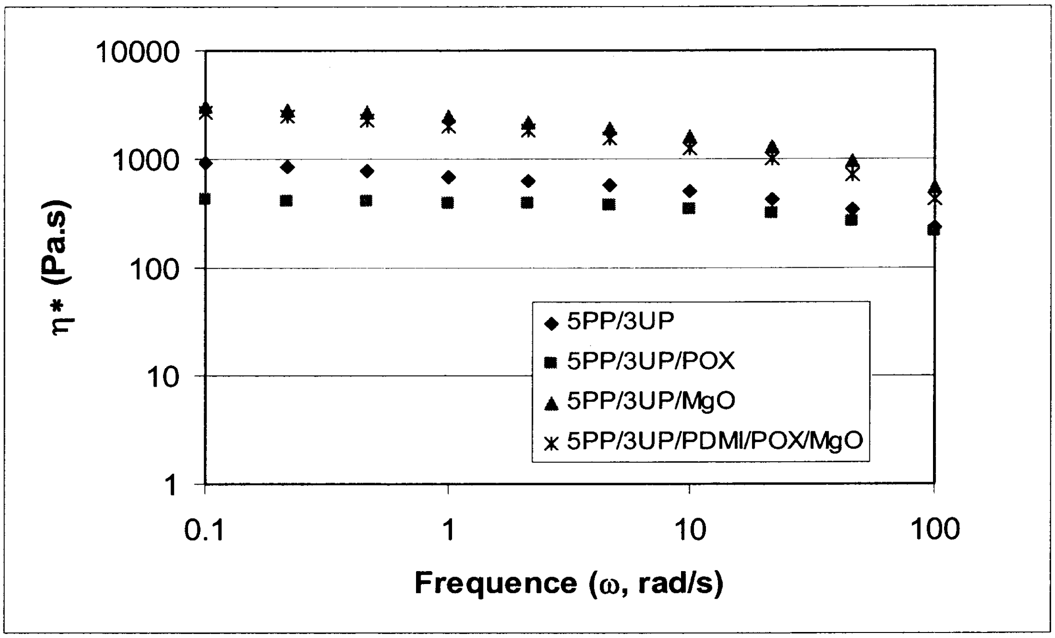

Figure 5.34b The effect of the addition of MgO and PDMI on the complex viscosity of the 5PP/3UP blends at 180°C testing temperature.

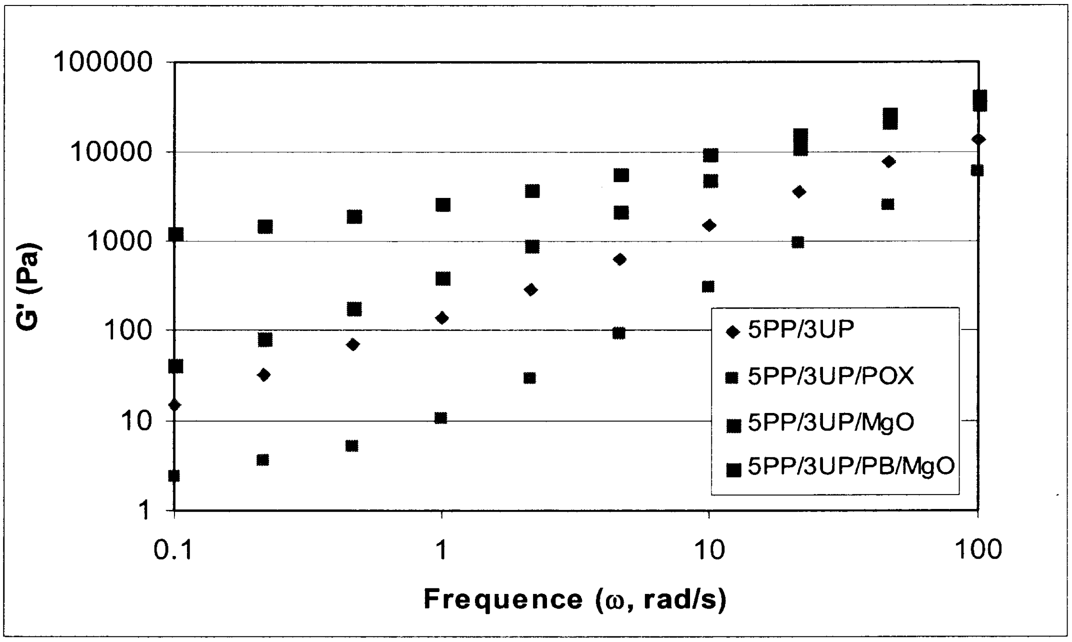

Figure 5.35a The effect of the addition of MgO and PB3200 on the storage modulus of the 5PP/3UP blends at 180°C testing temperature.

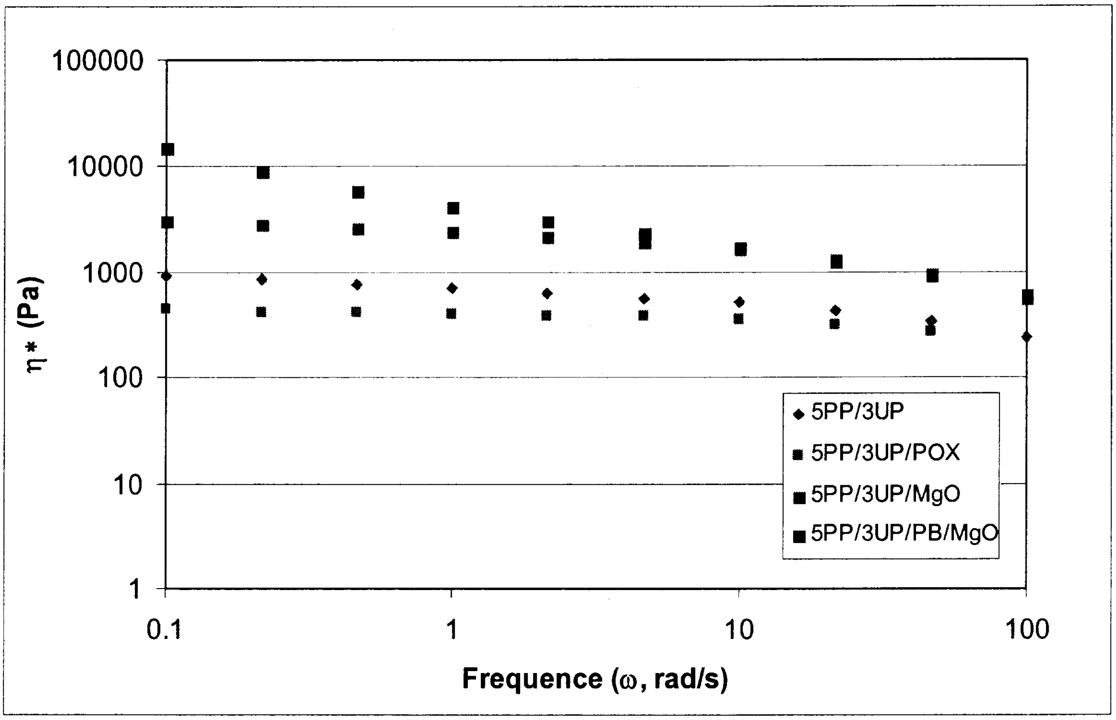

Figure 5.35b The effect of the addition of MgO and PB3200 on the complex viscosity of the 5PP/3UP blends at 180°C testing temperature.

Reactive modification of PP/UP blends through POX and MgO have several differences. From a chemistry point of view, these two methods represent two totally different approaches. During the reactive blending of PP/UP with POX, the POX will attack the PP backbone chain and the internal double bonds within the UP chains, leaving unreacted end-groups. While blending of PP/UP with MgO, the MgO will react with the end groups of UP and may also have an interaction/reaction with PP through coagents such as PDMI and PB3200, while possibly maintaining the double bond in the blend for further modification. The two modification routes can also be combined for tailoring the desirable properties of the final product.

5.3 Blends Prepared By Continuous Reactive Extrusion

Twin-screw extruders (TSE) are high-intensive mixing devices consisting of two screws with kneading sections for intensive mixing. The entire screw configuration can be built to fit a particular requirement, thus, offering a great flexibility in the process control (Todd, 1998). Compared to batch mixers, the better mixing effect provided by the kneading blocks of the twin-screw extruder is expected to produce a final product with a more stable morphology and better rheological properties. One limitation of using TSE during the present study of the reactive blending of PP/UP blends is the lack of flexibility in the feeding sequence design, i.e. all components were added together through a hopper.

