

3.0 Separation of a Thermotropic Liquid Crystalline Polymer from Polypropylene Composites

This chapter is focused on the first, third, and fifth objectives of this thesis. First, a process was developed to reclaim the expensive thermotropic liquid crystalline polymer from in situ composites. Second, the ability of the reclaimed thermotropic liquid crystalline polymer to make in situ composites with polypropylene was determined. Third, the economic feasibility of reclaiming and reprocessing the recovered thermotropic liquid crystalline polymer was examined. This chapter is organized as a manuscript and will be submitted to *Polymer Composites*.

Separation of a Thermotropic Liquid Crystalline Polymer from Polypropylene Composites

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SUMMARY

This work is concerned with determining how to effectively recycle wholly thermoplastic composites comprised of a polypropylene (PP) matrix reinforced with a thermotropic liquid crystalline polymer (TLCP). The composites of interest are generated by means of a patented, dual extrusion process in which TLCPs and TPs with non-overlapping processing temperatures can be utilized. In particular, fibers and strands are formed and then used to make composites with an excellent balance of mechanical properties. Because of the need to plasticate the TLCP and the TP components separately, a novel reclamation process was developed in which the TLCP could be recovered from the PP matrix. Reactive extrusion was used to reduce the molecular weight of the polypropylene (Montell PP 6523) and to facilitate phase separation. The melt was then extruded into a heated mineral oil bath, which separated the TLCP (DuPont HX8000) from the matrix by dissolving the polypropylene. It was found that greater than 70 wt% of the TLCP could be reclaimed from the PP matrix at a purity of greater than 96

wt%. In order to determine the ability to reuse the reclaimed HX8000, injection molded in situ composites were generated and their mechanical properties were determined. When the neat HX8000 component was partially replaced with reclaimed HX8000, the injection molded TLCP/PP composites showed no discernible difference in mechanical properties. With the current cost of neat HX8000 over \$8.00 per pound and with the projected cost of the reclaimed HX8000 under \$3.00 per pound, it is believed that this process is economically viable.

3.1 INTRODUCTION

TLCP / TP composites are typically generated by subjecting the blend of a thermotropic liquid crystalline polymer (TLCP) and a thermoplastic (TP) to an extensional flow during processing. During extensional flow, the thermotropic liquid crystalline polymer drops are elongated from spheres into fibrils. These fibrils are oriented and cooled to lock in orientation and morphology. Because the reinforcing fibrils are generated during the processing step, these composites are referred to as *in situ* composites. Generally, the main forms of processing these TLCP / TP composites are: 1) injection molding, 2) fiber spinning, 3) filament extrusion / drawing, and 4) film extrusion / drawing.

Much work has been done on the addition of thermotropic liquid crystalline polymers to enhance the overall mechanical properties of many thermoplastics (1-10). The composition and commercial names of a few of these thermotropic liquid crystalline polymers can be seen in Table 3.1. These studies showed that there are four main problems associated with *in situ* composites: 1) the mechanical properties of *in situ* composites were anisotropic in nature, 2) the highest possible mechanical properties were not being realized, 3) only TLCPs and TPs with overlapping processing temperatures and similar viscosities could be utilized, and 4) incompatibility was leading to poor dispersion of the TLCP within the TP matrix. However, some work has been done on improving the dispersion of the TLCP in injection molded plaques by blending the TLCP and TP in an extruder prior to injection molding (4, 11). In other cases, the extrusion system was fit with a static mixer to further disperse the TLCP throughout the thermoplastic matrix prior

Table 3.1 The Composition and Commercial Names for Some TLCPs (12).

Article name	Commercial name	Supplier	Composition
PET/60% HBA	—	Unitca	PET/HBA
Vectra A	Vectra A900/950	Hoechst-Celanese	HBA/HNA
Vectra B	Vectra B900/950	Hoechst-Celanese	HBA/HNA/AP
Vectra RD500	Vectra RD500	Hoechst-Celanese	HBA/HNA/HQ
SBH	—	Eniricerche	SA/HBA/BP
K161	—	Bayer	HBA/TA/TA/HQ/BP
—	Granular	Granmont	TA/PhHQ/StHQ
HX1000	—	DuPont	Based on HQ and TA ^a
HX4000	—	DuPont	Based on HQ and TA ^a

PET, poly(ethylene terephthalate); HBA, 4-hydroxybenzoic acid; HNA, 2-hydroxy-6-naphthoic acid; TA, terephthalic acid; SA, sebacic acid; AP, aminophenol; HQ, hydroquinone; IA, isophthalic acid; BP, 4,4'-dihydroxybiphenol; PhHQ, phenyl hydroquinone; and StHQ, styryl hydroquinone.

^aOther molar constituents are proprietary.

to injection molding (11, 13). While these methods were successful in dispersing the TLCP, they were unsuccessful in eliminating the problem of anisotropy and the limitation of only being able to use polymers with similar processing conditions.

However, there is one blending method that is very different from all of the typical processing methods used to make TLCP / TP composites. This method not only alleviates the processing condition problem, it also indirectly reduces the problem of anisotropy. This method is the dual extrusion technique patented by Baird and Sukhadia (14). In this system, the two extruders separately plasticate the thermotropic liquid crystalline polymer and the thermoplastic. Furthermore, the two extruders are connected to a phase distribution system and a set of static mixers, where the separate streams are subdivided into layers. The TLCP/TP composite melt is then extruded through a capillary die and then drawn into fibers. This process results in an axially continuous, fibril morphology of the TLCP which is not seen in the injection molded or extrusion mixed / injection molded samples (15).

There are numerous advantages to this system: 1) since the two composite components are extruded separately, a TLCP and a thermoplastic, whose processing temperature ranges do not ordinarily overlap, may still be processed into a composite, 2) strands of a matrix reinforced with nearly continuous fibrils of the thermotropic liquid crystalline polymer can be generated, 3) the composite fibers can be drawn to increase mechanical properties. The resulting composite fibers can be processed by means of several different methods. On one hand, they can be chopped into pieces and then injection molded. By being able to process at a temperature below the melting point of the TLCP, the reinforcing morphology generated in the dual extrusion step remains within

the injection molded plaque and higher mechanical properties can be realized (1, 2). Furthermore, the composite fibers can either be laid down into random mats or be woven into fabrics and then compression molded just above the melting point of the matrix (15). The resulting compression molded parts have higher mechanical properties and a lower amount of anisotropy than injection molded in situ composites (16). Overall, the dual extrusion process directly or indirectly leads to the reduction of the three main problems of in situ TLCP / TP composites.

Further advantages can be realized if a way to recycle thermotropic liquid crystalline polymer / thermoplastic composites can be developed. First, the ability to recycle would reduce the overall cost of producing the composite by being able to reuse the expensive TLCP component. Second, the ability to recycle represents an attractive concept to an industry that is becoming more environmentally conscious. Finally, the ability to recycle TLCP / TP composites would represent a technological advantage over traditional carbon or glass fiber composites.