Figures 5.36a and 5.36b show the final morphologies of extruded 5PP/3UP blends. The unreacted extruded 5PP/3UP blend (TU sample) has an almost identical morphology compared to those unreacted blends prepared in batch mixer (BU sample), as shown in Figure 5.36a and 5.17a. Since the large differences in their viscosity values and polarity are not really favoring dispersive mixing, it is expected that the aggressive mixing elements provided by the twin screw extruder will not promote to any large extent a more uniform mixture with a finer level of dispersion. However, Figure 5.36b shows the reacted 5PP/3UP blend (TR sample) possesses a better morphology than that made from the batch mixer (BR sample) (Figure 5.18d) in the absence of compatibilizers, which suggests better adhesion between the blend components and higher extent of reaction for the UP phase (less extraction vs. Fig. 5.18d and possibly finer domain size for the extracted product). This indicates that the different feeding protocols, shorter residence time, and better mixing due to the presence of aggressive mixing elements in the twin screw extruder are preferable vs. the corresponding batch mixer process conditions favor more UP crosslinking and apparently better compatibilization. The addition of PDMI will also have a bigger effect on the properties of final 5PP/3UP blends due to the better mixing effects which favoring the interphase reaction and formation of PP-UP copolymer, also resulting in much better adhesion between the blend components. The fracture surfaces are shown in Figures 5.37a and 5.37b, which is not directly comparable to Figure 5.28b since which was obtained by solvent extraction.

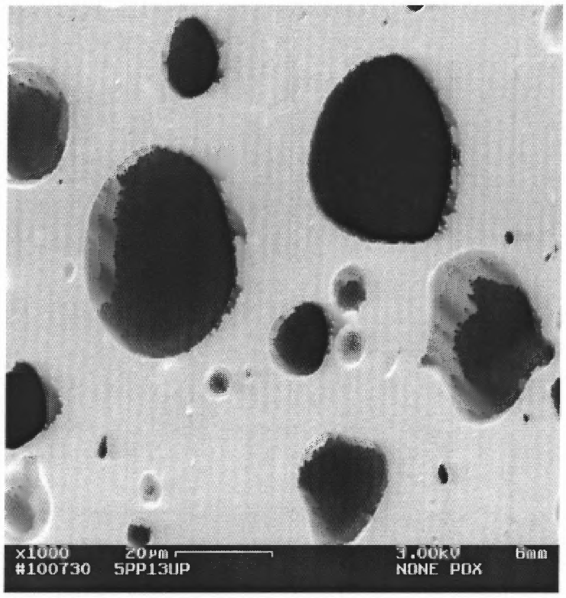

Figure 5.36a SEM of unreacted 5PP/3UP (blank, prepared in TSE, x1000).

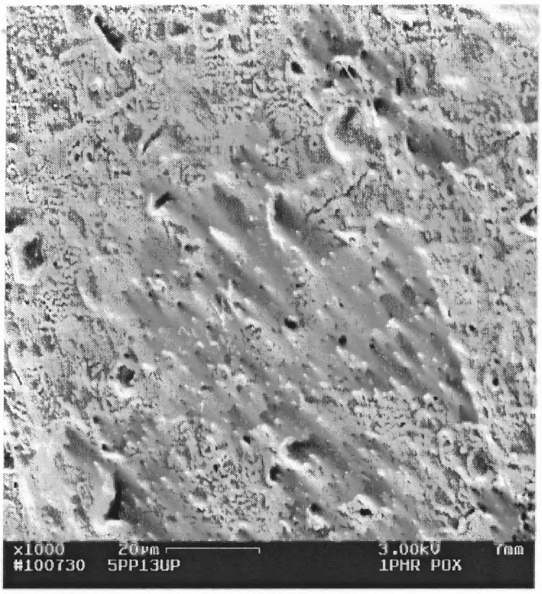

Figure 5.36b SEM of reacted 5PP/3UP (1phr POX, prepared in TSE, x1000).

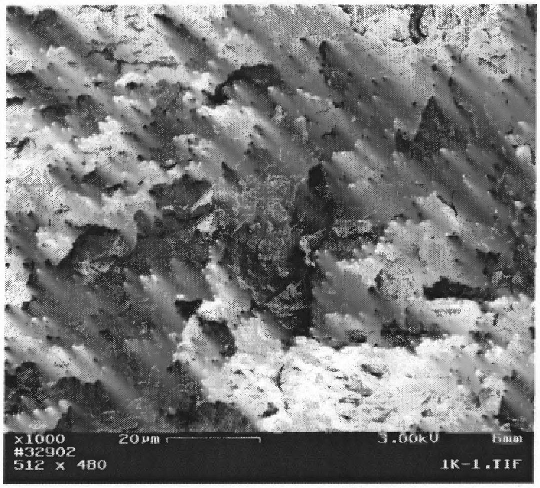

Figure 5.37a SEM of reacted 5PP/3UP (1phr POX and 1phr PDMI, prepared in TSE, x1000).

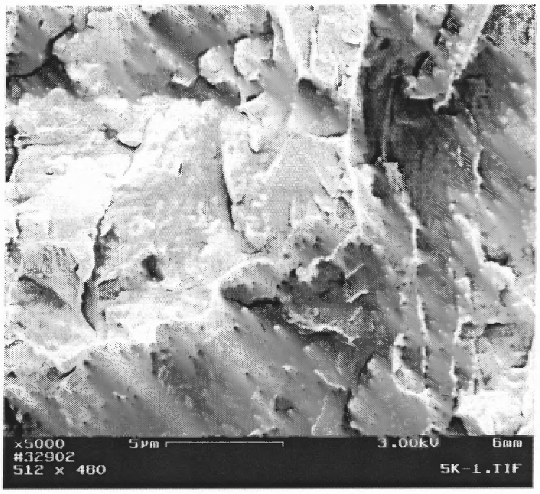

Figure 5.37b SEM of reacted 5PP/3UP (1phr POX and 1 phr PDMI, prepared in TSE, x5000).

Figures 5.38a and 5.38b show storage modulus (G') and complex viscosity (η^*) vs. frequency of the 5PP/3UP samples prepared in the batch mixer and twin screw extruder measured at 180°C. The values for the unreacted blends (U) prepared in the batch mixer (BU) and twin screw extruder (TU) are overlapping over the whole frequency of interest, indicating that the processing conditions have little effect not only on blend morphology, as shown earlier, but also on the rheological behavior. The reacted blend (R) prepared in the twin screw extruder (TR) shows a lower storage modulus in the high frequency region, compared to the unreacted blend (TU), apparently due to the excessive degradation of the PP matrix. In the low frequency region, the reacted TR blend shows a higher modulus than the BR sample and a distinct secondary plateau in its frequency curve. This may attribute to the better mixing effect promoting a higher possibility of the interfacial reaction with the blend components, resulting in the formation of graft or block PP-UP copolymers during the reaction.

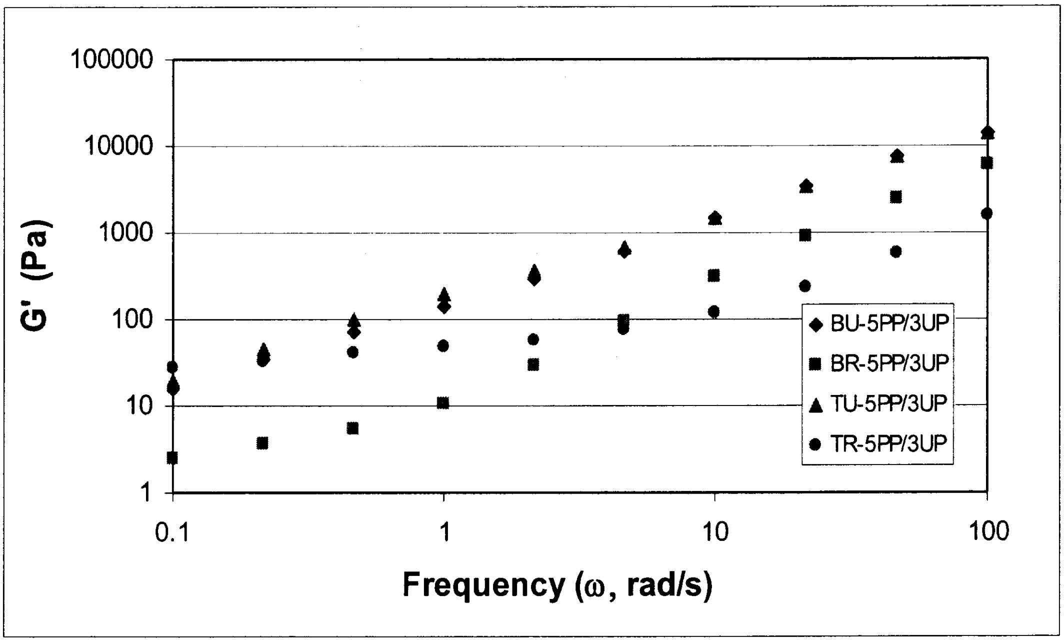

Figure 5.38a The effect of mixer type on the storage modulus of the 5PP/3UP blends at 180°C testing temperature.