In situ composites consisting of a TP and a TLCP (Hoechst Celanese Vectra A950) with overlapping processing temperatures have been reported to be directly recycled by grinding and then reprocessing the material (17). It was found that for a blend of PP and the Vectra A950 that the composite could be reprocessed up to 10 times without any losses in tensile strength. However, this approach is limited to in situ composites in which degradation of the matrix does not occur readily during recycling and to those in which anisotropic mechanical properties are acceptable. On the other hand, when the dual extrusion system is utilized to generate TLCP/TP composites, then a method for separating the two components must be developed.

The two main forms of separating well mixed polymers is to either reduce the composite to powder and then to use their differences in density to affect a separation or to selectively dissolve one polymer away from the other (18, 19). In order for the first method to work successfully, the size of the pure polymer phase must be larger than the size of the ground particle. Therefore, the distribution of pieces would contain no encapsulated phases and the differences in density could be used for separation. Currently, the best granulation-type device, a jet mill (air impact type), can only reduce a composite blend to a set of particles with an average diameter of 13.3 μm (18). In the case of the composites generated in the dual extrusion process, the size of the pure TLCP phase is much smaller than the 13.3 μm diameter of the jet mill particle. The average cross-sectional diameter of a pure TLCP fibril is on the order of 1 μm in size (15, 16). Therefore, this grinding method cannot be used to separate the thermotropic liquid crystalline polymer from the thermoplastic matrix.

In order for the selective dissolution method to work, three criteria must be met (19). First, the two species must not be miscible with each other and, therefore, a mixture of the two polymers must be heterogeneous. Second, the two materials must have melting points which are different enough to assist in the separation. Third, the two materials must be different enough in chemical structure so that selective dissolution will occur as a function of temperature. Only if a polymeric mixture meets these criteria, can this method be applied to separate the components of the mixture.

The selective dissolution method can be further broken down into two steps. The first step in the process consists of dissolving one or both of the polymers. A solvent is chosen that will either dissolve only one of the polymers, or will dissolve both of the

polymers at different temperatures. Once one of the polymers is completely dissolved, the solution is transferred away from the other polymer and sent to the next step. The second step, called flash devolatilization, consists of completely evaporating the solvent away from the polymer. The solids can be collected, and the evaporated solvent can be condensed and sent back to the dissolution chamber.

Some work has been done that utilized this selective dissolution process to separate a mixture of polymers. Lynch et al. (19) used this process, see Table 3.2, in an attempt to separate six, dry mixed thermoplastics by using tetrahydrofuran (THF) as the solvent. From Table 3.2, it can be seen that this process was > 99% effective in isolating both the low density polyethylene (LDPE) and the polyethylene terephthalate (PET) from the original mixture. While this particular study did demonstrate the partial effectiveness of the selective dissolution technique, it did not address the ability of this process to isolate polymers from a mixture in which one phase is dispersed within the other phase via melt blending.

Fortunately, some work has been done in which this process was used to reclaim the polypropylene and glass components from composites of polypropylene reinforced with glass fibers. Poulakis et al.(20) used xylene at 135°C to dissolve all of the polypropylene away from the glass fibers. The reclaimed fibers were reprocessed into composites with virgin polypropylene and no significant losses in tensile modulus, strength at yield, or strength at break were observed. However, there were losses seen in the izod impact strength of the recycled composites. While this study showed that the selective dissolution process was highly effective in isolating a dispersed, inorganic phase from a

Table 3.2. Experimental Extraction Efficiencies Using Single Solvent Selective Dissolution (19).^a

Material	Extraction	Temperature (°C)	Efficiency (%)
PVC	First	25	>99
PS	First	25	>99
LDPE	Second	70	>99
PP	Third	160	>99
HDPE	Third	160	>99
PET	Fourth	190	>99

a. Experiments were conducted using virgin polymers. Tetrahydrofuran was the solvent used in dissolution.

PVC is polyvinyl chloride, PS is polystyrene, LDPE is low density polyethylene, PP is polypropylene, HDPE is high density polyethylene, and PET is polyethylene terephthalate.

polypropylene matrix, it did not demonstrate the ability of this technique to separate a thermoplastic that was dispersed within another thermoplastic. Because the selective dissolution process proved to be successful in separating one type of a dispersed phase (an inorganic glass), this method was partially adapted for the reclamation of a TLCP from polypropylene / TLCP composites.

In this work, a new process is reported for the reclamation of a thermotropic liquid crystalline polymer (DuPont HX8000) from a polypropylene (Montell PP 6523) matrix. In order to eliminate the use of a volatile and toxic solvent such as xylene, mineral oil was chosen as the dissolution media. Because the virgin PP component would not completely dissolve into the mineral oil due to high molecular weight and phase constraint problems, reactive extrusion was used to lower the molecular weight of the PP and to increase phase separation between the HX8000 and the PP. The purity of the reclaimed HX8000 was determined by using density measurements and a general rule of mixtures, while the melt viscosity and solidification behavior of the reclaimed HX8000 were examined by using a parallel-plate rheometer. Tensile and flexural testing of injection molded composites was performed to determine any losses in mechanical properties due to the reclamation process. Finally, a brief cost analysis was done to examine the economic feasibility of the reclamation process.

3.2 EXPERIMENTAL

3.2.1 Materials

The composites used in this study consisted of 40 wt% DuPont HX8000 and 60 wt% Montell PP 6523. HX8000 is a semi-crystalline TLCP which has two melting

temperatures (one at 228°C and the second at 278°C) and a density of 1.38 g/cm³. It is believed to be composed of an unspecified ratio of terephthalic acid, 4-hydroxybenzoic acid, hydroquinone, and hydroquinone derivatives (21). To process this TLCP, a melt temperature of at least 290°C is required. PP 6523 is a semi-crystalline polyolefin which has a melting point of 165°C and a density of 0.90 g/cm³.

The composites were in the form of 1.0 mm diameter fibers that had been compression molded at 200°C into random-mat plaques by a Carver Laboratory Hot Press (Model 2696). The plaques were then shredded in a Cumberland Granulator (Model 618 D) in order to fit into the extruder. The resulting pieces consisted of shavings with the following average dimensions: 5.0 mm long, 3.0 mm wide, and 2.0 mm thick. The granulated shavings were then used as the feedstock for the novel separation process.

3.2.2 Reactive Extrusion

A Killion, single screw extruder was used, which contained a general purpose, 2.54 cm diameter screw ($L/D = 24$) with a compression ratio of 2.5, three heating zones, and one heating zone for the die. A 90° elbow-shaped, 2.0 cm inner diameter die was used to discharge the melt into the mineral oil separation process. The processing temperatures for the reaction were: Zone 1 = 120°C, Zone 2 = 300°C, Zone 3 = 300°C, and the die = 300°C; which were chosen to thoroughly melt both polymers and to increase phase separation. The other processing parameters were: a screw speed of 10 rpm and a mass flow rate of 12.0 g/min. The starting material was dry blended with 1.0 wt% dicumyl peroxide (Aldrich 32,954-1, CAS # 80-43-3) and then fed into the reactor.