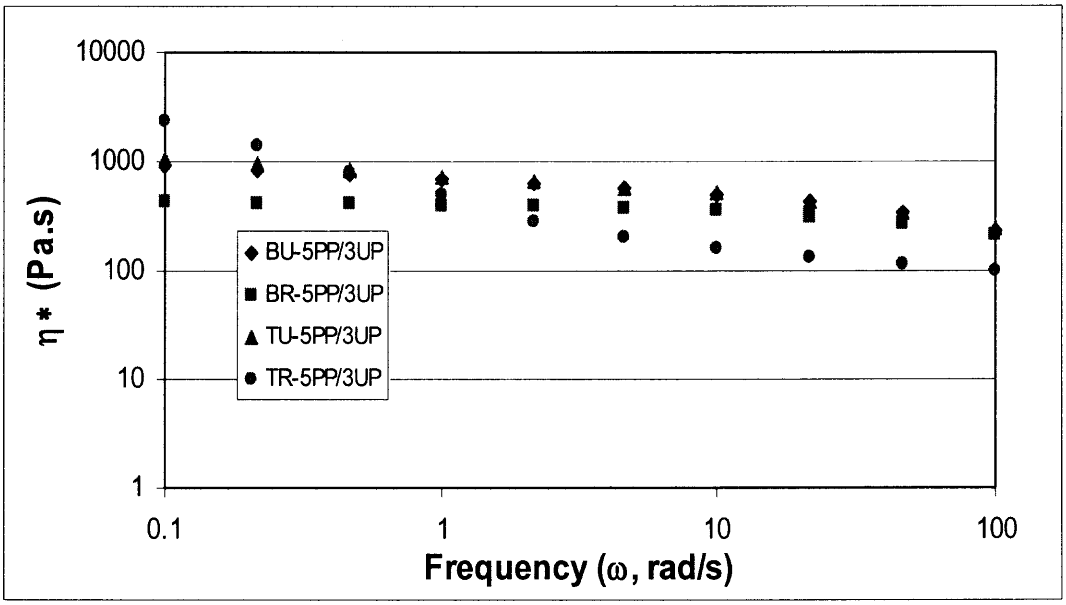

Figure 5.38b The effect of mixer type on the complex viscosity of the 5PP/3UP blends at 180°C testing temperature.

The effects of PDMI on the viscoelastic properties of the reacted 5PP/3UP blend also depended on the processing equipment. As mentioned in the morphology comparison, TSE provides much intensive mixing effect promoting a higher possibility of interfacial reaction within the blend components, compared to the batch mixer. Figures 5.39a and 5.39b show a slight difference in the low frequency region, where the TR sample in the presence of PDMI has the higher values of viscosity and storage modulus.

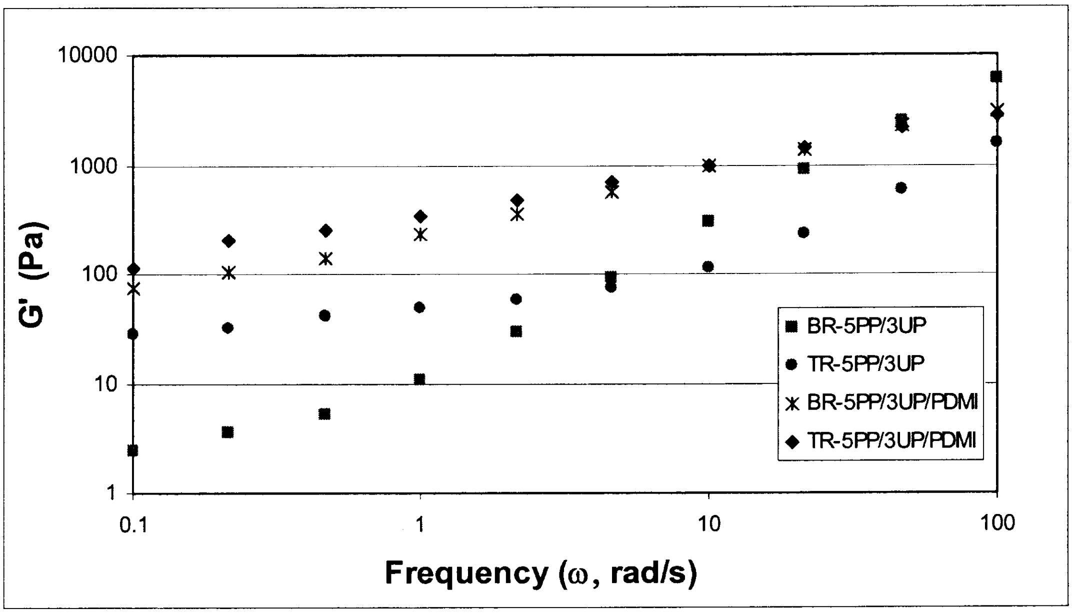

Figure 5.39a The effect of mixer type on the storage modulus of the POX reacted 5PP/3UP blends with or without PDMI at 180°C testing temperature.

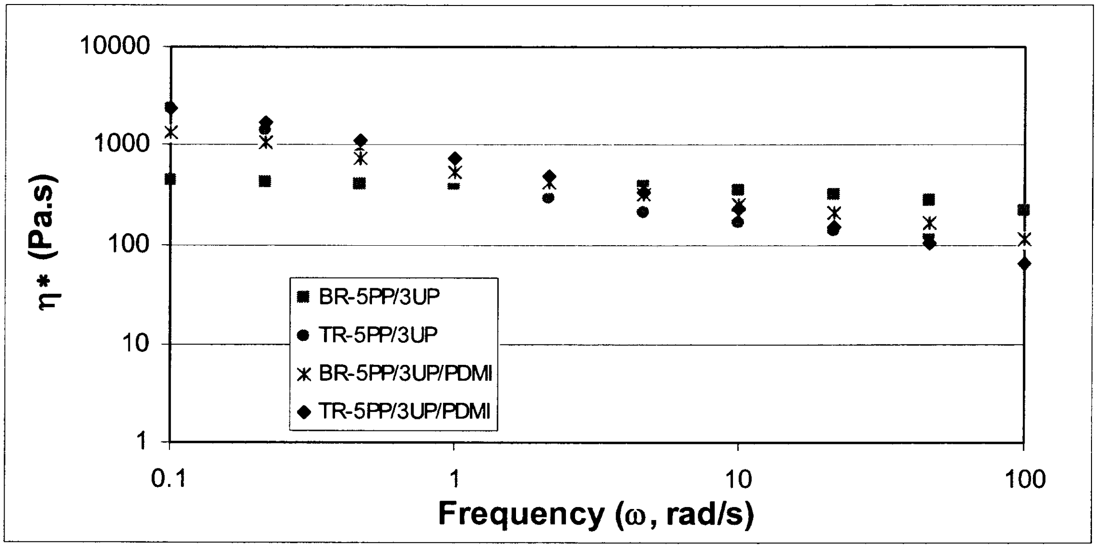

Figure 5.39b The effect of mixer type on the complex viscosity of the POX reacted 5PP/3UP blends with or with PDMI at 180°C testing temperature.

5.4 FT-IR Characterization of the Extruded PP/UP Blends

The IR spectra of:

(a) neat PP film from compression molded pellets;

(b) degraded PP initiated by 1phr POX in batch mixer;

(c) PP filtered from unreacted U-5PP/3UP sample blended in twin screw extruder;

(d) PP and PP-UP, xylene insoluble fraction at 50°C, filtered from reacted R-5PP/3UP sample blended in twin screw extruder;

are shown in Figure 5.40a and their subtracted spectra by differentiating from the original neat PP spectrum are also recorded in Figure 5.40b in an expanded scale. The original PP spectrum (a) does not show any significant peaks over a frequency range from 1600-1800 cm^{-1}. The spectrum of the degraded PP (b) is similar to that of (a). After subtracting it from (a), peaks appear at 1781cm^{-1}, 1723.17cm`1 and 1645cm^{-1}, which may be assigned to γ-lactone, ketone or aldehyde and unsatured carbon double bond, respectively. These may be due to residues of the decomposed peroxide and degradation of PP leading to carbonyl and unsaturation formation (Hinsken, et al., 1991). Spectrum (c) is almost identical to (a) and there are no additional peaks appearing in its subtracted spectrum, indicating that unreacted UP can be totally removed from the non-reacted blend by repeatedlly washing with warm xylene for at least 4 times. This confirms that no grafting reactions occurred between PP and UP during melt blending in the absence of peroxide. Minor peaks around 1700cm^{-1} may be due to thermo-oxidative degradation during melt blending. Then, the strong carbonyl absorption at 1728cm^{-1} in spectrum (d) and the peak appearing at 1735cm^{-1} in its subtracted spectrum, which corresponds to the PP carefully filtered from the reacted R-5PP/3UP blend can only be due to UP grafted onto the PP chains, after differentiating with respect to the carbonyl absorption due to degradation of PP and peroxide residue. This appears to offer a strong evidence of the existence of the graft or block PP-UP copolymer in the reaction product.