3.2.3 Mineral Oil Separation

Once the starting material had reacted with the dicumyl peroxide, the melt was extruded into the light mineral oil. Specifically, the light mineral oil used was Fisher O121-4 (CAS # 8042-47-5), which was heated to 200°C in a 6 liter tank with a 1600 W heater on the bottom. The mineral oil was stirred at 1550 rpm by an impeller with the following dimensions: 55.13 blade diameter, 21.13 outer blade width, and 1.0 mm thickness. The extruded material was stirred in the mineral oil for the duration of the batch extrusion process, which was typically 3 hours long. With the degraded PP dissolved, the remaining HX8000 particles were strained out of the oil bath at 200°C using a 200x200 count wire mesh screen. The solids were then centrifuged (Fisher Scientific Marathon 21K/R centrifuge) at 3000 rpms (1700 g-force) and 25°C for 10 minutes. The oil was decanted off and the remaining particles were boiled (175°C) in kerosene for 10 minutes to selectively dissolve only the mineral oil. This process was repeated twice, and then the remaining particles were washed with hexane to remove the kerosene. The particles were then dried in a convection oven for 30 minutes at 115°C to remove all of the hexane.

3.2.4 Physical Properties

The purity of the reclaimed HX8000 was determined by making density measurements using a pycnometer (Micrometrics Accupyc, Model 1330). The densities of pure PP 6523 and HX8000 were determined and the following rule of mixtures was used to calculate the purity:

$$wt\% HX8000 = 100\% \left[\frac{\rho - \rho_{PP}}{\rho_{HX8000} - \rho_{PP}} \right] \quad (1)$$

where ρ was the density of the reclaimed pieces, ρ_{PP} was the density of the pure PP, and ρ_{HX8000} was the density of the pure HX8000.

A Rheometrics Mechanical Spectrometer (Model 800) was used to determine the viscoelastic properties of the materials. All dynamic rheological tests were run using 25.0 mm diameter plates, with a 1.0 mm gap, and at a 5 % strain. The steady shear viscosity tests were run using the parallel plate tooling, and samples were tested from of a shear rate of 0.001 sec^{-1} to 1.0 sec^{-1} and at a temperature of 290°C . Each sample was sheared steadily at each rate for 10 minutes before increasing the shear rate. A test sample of the pure reclaimed HX8000 was cut from a compression molded plaque, while a test sample of the pure HX8000 was cut from an injection molded plaque.

3.2.5 Injection Molding

Blends of polypropylene with the reclaimed HX8000 and the pure HX8000 were injection molded in an Arburg Allrounder (Model 221-55-250). The screw diameter was 22.0 mm with a fluted screw tip and a check ring non-return valve. The polymer was injected into a film-gated mold with the following dimensions: 80.0 mm long, 75.0 mm wide, and 1.6 mm thick. The processing temperatures used for generating the in situ composites were: Zone 1 = 200°C , Zone 2 = 290°C , Zone 3 = 285°C , and the Nozzle = 270°C . The same processing conditions were used throughout with a screw speed of 200 rpm, a mold temperature of 22°C , a hold pressure of 10 MPa, and an injection pressure of 2-4 MPa. The cooling time in the mold for the plaques was 30 seconds.

The pure and reclaimed HX8000 were dried in a vacuum oven at 120°C and for 18 hours prior to injection molding. The in situ composites produced in this study were

prepared by dry mixing the pure resin, the reclaimed resin, and the polypropylene into four concentrations prior to injection molding:

- 1) 40 wt% pure HX8000 / 60 wt% PP 6523 (Control Sample)
- 2) (30 % reclaimed / 70 % pure) of the 40 wt% HX8000 / 60 wt% PP 6523
- 3) (40 % reclaimed / 60 % pure) of the 40 wt% HX8000 / 60 wt% PP 6523
- 4) (83 % reclaimed / 17 % pure) of the 40 wt% HX8000 / 60 wt% PP 6523.

In situ composites were prepared in an effort to assess the quality of the reclaimed HX8000.

3.2.6 Mechanical Properties

The tensile and flexural properties were measured using an Instron Mechanical Tester (Model 4204). The load cell used for tensile testing was an Instron Static Load Cell with a 5 kN capacity; a 1 kN load cell was used for the flexural testing. ASTM standard, D 638-87b, was followed for the tensile testing and ASTM standard, D 790-86, was followed for the flexural testing. A cross-head speed of 1.27 mm/min and an extensometer (Instron, Model 2630-25) were used for the tensile testing. All of samples were prepared by cutting injection molded plaques, along the machine direction, into 8 strips with the following average dimensions: 7.8 cm long, 8.6 mm wide, and 1.6 mm thick. Note that for all of the tensile and flexural test results, the reported values were an average of at least five samples.

3.3 RESULTS AND DISCUSSION

3.3.1 Development of the Reclamation Process

The first step in the development of this reclamation process was to examine the physical characteristics and properties of the two polymers used to produce the in situ composites. From Table 3.3, it can be seen that there are many important physical differences between these two polymers. First, the basic chemical structure for each of these polymers is very different. The backbone of polypropylene contains only aliphatic linkages, whereas the backbone of HX8000 is believed to contain only non-aliphatic linkages. There is also a 0.4 g/cm^3 difference in densities and about a 100°C difference in their melting points. Noting these differences, various hydrocarbon, aromatic, and chlorinated solvents were examined for their potential to bring about an effective dissolution of the polypropylene.

Much work has been done on the dissolution of polypropylene (22, 23). From these and other studies, a value of $16.8 \text{ (J/cm}^3)^{1/2}$ was obtained for the solubility parameter of polypropylene (23, 24). It was shown that the best solvents for the dissolution of polypropylene came from high boiling, aromatic solvents, whose solubility parameters were close to that of the polypropylene's (20, 23). It is well known that the solubility of a polymer is strongly influenced by the similarity of the solubility parameters (25). Furthermore, the solubility of the polymeric material is enhanced when the size of the polymeric chain is closer to the size of the solvent molecule and when the temperature of the solution is increased (25). Based on this and the information obtained from a previous work on polypropylene dissolution, a high boiling, aromatic solvent needed to be used in order to utilize the selective dissolution technique (20, 23).

Table 3.3. Properties of the Thermotropic Liquid Crystalline Polymer (HX8000) and the Polypropylene Matrix (PP 6523).

Polymer	Basic Chemical Structure	Density (g/cm³)	Melting Point (°C)	Glass Transition Temperature (°C)
DuPont HX8000	Aromatic Co-polyester	1.38 (0.03)	278 (5)	~ 100
Montell PP 6523	Polyolefin	0.90 (0.02)	165 (4)	< 0

* numbers in parenthesis represent the error associated with the measurement.

An examination of aromatic solvents and oils led to the selection of light ($\rho = 0.83\text{-}0.86 \text{ g/cm}^3$) mineral oil as the best, non-toxic and non-volatile solvent to effectively dissolve the polypropylene. Light mineral oil consists of a number of n-paraffins or naphthalenes and has a solubility parameter around $17.2 \text{ (J/cm}^3\text{)}^{1/2}$; which is very close to the solubility parameter of polypropylene (23, 26). This solvent also has some other beneficial characteristics for the solubility and separation process. The boiling point of this solvent is around 220°C and it has an average density of 0.85 g/cm^3 . This high boiling point will lead to better solubility, and it can also be used to selectively melt only the degraded polypropylene. In addition, the density of the mineral oil is nearly equal to that of the degraded polypropylene but lower than the density of the HX8000. Therefore, any polypropylene that does not dissolve will float and the solid HX8000 will sink. This separation, due to dissolution and differences in densities, allowed for the collection of relatively pure HX8000 particles from the bottom of the mineral oil bath.

In order to maximize the ability of the mineral oil to dissolve all or most of the polypropylene, the size or molecular weight of the PP must be reduced to increase solubility. Fortunately, much work has been done on the controlled degradation of PP (27-30). It has been shown that the addition of a small amount of an organic peroxide during extrusion results in a large reduction in the molecular weight of polypropylene (27). The peroxide radical attacks an aliphatic hydrogen by abstracting it, and thus forms a carbon radical. This highly unstable carbon radical leads to chain scission, and the backbone of the chain begins to break down. The level of degradation, or the molecular weight reduction, can be controlled by the amount of peroxide added and by the length of

residence time (27, 28). Therefore, the size of the polymer chains can be controlled in order to maximize the dissolution of the polypropylene into the solvent.

By using the gathered information on reactive extrusion and polypropylene dissolution, a novel process was developed (see Figure 3.1) to effectively reclaim the HX8000 from composites generated from polypropylene and HX8000. First, the composite materials were granulated into a size small enough for extrusion. Next, the granulated composite was mixed with dicumyl peroxide and then fed into the extruder. The extrudate was then allowed to fall into a mineral oil bath. This solution was stirred vigorously for the length of the batch process and then the pieces of HX8000 were screened out. The pieces were centrifuged, and then separated from the liquids. The leftover oily pieces were then stirred and boiled in kerosene to remove the mineral oil. The kerosene/mineral oil solution was decanted off and then the pieces were washed with hexane to dissolve the kerosene. The liquid solution was decanted off and the pieces of HX8000 were dried in a convection oven.

3.3.2 Physical Properties of the Reclaimed HX8000

Density tests run on the reclaimed pieces of HX8000 resulted in an average density of around 1.3630 (0.0003) g/cm³. Based on equation (1), this density represented a material that was 96.80 wt% HX8000 and 3.2 wt% degraded PP. In order to determine the accuracy of this purity measurement, a control sample was prepared by dry mixing and injection molding 40 wt% pure HX8000 with 60 wt% pure PP. The density for this sample was found to be 1.0815 (0.0003) g/cm³, which represented a material that was

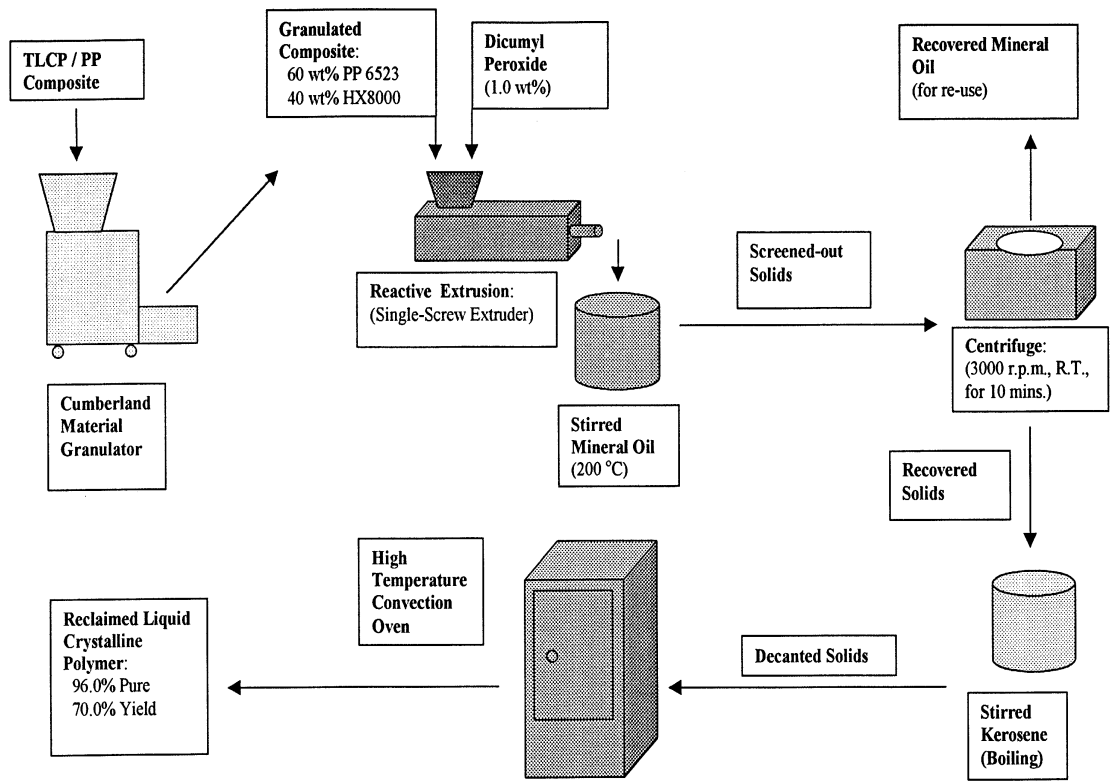


Figure 3.1 Schematic of the Reclamation Process.

37.92 wt% HX8000 and 62.08 wt% PP. Based on these results, it seemed that this form of purity determination was a viable method. The purity of the reclaimed HX8000 was also verified via thermogravimetric analysis by Collier and Baird (31).

3.3.3 Mechanical Properties of the (Reclaimed/Pure) HX8000/PP Plaques

In this work, only in situ composite plaques were generated and tested in order to initially determine the ability of the reclaimed HX8000 to be reused as a blending resin. Future work will deal with using the reclaimed resin in the dual extrusion technique, thereby completing the process of recycling. The reclaimed HX8000 was blended with pure HX8000 and then injection molded along with pure PP 6523 to generate in situ composite plaques for mechanical testing.