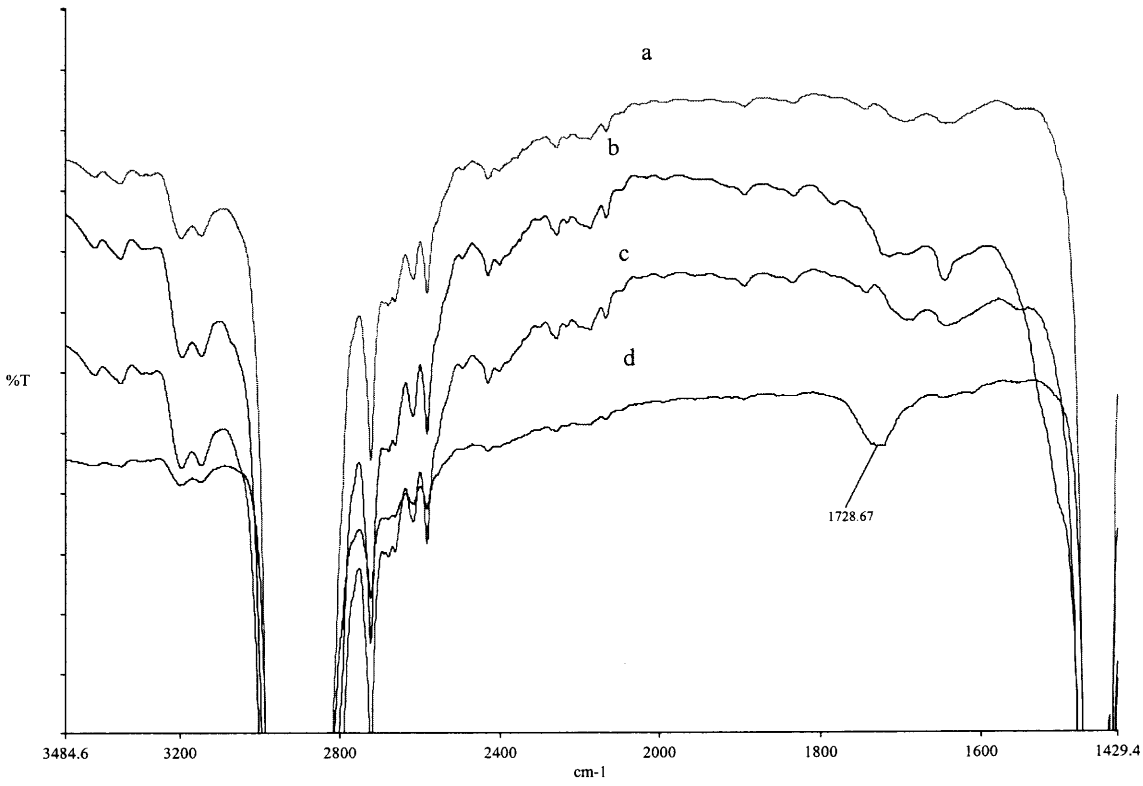

Figure 5.40a FT-IR spectra of different PP samples

(a)-neat PP;

(b)-peroxide degraded PP;

(c)-PP, xylene insoluble fraction of unreacted U-5PP/3UP blend at 50°C;

(d)-PP, xylene insoluble fraction of reacted R-5PP/3UP blend at 50°C, after filtering out the fraction of crosslinked UP

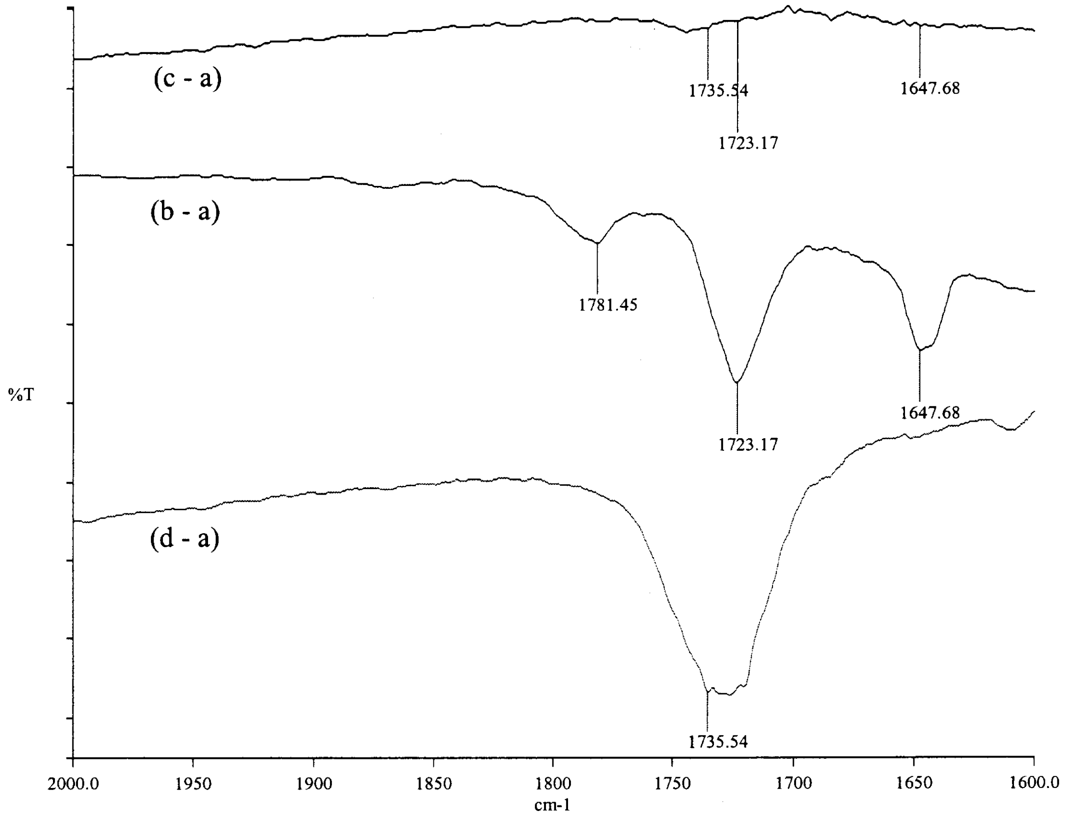

Figure 5.40b FTIR spectra of (b), (c) and (d) subtracted from that of (a).

5.5 Reactive Modification of High MW Polyester (PET) and its Blends With PP

High MW polyesters such as PET have similar end groups as those present in unsaturated polyesters and that makes end-group modification possible. All reactive modification such as chain extension and reactive blending in this section are based on that. However, due to the lack of unsaturated double bond, the reactive approaches will be different than those applicable in UPs. Other factors such as higher MW and high melting temperature result in large differences in the reactive modification process.

5.5.1 Chain Extension of PET and One-step Chain Extension/Foaming

Five additives, TGIC, PMDA, BDTA, BGPM and TGDDM, which posses different functionalities are selected for the study of chain extension of PET. Table 5.7 shows the results of the thermogravimetric analysis of the above five additives at process temperature (270-300°C). Despite significant differences in their thermal characteristics, all these additives will be in their liquid form at the processing conditions. The isothermal experiments were conducted in a non-pressurized system under nitrogen for a total time of 10 minutes (5 min heating followed by 5 min. at the selected temperature). The results indicated very high weight retention for BTDA, BGPM and TGDDM, lower weight retention for the TGIC and high weight losses for the PMDA. Excessive weight losses for TGIC and PMDA may be due to chemical degradation, which could cause possible changes in the reactivity of these additives, or may be simply due to their partial evaporation/sublimation. For all additives, assuming that high temperatures do not affect their reactivity over short time periods, no weight losses are anticipated in the pressurized environment of the extruder.