The plaques were first tested for their machine direction, tensile properties. From Figure 3.2, it can be seen that as the weight fraction of reclaimed HX8000 was increased, within the 40 wt% HX8000 component of the composite, there was no loss in tensile modulus and in fact there was an increase. The average value for the pure 40 wt% HX8000 / 60 wt% PP 6523 composite (Control) was 3.40 (0.23) GPa, while the average value for the 0.3 weight fraction of reclaimed HX8000 was 4.05 (0.18) GPa, for the 0.4 weight fraction was 3.80 (0.21) GPa, and for the 0.83 weight fraction was 3.62 (0.33) GPa. From Figure 3.3, it can also be seen that here were no losses in tensile strength. The average tensile strength for the control composite was 29.8 (2.0) MPa, while the average tensile strength for the 0.3 weight fraction composite was 33.8 (1.8), for the 0.4 weight fraction was 32.0 (1.5), and for the 0.83 weight fraction was 31.7 (1.8) MPa. From

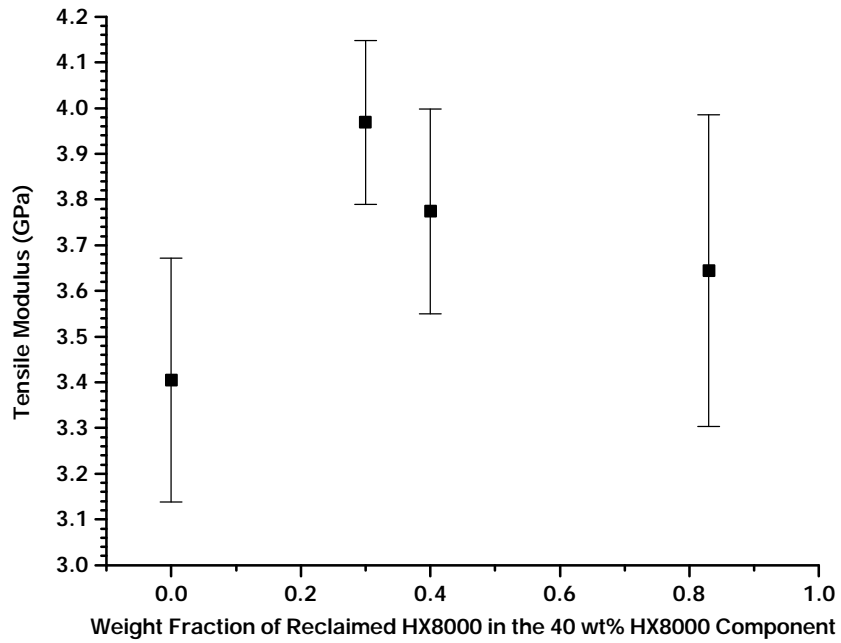


Figure 3.2 A Comparison of the Machine Direction, Tensile Modulus of In situ Composites of 40 wt% Pure HX8000 / 60 wt% PP 6523 (Control) and Three Composites whose 40 wt% HX8000 Component contains Various Fractions of Reclaimed HX8000.

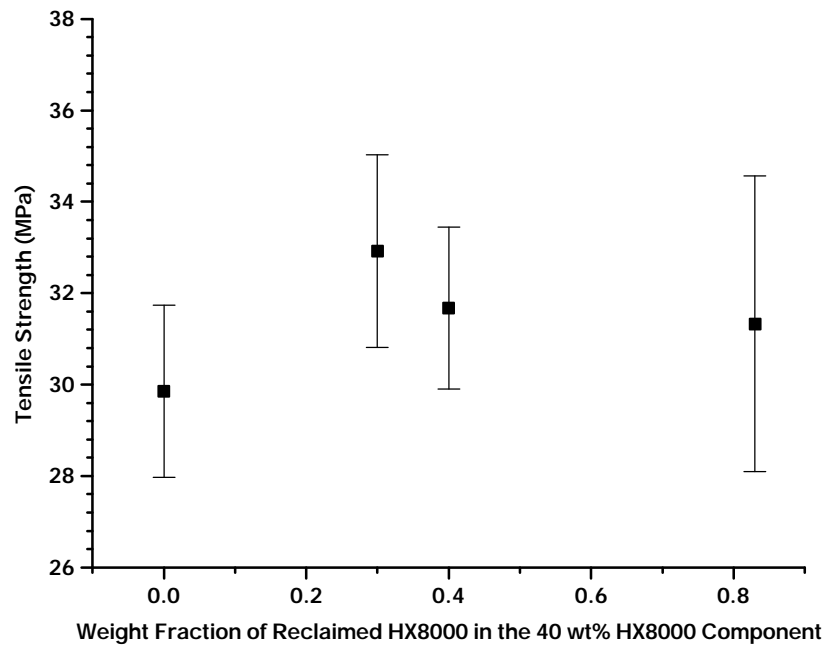


Figure 3.3 A Comparison of the Machine Direction, Tensile Strength of In situ Composites of 40 wt% Pure HX8000 / 60 wt% PP 6523 (Control) and Three Composites whose 40 wt% HX8000 Component contains Various Fractions of Reclaimed HX8000.

Figure 3.2, it can be seen that the composite with the 0.3 weight fraction of reclaimed HX8000 (in the 40 wt% HX8000 component) exhibited a higher tensile modulus than the control composite. Although this can not be readily explained, it can be seen that the addition of the reclaimed HX8000 does not lower the mechanical properties of these HX8000 / PP in situ composites.

Next, flexural testing was run on this set of injection molded composites. From Figure 3.4, it can be seen that as the loading of reclaimed HX8000 was increased up to 83% in the 40 wt% HX8000 component, there were no losses in flexural modulus and in fact there were increases. The average value for the control composite of 40 wt% pure HX8000 / 60 wt% PP 6523 was 3.88 (0.24) GPa, while the average value for the 0.3 weight fraction was 4.24 (0.28) GPa, for the 0.4 weight fraction was 5.08 (0.24) GPa, and for the 0.83 weight fraction was 4.44 (0.12) GPa. From Figure 3.5, it can also be seen that there were no losses in flexural strength. The average flexural strength for the composite of 40 wt% pure HX8000 / 60 wt% PP 6523 was 45.2 (1.6) MPa, while the average value for the 0.3 weight fraction composite was 47.0 (1.8) MPa, for the 0.4 weight fraction was 53.0 (1.4) MPa, and for the 0.83 weight fraction was 51.6 (1.6) MPa. From Figure 3.4 and from Figure 3.5, it can be seen that the composite with the 0.4 weight fraction of reclaimed HX8000 (in the 40 wt% HX8000 component) showed a marked increase in both flexural modulus and strength over the control composite. Although this can not be easily understood, it can be seen that the addition of the reclaimed HX8000 does not lower the mechanical properties of these HX8000 / PP in situ composites and in fact seems to increase them.