Table 5.7 Thermogravimetric Characteristics of Modifiers

Modifier	*MW*	*Form*	*Functionality*	*Reported M.P/B.P (°C)*	*Iso. TGA thermal stability****
PMDA	218	White powder	Tetra-	283-286 (397-400)*	31.3
BTDA	322	Beige powder	Tetra-	215-217*	97.4
BGPM	569	Yellow powder	Bi-	270**	99.6
TGIC	297	White powder	Tri-	100**	84.7
TGDDM	423	Clear brown viscous liquid	Tetra-	Not available	99.0

* Suppliers data
** Measured
*** (Wt.% residual following heating at 300°C and holding for 300s under nitrogen)

Several complex reactions are involved in the melt modification of polyesters with polyanhydrides or polyepoxides. As mentioned in the Chapter 3, a suggested reaction mechanism, with PMDA involves as a first step linear extension through reaction of terminal polyester hydroxyl end groups with the anhydride functionalities and the formation of two carboxyl groups per incorporated PMDA moiety; subsequent reactions may involve all four functionalities of the PMDA molecule through esterification and transreactions to yield branched or even cross-linked structures (Xanthos, 2002, Khemani, 1998, see Figure 3.3b). In the case of epoxides, a suggested mechanism for melt chain-extension reactions with the glycidyl functionality includes preferential esterification of carboxyl end groups followed by etherification of hydroxyl end groups; secondary hydroxyls formed from these reactions may further react with carboxyl or epoxy groups leading to branching or crosslinking as shown in Figure 3.3a. Transesterification reactions may also be important as well as subsequent reactions with the hydroxyl end groups of the polyester (Japon, 2001). It has been shown that the net effect of such reactions is a decrease in carboxyl content and an increase in hydroxyl content (Xanthos et al., 2001). It should be noted that in the absence of hydrolytic degradation, thermal degradation of the PET itself in melt processing equipment does occur; this is accompanied by increase in carboxyl content and decrease in hydroxyl content (Japon et al., 1998, Xanthos et al., 2001). Thus, changes in the instantaneous concentration of the resin end groups available for reaction with the additives are to be expected. During the extrusion runs, all those five additives are added by the concentration representing 50% excess of the stoichiometric amount to ensure the highest extent of reaction within the extruder residence time. These concentrations, in parts per hundred resin (phr), were based on the initial carboxyl or hydroxyl end group content (EG) values in the following generalized equation adapted from Refs. (Xanthos et al., 2001, Bikiaris et al., 1995).

$$\text{phr} = (\text{MW} \times \text{EG}) / f \quad \times\ 104 \qquad (5.11)$$

No corrections were made for new groups appearing in the reaction products as a function of time or in the base resin as a result of thermal degradation. Extrusion data related to die pressure and extrudate appearance shown in Table 5.8 clearly indicate that branching/crosslinking reactions did take place with all modifiers under the used process conditions. The relatively long residence time, estimated to at least 9 minutes, was considered to be sufficient for complete melting and mixing, and to advance/complete most reactions. Die pressures (taken as a measure of melt viscosity and, hence, MW) for the reacted systems were significantly higher than the die pressure for the unmodified resin control. Extrudate appearance was also significantly different for all reacted systems, particularly the PMDA and TGIC systems that showed the highest die pressures.

Table 5.9 contains a comparison between the anhydride modified products and the unmodified melt processed PET control. All on-line and off-line melt measurements point out to significant differences among the PMDA and BTDA modified products and their PET control with respect to parameters related to viscosity/MW (die pressure, Melt Flow Index, IV) and branching/MWD (die swell, sag, melt strength). By contrast to the control, the chemically modified extrudates showed significant degrees of swell upon exiting the die and exhibited less sag. Within standard deviation, sag was not much different among the two additives. Thermal analysis suggests that MW increases and broadening of the MWD as a result of chemical modification lower the onset and peak

Table 5.8 Extrusion Characteristics With Different Modifiers

Modifier	*Concentration, phr (1.5X stoichiometric amount)*	*Die Pressure (MPa)*	*Die Temperature (°C)*	*Extrudate appearance*
None	-	0.96	270.6	Smooth, thin, low viscosity
Anhydrides				
PMDA	0.7	12.8	269.3	Wavy, variable diameter (melt fracture)
BTDA	1.1	3.38	274.1	Smooth
Epoxides				
BGPM	1.1	4.68	275.6	Smooth
TGIC	0.4	15.2	279.6	Wavy, variable diameter (melt fracture)
TGDDM	0.45	11.5	270.3	Smooth

crystallization temperatures, increase the onset melting temperature and appear to reduce peak melting temperature on second heating. Glass transition temperature on second heating and % crystallinity were relatively unaffected for all samples ranging from 82.3 to 83.9 °C and 24.0-25.3 %, respectively (data not shown). Carboxyl content of the PET resin has also increased after processing versus that of the original pellets. Based on the proposed reaction mechanism of PET with polyanhydrides, any measurable carboxyl content at the end or reactive processing would reflect unreacted or thermally degraded PET macromolecules containing such groups, unreacted anhydride, and reaction products containing carboxyl groups. The difference in residual carboxyl content between the PMDA and BTDA reacted products coupled with the observed differences in rheology suggest different reactivity and conversion between the two additives. However, in the absence of reliable hydroxyl content data further speculation on the structural differences between the products is not possible.

Table 5.9 Comparison of Anhydride Modified PET Resins With PET Control

	Unmodified processed PET	PMDA modified	BTDA modified
On-line Measurements			
Die Pressure, (MPa)	0.96	12.8	3.38
Die Swell Aver., (SD)	0.82 (0.04)	3.32 (0.18)	2.65 (0.19)
Sag - Diameter Ratio Aver. (SD)	1.50 (0.03)	1.10 (0.06)	1.17 (0.12)
Off-line Melt Rheology			
Melt Flow Index Initial, (g/10 min)	>200	3.48	5.18
Melt Flow Index Aver. , (g/10 min)	>200	4.35	6.69
Melt strength, (10^{-3} N)	Not measurable	105	13.0
Off-line Thermal Analysis			
T_c, °C (onset/peak)	(187.9/176.4)	(182.5/166.6)	(181.7/164.9)
T_m, °C (onset/peak)	(195.6/245.2)	(226.2/240.5)	(226.8/243.2)
Off-line Structural Analysis			
IV, (dL/g)	0.68	1.13	0.90
Gel Content (%)	0	0	0
[COOH] (eq/10^6g)	36	108	77

Table 5.10 contains a comparison between the epoxide modified products and their unmodified melt processed PET control counterpart. As in the case of the anhydride modified materials, all on-line and off-line melt measurements point out to significant

differences among the epoxide modified products and their PET control with respect to parameters related to viscosity/MW (die pressure, Melt Flow Index, IV) and branching/MWD (die swell, sag, melt strength). TGIC and TGDDM modified products show the highest extent of reaction which is also confirmed by excessive gel formation and, as anticipated, a significantly reduced carboxyl content. Note that in both Tables 5.9 and 5.10 the average MFI values are higher than the initial values, apparently due to the continuing thermal degradation of the resins in the plastometer barrel; this is in contrast with data reported in (Japon, 2001) where incomplete reactions in the extruder led to further viscosity increases during melt rheological characterization. As in the case of anhydride modified PET's, thermal analysis suggests that MW increases and broadening of the MWD as a result of chemical modification lower the onset and peak crystallization temperatures, increase the onset melting temperature and appear to reduce peak melting temperature on second heating. Glass transition temperature on second heating and % crystallinity were relatively unaffected ranging for all samples from 81.7 to 83.9 °C and 23.5-25.3 %, respectively (data not shown)

Table 5.10 Comparison of Epoxide Modified PET Resins With PET Control

	Unmodified processed PET	BGPM modified	TGIC modified	TGDDM modified
On-line Measurements				
Die Pressure, (MPa)	0.96	4.68	15.2	11.5
Die Swell Aver. (SD)	0.82 (0.04)	2.94 (0.08)	3.07 (0.11)	3.09 (0.04)
Sag - Diameter Ratio Aver. (SD)	1.50 (0.03)	1.11 (0.05)	1.05 (0.04)	1.14 (0.03)
Off-line Melt Rheology				
Melt Flow Index Initial, (g/10 min)	>200	4.30	1.06	2.14
Melt Flow Index Aver., (g/10 min)	>200	4.57	1.09	2.97
Melt strength, (10^{-3} N)	Not measurable	18.5	332	289
Off-line Thermal Analysis				
T_c, °C (onset/peak)	(187.9/176.4)	(179.2/162.0)	(180.9/162.8)	(180.4/163.9)
T_m, °C (onset/peak)	(195.6/245.2)	(222.9/239.5)	(222.9/239.2)	(227.3/242.7)
Off-line Structural Analysis				
IV, (dL/g)	0.68	0.95*	0.82* (1.00)**	0.89* (1.00)**
Gel Content (%)	0	0.42	18.4	11.2
[COOH] (eq/10^6g)	36	20	9	13

* measured before gel removal

** measured after gel removal

Figures 5.41 and 5.42 contain plots of selected properties representing melt viscosity or MW changes versus properties representing melt elasticity or MWD changes for all five modified products and the unmodified control. A comparison of MW (expressed as die pressure) versus MWD (expressed as initial die swell) is shown in Fig. 5.41. The curve resembles curves in the "viscoelastic grid" of Kowalsky (Kowalsky, 1992) where two rheological parameters (and, therefore, two molecular variables) were used to define products with low MW and narrow MWD obtained by the peroxide modification of polypropylene (PP) in extruders. Although in our case high MW and broad MWD are required, the methodology applied to "controlled rheology" PP is still applicable, i.e., the level of MW and MWD needed for a given final product application dictates the required MW of the starting PET material and the type and concentration of the modifier. Similar information may be obtained from the Melt Strength vs. Melt Flow Index plot in Figure 5.42. In this Figure, data for the unmodified PET were omitted since melt strength was not measurable.

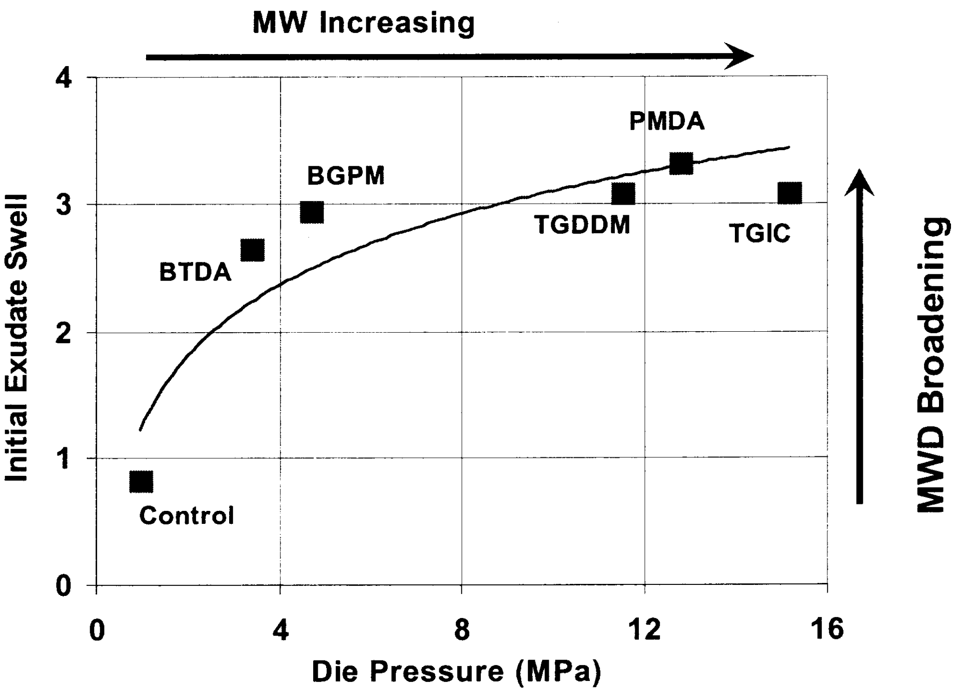

Figure 5.41 Die melt pressure versus die swell for PET control and PET reacted with anhydride and epoxy modifiers.

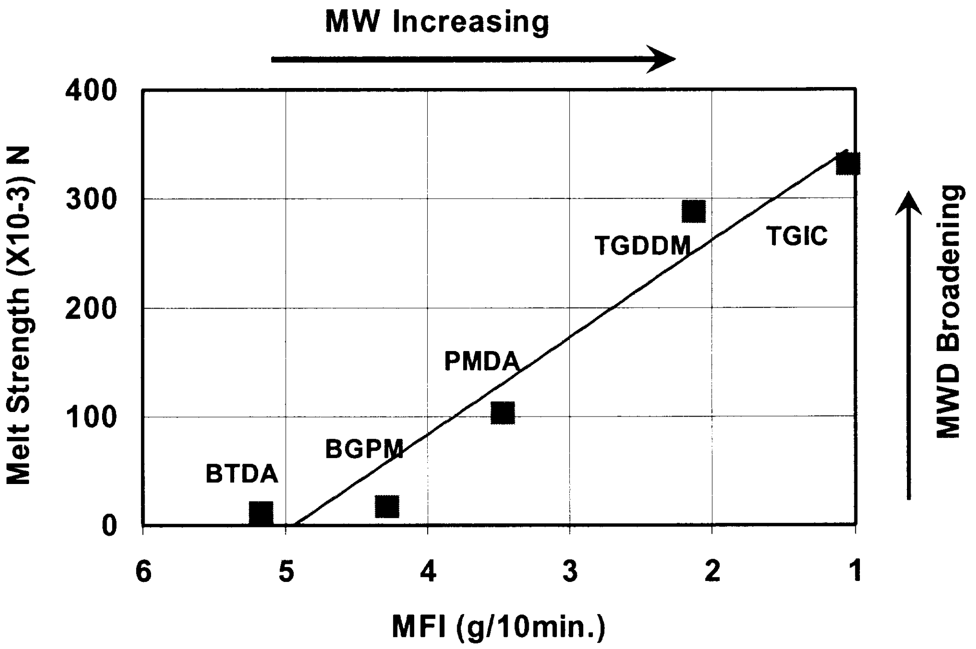

Figure 5.42 MFI versus melt strength of PET reacted with anhydride and epoxy modifiers.

One-step reactive extrusion/foaming results, mostly involving PMDA, have been already reported in the patent literature (Xanthos et al., 2000). However, limited or no data have been reported for most of the other four modifiers used in this work. Among the five modifiers, the BTDA system with a reasonably high IV of 0.9, zero gel content and medium degree of branching based on on-line and off-line measurements was used in a series of successful experiments with isobutane as the physical blowing agent. Extrudates with density of about 0.13 g/cc, expansion of 540% and reasonably uniform cells were produced, indicating that a foamable composition could be specified in terms of the rheological and structural parameters shown in Table 5.9 for this particular system. By contrast, the unmodified PET showed an expansion of only 120% with only few non-uniformly distributed cells. Our results suggest that the BGPM system having MFI, melt strength and IV not much different than the BTDA system would be a good candidate for foaming. It should be noted that, by contrast to foam extrusion by gas injection of non-reacting polymeric materials (Xanthos et al., 2000 and Zhang et al., 2001), analysis of the one-step process presents several challenges; one of them is that the dissolution and, perhaps, expansion of the blowing agent occurs in a continuously reacting, often multicomponent (Zhang et al., 2002), melt of increasing viscosity and elasticity, and changing structural characteristics including polarity.

5.5.2 One Step Reactive Blending/Foaming of PET/PP Blends

As mentioned in Chapter 3, PET homopolymers can not produce good quality foams due to their insufficient rheological properties. In the present study, the foamed product had an average density of 0.41 g/cc with uneven diameter, rough skin and non-uniform cell size. The die pressure was also found to fluctuate widely. In foaming experiments with binary blends of PP and PET, it was observed that the density of foams went through a minimum at 20% by wt. PP to a value of about 0.26 g/cc. For this composition, operating conditions were stable and extrudate surface was relatively smooth. However, cells were coarse and the average cell size of the foam increased from about 0.95 mm for PET to about 1.5 mm at 20 wt% PP.

In subsequent runs, a dry blend of 80% PET, 15% PP and 5% compatibilizer, a polyolefin based copolymer containing around 1~2% acrylic acid (Primacor 3460), was used and a foam of density of 0.25 g/cc was obtained, as shown in Figure 5.37. The extrusion process was also found to be very stable (Table 5.11). Though the decrease in density was marginal, the average cell size of the compatibilized foamed blend was found to be about 900 μm versus about 1500 μm for the uncompatibilized foamed blend (Figure 5.38). The use of the reactive coagent (TGIC) to enhance compatibility had a great effect on both density (0.17 g/cc) and cell size (180 μm) as shown in Figures 5.43 and 5.44. The peak melting temperatures of PET and PP and the % crystallinity of PET were not significantly affected by the addition of compatibilizer as shown in Table 5.11. However, when the compatibilizer or compatibilizer/coagent combination was used, the crystallization peak temperatures of PET and PP were shifted to much lower values. This is presumably the result of enhanced interactions between the blend components delaying their ability to crystallize. These results are in agreement with DSC data reported earlier on PET/PP and PET/PP-g-AA unfoamed blends (Young, 1989).