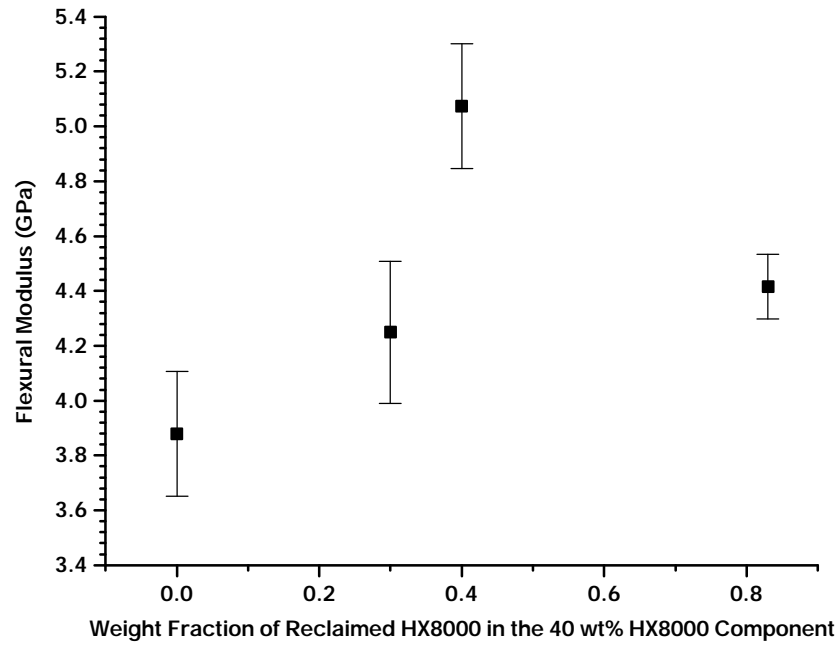


Figure 3.4 A Comparison of the Machine Direction, Flexural Modulus of In situ Composites of 40 wt% Pure HX8000 / 60 wt% PP 6523 (Control) and Three Composites whose 40 wt% HX8000 Component contains Various Fractions of Reclaimed HX8000.

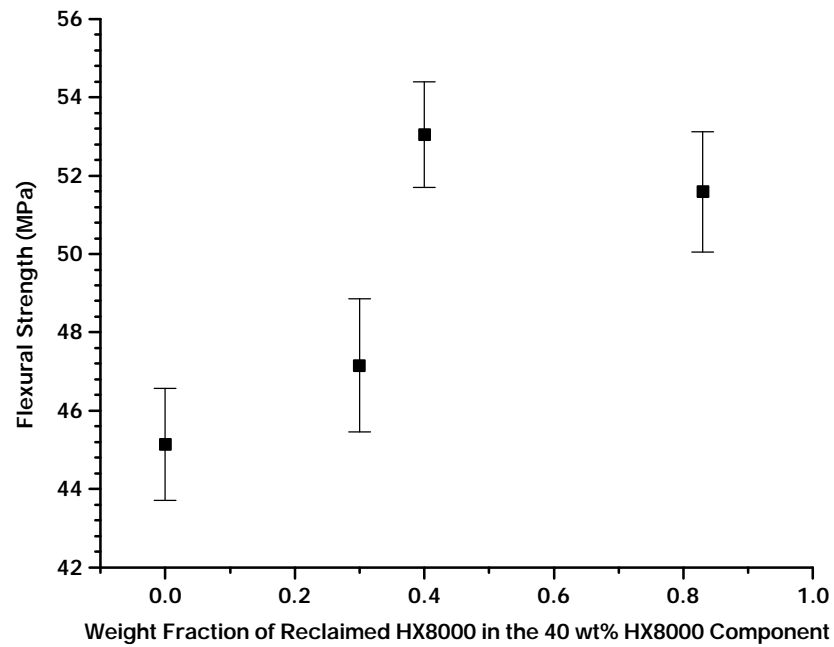


Figure 3.5 A Comparison of the Machine Direction, Flexural Strength of In situ Composites of 40 wt% Pure HX8000 / 60 wt% PP 6523 (Control) and Three Composites whose 40 wt% HX8000 Component contains Various Fractions of Reclaimed HX8000.

3.3.4 Rheological Testing of the Reclaimed HX8000

Due to a problem of the melt flashing out of the sides of the mold, higher loadings of the reclaimed HX8000 were not injection molded and tested. At these higher blends, it appeared that a reduction in viscosity occurred which did not allow for proper filling of the mold. More specifically, an in situ composite consisting of 40 wt% reclaimed HX8000 and 60 wt% PP 6523 was attempted but was not successful due to this viscosity problem.

This apparent reduction in viscosity was investigated by performing a series of dynamic and steady shear rheological tests on the reclaimed and pure HX8000. Dynamic oscillatory tests were carried out using the parallel plate geometry of a RMS-800. Because the reclaimed material could not be injection molded, a sample for the rheological tests was prepared by compression molding. Even though the thermal and deformation histories would be different between this sample and the injection molded plaques, it was important to get a qualitative response of the reclaimed HX8000. From Figure 3.6, it can be seen that the pure HX8000 exhibited the highest complex viscosity. There was almost an order of magnitude drop in the complex viscosity for the reclaimed HX8000 as compared to the pure HX8000. Another major difference between these two materials was in the shape of the response curves. The pure HX8000 showed Newtonian behavior over a frequency range of 0.1 to 1.0 rad/sec, but showed a loss in complex viscosity with increasing angular frequency after a frequency of 1.0 rad/sec. However, the reclaimed HX8000 showed a loss in complex viscosity with increasing angular frequency over the entire frequency range tested, and there was an absence of a Newtonian plateau at lower frequencies.

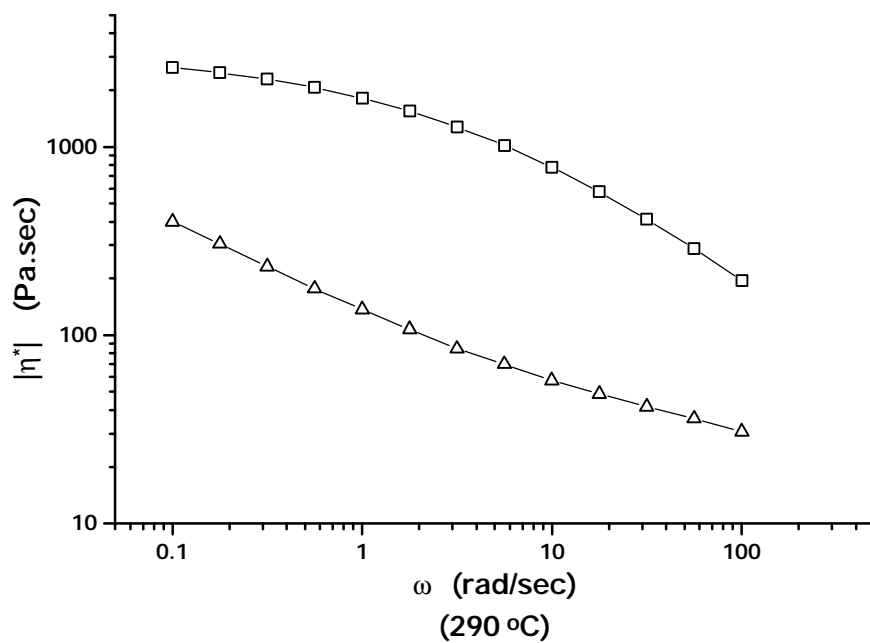


Figure 3.6 Complex Viscosity ($|\eta^*|$) vs. Angular Frequency (ω) Comparison between Pure HX8000 = (—□—) and 97% Pure Reclaimed HX8000 = (—△—).

The reduction in viscosity was also investigated by performing steady shear rate sweeps on the pure and reclaimed samples. From Figure 3.7, it can be seen that the reclaimed HX8000 showed almost a two order of magnitude drop in shear viscosity. As was also seen in the dynamic tests, the pure HX8000 was the most viscous of all the samples tested. However, there was a difference in the response of the reclaimed HX8000 in this test as compared to the dynamic test. The reclaimed HX8000 showed a constant loss in complex viscosity as a function of angular frequency in the dynamic test, but showed the onset of a Newtonian plateau at a shear rate of 0.01 sec^{-1} in the steady shear test. In addition, there was an order of magnitude increase in the difference between the viscosity response of the pure and reclaimed HX8000, which was much larger than the difference seen in the dynamic tests.

Further rheological investigation was performed by running a cooling curve on the pure and reclaimed HX8000. In this test, the material was placed between parallel plates and the change in complex viscosity was monitored as a function of temperature in order to determine the onset of solidification. From Figure 3.8, a difference in solidification temperatures was observed between the pure and reclaimed HX8000. The reclaimed material appeared to solidify around 258°C , while the pure material began to solidify around 248°C . This difference in cooling behavior also seemed to represent a difference in the reclaimed and pure HX8000, as was seen with the frequency and steady shear rate sweeps. This change in the solidification temperature of the reclaimed HX8000 would be significant in that it could affect the processing behavior (such as super-cooling) of the material, which is important in the dual extrusion process (15, 16).

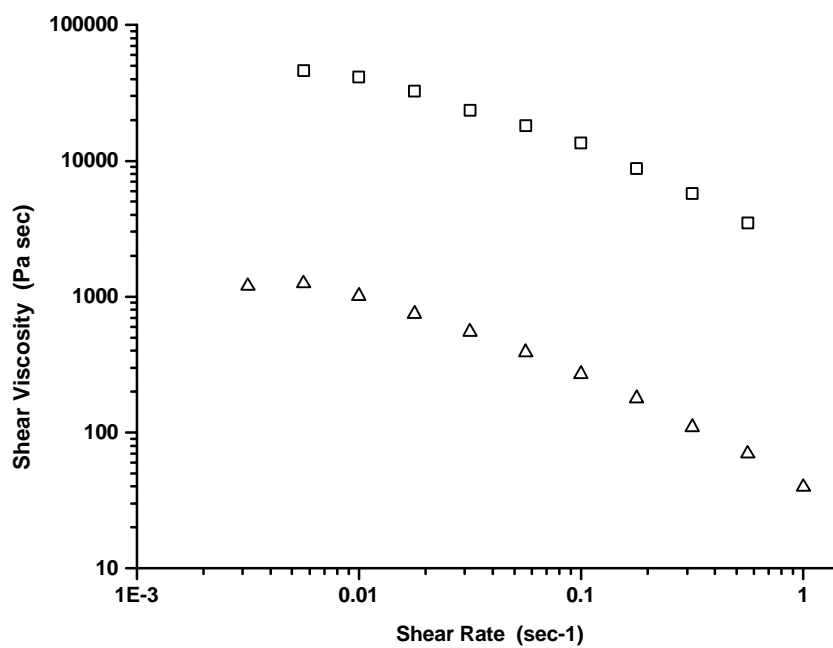


Figure 3.7 Shear Viscosity vs. Shear Rate Comparison between the Pure HX8000 = (—□—) and the 97 wt% Pure, Reclaimed HX8000 = (—△—). Run at 290°C.

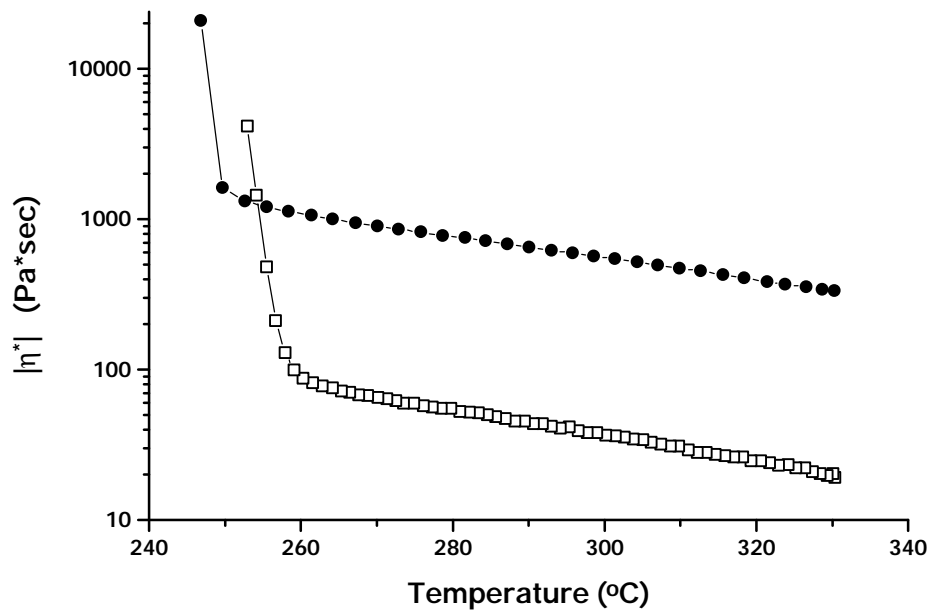


Figure 3.8 Complex Viscosity ($|\eta^*|$) vs. Temperature (Cooling Curve) for Pure HX8000 = (—●—) and Reclaimed HX8000 = (—□—). Run at 2.3 °C/min and 10 rad/sec.

3.3.5 Proposed Explanations for the Differences in Rheological Properties

These differences in complex and shear viscosity, frequency and steady shear rate behavior, and solidification temperature could be explained by two opposing theories. The first theory was that the HX8000 was undergoing a reduction in molecular weight during the reactive extrusion. This subsequent reduction in molecular weight could result in the order of magnitude drop in complex viscosity, and it would explain the solidification behavior observed when the melt was cooling. Degradation of the HX8000, however, could not explain the behavior of the complex viscosity as a function of frequency. Though the complex viscosity could drop an order of magnitude, the degraded HX8000 would still have the same frequency behavior and would still reach a Newtonian plateau at the lower rates as with the pure HX8000. Also, the degradation of the HX8000 would be expected to result in a reduction of mechanical properties, which contradicts the results from the mechanical property testing.