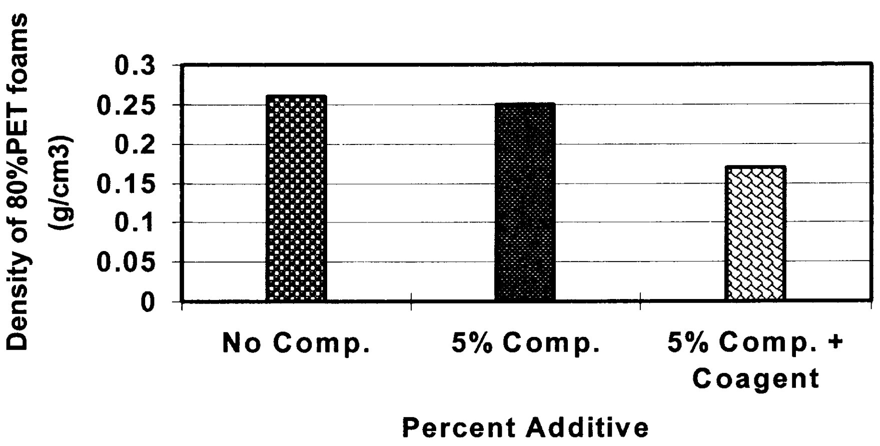

Figure 5.43 Blend foam density vs. % and type of additives.

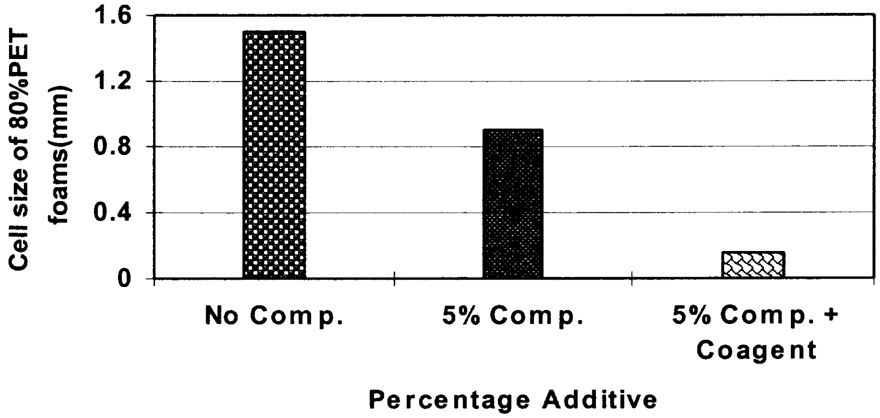

Figure 5.44 Blend foam cell size vs. % and type of additives.

Table 5.11 Properties of Carbon Dioxide Foamed PET/PP (80/20) Blends with/without Compatibilizer

Composition	Melting Peak (°C)		Crystallization. Peak (°C)		Crystallinity of PET(%)	Surface appearance	Process stability
	PP	PET	PET	PP			
PET	N/A	250.2	196.9	N/A	30.1	Unacceptable	Unstable
80%PET + 20%PP	145.3	248.8	199.2	109.0	30.3	Smooth	Stable
80%PET + 15%PP + 5%comp.	146.1	250.9	179.3	91.2	31.7	Smooth	Stable
80%PET+ 15%PP + 5% (comp.+ coagent)	145.3	246.3	161.5	102.2	26.4	Very smooth	Stable

5.5.3 Summary of the Reactive Blending/Foaming PET and its Blend With PP

Low IV polyethylene terephthalate (PET) can be reactively modified through low molecular weight multifunctional anhydride and epoxy compounds (chain extension/branching) or by blending with a second component such as PP in the presence of compatibilizers (reactive blending). During the chain extension of PET, melt viscosity and melt strength, and intrinsic viscosity and carboxyl group content were used as criteria of the extent of the modification. Correlations of die pressure with extrudate swell, and correlation of melt flow index with melt strength by off-line testing of the extrudates showed that the most reactive modifiers were pyromellitic dianhydride, a tetrafunctional epoxide and a trifunctional epoxide. For all systems molecular weight increases (related to die pressure/MFI/IV) are accompanied by broadening of the molecular weigh distribution (related to die swell/melt strength). The less reacted BTDA system was used satisfactorily in the production of low-density foams by one-step reactive modification/gas injection foaming at extrusion conditions not significantly different than those employed in the simple reactive modification. This indicates that foamable compositions could be specified in terms of the rheological and structural property values corresponding to the BGPM and BTDA systems; also, that excessive modification with the used high concentrations of PMDA, TGIC and TGDDM is not necessary.

Reactive blending of PET with PP offers another approach for modifying PET for extending its application in extrusion foaming. However, due to their totally different molecular structure, compatibilizers are needed in order to form a useful blend structure. In the present study, a low density foam with fine cell size can be obtained by blending PET, PP, compatibilizer (Primacor 3460) and a suitable coagent (TGIC) followed by foaming with carbon dioxide in a twin screw extruder. The use of PP or polyolefinic based compatibilizer did not affect the melting peak temperature of PET or the PET crystallinity in the foam, although it decreased its crystallization temperature.

CHAPTER 6

CONCLUSIONS

A low MW unsaturated polyester (UP) was shown to be effectively modified through reactive melt processing. The viscosity of UP can be increased through the chemical reactions between POX or MgO and functional groups of UP such as unsaturated double bond and carboxyl/hydroxyl end groups. While POX will attack the double bond within the UP backbone chains and leave most of end groups untouched, MgO will interact with acid groups of UP and maintain, in principle, the unsaturated structure, if the effects of thermal degradation can be neglected. Both chemical modifications can take place in melt processing equipment and are fast enough to be carried out in continuous extruder reactors. The concentration of POX or MgO and the choice of processing conditions play an important role in the crosslinking reaction.

Organic peroxides appear to be very effective compatibilizing agents during the reactive blending of PP/UP. PP and UP respond to POX in opposite ways during reactive blending: PP degrades and UP crosslinks. As a result of these two opposite reactions, the vastly different rheological properties of the blend components can be adjusted during reactive melt blending to produce a much finer and more uniform morphology in the reacted PP/UP blends. This is due to the continuously decreasing viscosity ratio of PP/UP towards unity by the competing reactions between POX and the blend components; this has a remarkable effect on the morphology of the dispersed phase. Another important factor is the formation of PP-UP copolymers during the reactions, which serve as *in situ* compatibilizers to promote better adhesion and strengthen the weak interface between the PP and UP.

Reactive blending of PP/UP blends with POX is affected by many factors such as the concentration of POX, mixing efficiency and addition of coagents. With PP as the matrix, the effect of the POX concentration is not that pronounced in terms of the morphological and rheological properties of the final reacted blend systems due to the excessive degradation of PP matrix. However, large differences are observed with UP as the matrix during reactive blending. In this case, the higher the POX concentration, the higher the viscosity and better rheological properties of the blend and the finer and more uniform the morphology of the final products, since the UP crosslinking reaction is predominant among the peroxide reactions. The mixing efficiency also plays an important role on the properties of the final reacted blends, particularly on the formation of PP-UP copolymer during processing. Intensive mixing is needed to promote interfacial reactions, which is one of the keys to make the *in situ* reactive compatibilization process possible. Due to the much better mixing efficiency in the twin screw extruder than in the batch mixer, the blends prepared by twin screw extruder (TR blends) have a more stable morphology and a more thermoplastic elastomers-like rheological behavior than those prepared through the batch mixer (BR blends). TR blends show a higher modulus and complex viscosity than the BR samples and a distinct secondary plateau in the low frequency region.

Addition of coagents during the reactive blending offers a great flexibility and effective means for tailoring the desired properties of the final blends. PDMI has been shown to be an efficient coagent for suppressing the degradation of the PP matrix and the crosslinking of UP domains and increasing the possibilities of the interphase reactions; thus, it is possible to generate more PP-UP copolymers serving as compatibilizers and promoting a more uniform and finer morphology. MgO can be used to increase the viscosity of the UP domains and interact with PP through PDMI or PB3200, thus, bridging the PP and UP phase to minimize interfacial energy between the two immiscible blend components. PB3200 is also a promising coagent and gives the best results in terms of morphology and rheological properties during the reactive blending of PP/UP blends together with MgO. This is mainly because that there is no POX induced degradation of the PP phase during processing.

A high MW saturated polyester (PET) at relatively low I.V. can also be modified through low MW multifunctional anhydride and epoxy compounds by chain extension/branching. Correlations of die pressure with extrudate swell, and correlation of melt flow index with melt strength by off-line testing of the extrudates showed that the most reactive modifiers were pyromellitic dianhydride, a tetrafunctional epoxide and a trifunctional epoxide, resulting in excessive viscosity increase. The less reacted BTDA system was used satisfactorily in the production of low-density foams by one-step reactive modification/gas injection foaming at extrusion conditions not significantly different than those employed in the simple reactive modification without foaming.

Reactive blending of PET with PP offers another approach for modifying the PET and extending its application in extrusion foaming. Thermal analysis results gave an indication of a stable compatibilized PET/PP blend by using polyolefinic based polar compatibilizer with coagents during the mixing/reaction process. Low density foams with fine cell size can be obtained by blending PET, PP, compatibilizer and the coagent followed by foaming with carbon dioxide in a twin screw extruder.

Recommendations for future work:

1. Detailed structural characterization of the reacted blends by FTIR and NMR.
2. Explore the remaining reactive functionalities of UP after reaction with POX or MgO, respectively, in attempts to produce novel blends.
3. More experiments, preferably at the pilot scale should be carried out to ascertain the technical and economic feasibility of the reactive blending process in the twin screw extruder and evaluate compatibilization in terms of mechanical properties.
4. Explore promising blends such as PP based compositions of low and high UP content with modified structural and rheological characteristics to be used as: (a) compatibilizers in PP/high MW polyester blends and (b) rheological modifiers in extrusion foaming.
5. Study the effects of other different coagents for better product design.

APPENDIX

MODEL DEVELOPMENT FOR THE DEGRADATION OF PP AND CROSSLINKING OF UP IN THE PRESENCE OF POX

In this appendix, models were developed for PP degradation and UP crosslinking. For the degradation of PP, a general mechanism of chain scission using a free radical initiation is represented by the following elementary reactions (assuming the POX is well distributed in the PP or UP and neglecting the thermal and shear-induced degradation):

Initiator decomposition:

$$I \xrightarrow{kd} 2I\cdot \tag{A.1}$$

The POX (Luperco 101XL) dissociates into two initiator radicals with the rate coefficient for initiator dissociation k_d. The initiator radicals are able to initiate the polymer degradation reaction and may be lost in unspecified side reactions. This is usually taken into account by the initiator efficiency *f* (number of polymer chains broken after hydrogen abstraction through initiator radicals divided by the number of initiator radical formed). *f* is usually a function of the peroxide concentration and reaction temperature.

Hydrogen abstraction by primary radicals:

$$P_n + I\cdot \xrightarrow{ki} P_n\cdot + IH \tag{A.2}$$

The initiator radical abstracts a H-atom from PP (P_n) with chain length *n* leading to non-reactive initiator fragment IH and a PP macroradical $P_n\cdot$ (radical function along with the chain) with chain length *n*. Tertiary hydrogen atoms are preferentially attacked and the abstraction of primary and secondary H-atoms can be neglected.

Chain scission (β-scission):

$$P_n \cdot \xrightarrow{ks} P_m \cdot + P_{n-m} \tag{A.3}$$

Since this reaction is extremely fast, the above two equations (A.2 and A.3) can be combined as follows:

$$P_n + I \cdot \xrightarrow{ki} P_m \cdot + P_{n-m} + IH \tag{A.4}$$

The PP chains can also abstract H-atoms from other PP chains with a rate coefficient k_{tr}, as called chain transfer as follows:

$$P_m \cdot + P_n \xrightarrow{ktr} P_m + P_n \cdot \tag{A.5}$$

Termination

PP macroradicals can be terminated by disproportionation:

$$P_n \cdot + P_m \cdot \xrightarrow{ktd} P_n + P_m \cdot \tag{A.6a}$$

or by recombination:

$$P_n \cdot + P_m \cdot \xrightarrow{ktc} P_{n+m} \tag{A.6b}$$

As proposed by Tzoganakis *et al* (1988), the changes of concentration of the different species with time are the following:

POX balance:

$$\frac{d[I]}{dt} = -k_d[I] \tag{A.7}$$

Free radical balance:

$$\frac{d[I\cdot]}{dt} = 2fk_d[I] - k_i[I\cdot]\sum_{n=2}^{\infty}(n-1)[P_n] \tag{A.8}$$

PP balance:

$$\begin{aligned}\frac{d[P_n]}{dt} &= k_i[I\cdot]\{\sum_{i=n+1}^{\infty}[P_i]-(n-1)[P_n]\}\\ &\quad -k_{tr}\{(n-1)[P_n]\sum_{i=1}^{\infty}[P_i\cdot]-[P_n\cdot]\sum_{i=1}^{\infty}(i-1)[P_i]-\sum_{i=1}^{\infty}[P_i\cdot]\sum_{j=n+1}^{\infty}[P_j]\}\\ &\quad +(k_{td}+k_{tc})[P_n\cdot]\sum_{i=1}^{\infty}[P_i\cdot]\end{aligned} \tag{A.9}$$

In order to reduce the dimensions of the infinite set of the obtained coupled differential equations, the majority of authors takes only into account the free radical initiation and chain scission and neglect the contribution from transfer and termination reactions. During this particular study, the free radical is the limiting reagent; the differential expression for P_n can be rearranged as follows:

$$\frac{d[P_n]}{dt} = \{k_i[I]^{\frac{k_iC_1}{k_d}} - 2f\frac{k_ik_d}{-k_iC_1+k_d}[I]\}C_2 \tag{A.10}$$

where $C_1 = \sum_{n=2}^{\infty}(n-1)[P_n]$

$$C_2 = \sum_{i=n+1}^{\infty}[P_i]-(n-1)[P_n]$$

Since it is shown experimentally that the free radical initiation is the controlling step, which means $k_i >> k_d$, equation A.10 can be reduced to:

$$\frac{d[P_n]}{dt} = 2fC_3k_d[I] \tag{A.11}$$

where $C_3 = \frac{C_2}{C_1}$

Since at the steady shear mode, the viscosity is a function of molecular weight of PP, then:

$$\eta = f_cM_w^{\ C_4} = f_c(M_0P_n)^{C_4} \tag{A.12}$$

where C_4 is a constant and its value is between 1~3.4 and M_0 is the MW of PP monomer So, Eq. A.12 can be modified into:

$$\frac{d\eta}{dt} = 2fC_5 k_d [I] \tag{A.13}$$

where $C_5 = \dfrac{f_c C_2}{C_1 \times C_4 \times M_0}$

Equation A.13 theoretically shows the degradation of PP in the presence of POX is controlled by the decomposition of POX.

Very few studies for the kinetics of UP crosslinking have been published. However, it can be treated as a macroradical polymerization reaction and, thus, the following elementary reactions can be used to represent the UP crosslinking initiated by POX.

Initiator decomposition

$$I \xrightarrow{kd} 2I \cdot \tag{A.1}$$

The above free radicals initiation is exactly same as that of degradation of PP. However, the initiator radical will attack UP preferentially at the double bond sites.

$$U_n + I \cdot \xrightarrow{ki'} U_n \cdot + IH \tag{A.14}$$

The polymeric radicals propagate through further reactions at the double bonds of the polyester chains and build up the MW of UP before terminating through recombination with another polymer radical.

Crosslinking of UP:

$$U_n \cdot + U_m \xrightarrow{ks'} U_{n+m} \cdot \tag{A.15}$$

Termination of UP radicals:

$$U_n \cdot + U_m \cdot \xrightarrow{ktc'} U_{n+m} \tag{A.16}$$

In this mechanism, hydrogen abstraction and scission of polymer chains are neglected. Intramolecular cyclization reactions are also neglected in the kinetic mechanism. Also in this particular study, the "steady-state" assumption is not valid since there is no adequate mixing during the crosslinking reaction under the current experimental conditions. In fact, the crosslinking of UP with POX is very similar to PP degradation, if only free radical initiation and the crosslinking reaction are taken into account. The changes of concentration of the UP_n with chain length *n* at time *t* are the following:

$$\frac{d[U_n]}{dt} = \{k_i'[I]^{\frac{k_i'C_1'}{k_d}} - 2f'\frac{k_i'k_d}{-k_iC_1' + k_d}[I]\}C_2' \tag{A.17}$$

where $C_1' = \sum_{n=2}^{\infty}(n-1)[U_n]$

$$C_2' = \sum_{i=n+1}^{\infty}[U_i] - (n-1)[U_n]$$

Similarly to the degradation of PP and considering that the free radical decomposition is the controlling step and $k_i' >> k_d$, the Eq. A.17 can be reduced to the following equation:

$$\frac{d[U_n]}{dt} = 2f'C_3'k_d[I] \tag{A.18}$$

where $C_3' = \frac{C_2'}{C_1'}$

Equation A.18 can also be transformed into the following expression of viscosity versus time by treating in a similar way to degradation of PP:

$$\frac{d\eta}{dt} = 2f'C_5'k_d[I] \tag{A.19}$$

where $C_5' = \dfrac{f_c C_2'}{C_1' \times C_4' \times M_0'}$

M_0' is the MW of UP monomer

Equations A.13 and A.19 are almost identical except that they have different initiator efficiencies, which are not only a function of the polymer matrix and POX concentration but also of the processing temperature. However, combined with constants such as C_5 and C_5', this only unknown parameter can be determined by fitting the kinetic model to the experimentally measured steady-shear viscosity, given the value of k_d.

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