On the other hand, this same order of magnitude drop in viscosity could also be explained by the small volume of degraded polypropylene, 5 vol%, still left in the reclaimed HX8000. A method for evaluating the viscosity of heterogeneous blends is to use the following rule of mixtures (parallel arrangement):

$$\frac{1}{\eta_{blend}} = \frac{f_{d-PP}}{\eta_{d-PP}} + \frac{f_{HX8000}}{\eta_{HX8000}} \quad (2)$$

where η is the viscosity, d-PP is the degraded polypropylene, and ϕ is the volume fraction. From this mathematical relationship, it was easy to deduce that a small volume of degraded polypropylene could drop the overall viscosity of the blend an order of magnitude. The complex viscosity of degraded polypropylene, at 290 °C and 1.0 rad/sec,

was around 12.0 (0.3) Pa.sec. If there was around 5.0 vol% of this degraded PP in the pure HX8000, then this rule would predict a complex viscosity for the blend to be around 201.7 (5.0) Pa.sec. From Figure 3.6, the measured viscosity for the reclaimed HX8000 was around 200 Pa.sec. This was in very good agreement with the predicted value. Therefore, the order of magnitude drop in complex viscosity would be accounted for by the presence of a small amount of encapsulated polypropylene. The presence of a small amount of encapsulated spheres of degraded polypropylene was established via scanning electron microscopy by Collier and Baird (31).

However, this mixing rule would not necessarily account for the higher solidification temperature observed by the reclaimed HX8000. It has been shown that the contamination of a pure substance would result in a depression of the solidification temperature for the material (32). Therefore, any contamination by the degraded polypropylene would result in lowering the solidification temperature. As can be seen in Figure 3.8, this was not the case and instead the solidification temperature was raised. A possible explanation for the higher solidification temperature was that the degraded polypropylene, which may contain some cumene groups from the reactive extrusion, would be acting as a nucleating agent for the aromatic liquid crystalline polymer. Though these differences in rheological properties could not be readily explained, it was important to remember that the reclaimed material could be successfully reused as a blending resin.

3.3.6 Projected Material Cost Analysis

In order to determine a basic value for the cost of reclaiming the thermotropic liquid crystalline polymer, a material cost was calculated on the projected ability to process in

bulk. First, the reactive extrusion part of the reclamation process was modeled after the large scale reactive extrusion of polypropylene found in the literature (30, 33). The assumption was made that the reactive extrusion of the composite material was inherently the same as the reactive extrusion of pure polypropylene. This assumption was based on the knowledge that only the aliphatic linkages of the PP, which are not present in the HX8000, were susceptible to peroxide attack. Some work done by Dorn et al. (30) showed that the reactive extrusion of polypropylene could be run at throughputs of up to 25 tons/hr in a large capacity, co-rotating twin screw extruder. At this rate, the peroxide was fed at 30 lb/hr (0.1 wt%) and the starting material was fed at 50000 lb/hr of PP. For the reclamation process, this correlated to a feed rate of 20000 lb/hr of the HX8000 (40 wt%) and 30000 lb/hr for the polypropylene (60 wt%) in the form of in situ composite pieces. Without being able to purchase in bulk, the costs for the supplies that are used in the reclamation process were as follows: 1) Dicumyl Peroxide was \$36.77 per pound, 2) Oil was \$0.58 per pound, 3) Kerosene was \$0.55 per pound, and 4) Hexanes were \$1.57 per pound. These prices were obtained from Aldrich Chemical Company, Inc. and VWR Scientific Products and represented the lowest prices found within the catalogs.

The following assumptions, which need to be validated in a future work, were made in order to arrive at the final cost for the reclaimed HX8000:

- 1) a 70% yield of reclaimed HX8000 or 1,400 lb/hr
- 2) a 1:1.2 ratio of degraded polypropylene to oil for the dissolution of the PP or 36,000 lb/hr of oil
- 3) a 1:1 ratio of the volume of kerosene to oil needed to dissolve the leftover oil after centrifugation or 7,971 lb/hr of kerosene

- 4) a 1:1 ratio of the volume of hexanes to kerosene needed to dissolve the leftover kerosene after centrifugation or 6,745 lb/hr.

Based on these assumptions and the prices obtained, the total material supply cost was \$36,995 per hour. Therefore, the total material cost of producing the reclaimed HX8000 was \$2.64 per pound. Obviously, this value did not include capital costs nor did it include the cost of manpower and energy. However, it also did not include the ability to purchase supplies in bulk and the ability to recycle the oil, kerosene, or hexanes. What this cost analysis did demonstrate was that the reclamation process seems to be economically feasible and, therefore, TLCP / PP composites could represent an advantageous, engineering material in the composites industry.

3.4 CONCLUSIONS

In this study, a dual extrusion process was used to generate composite strands of HX8000 (a thermotropic liquid crystalline polymer or TLCP) and polypropylene (PP). Because these composites were extruded separately in order to realize the highest mechanical properties, a recycling process was developed to facilitate this dual extrusion form of processing. Furthermore, the development of the recycling process was concerned with using existing technologies and with eliminating expensive, toxic, and volatile organic solvents (such as xylene) as much as possible. The novel recycling process developed in this work, which included the selective degradation and dissolution of the polypropylene, proved to be an effective method for the reclamation of a thermotropic liquid crystalline polymer. Small amounts of an organic peroxide, along with reactive extrusion, can be used to selectively degrade the polypropylene of HX8000 / PP composites. Subsequent

mineral oil dissolution, at a temperature above the melting point of polypropylene and below the melting point of the HX8000, showed this process to be a novel method for the separation of these two materials.

This process resulted in a product that was 97 wt% pure HX8000, and it separated over 70 % of the HX8000 from the composites. The reclaimed material was blended with pure HX8000 and pure PP 6523 and then reprocessed to form an in situ composite without any losses in mechanical properties. Although the reclaimed HX8000 exhibited rheological behavior that was different than the pure HX8000, it was probable that this behavior was due to the presence of trace quantities of polypropylene rather than the degradation of the thermotropic liquid crystalline polymer.

It can also be concluded that this process could be used on other wholly thermoplastic composites if the following criteria are met:

- 1) the thermotropic liquid crystalline polymer should not contain any aliphatic linkages (Ex: Hoechst-Celanese Vectra Series)
- 2) the TLCP should not be susceptible to peroxide attack
- 3) the matrix material should contain aliphatic linkages
- 4) the matrix material should have a different density than the TLCP
- 5) only the matrix material should be soluble in light mineral oil.

If these five criteria are met, then it is reasonable to believe that this process would work for other composite systems. Furthermore, it was seen that the projected material cost for the reclaimed HX8000 was much lower than the cost of the pure HX8000. In conclusion, this novel process represents a cost effective and beneficial development in the field of polymer and composites recycling.

3.5 ACKNOWLEDGEMENTS

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