

4.0 Reprocessing of a Recycled Thermotropic Liquid

Crystalline Polymer

This chapter is focused on the second and fourth objectives of this thesis. First, the purity of a thermotropic liquid crystalline polymer (TLCP) reclaimed from polypropylene / TLCP composites was determined. Second, the processability and mechanical properties of the TLCP were examined by injection molding the reclaimed TLCP with neat TLCP pellets. This chapter is organized as a manuscript and will be submitted to the *Journal of Applied Polymer Science*.

Reprocessing of a Recycled Thermotropic Liquid Crystalline Polymer

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SYNOPSIS

This work is concerned with determining the purity of a reclaimed thermotropic liquid crystalline polymer (DuPont HX8000), which was recycled from 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 thermoplastics 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. In other work, a process was developed to recycle the TLCP from these TLCP/PP composites. In this work, 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%. Because of a need to better understand how this reclamation process affected the HX8000, work was

performed in order to determine the processability of the reclaimed HX8000. In order to determine the ability to reuse the reclaimed material, injection molded plaques were generated and their mechanical properties were determined. When the neat HX8000 was partially replaced with reclaimed HX8000, the injection molded plaques showed no discernible difference in mechanical properties. Furthermore, the effects of the reclamation process on the recovered HX8000 were investigated by using pycnometry (density), thermogravimetric analysis (TGA), parallel plate rheometry, scanning electron microscopy (SEM), and differential scanning calorimetry (DSC).

4.1 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 work¹⁻¹⁰ has been done on the addition of thermotropic liquid crystalline polymers to enhance the overall mechanical properties of many thermoplastics. The composition and commercial names of a few of these thermotropic liquid crystalline polymers can be seen in Table 4.1. These studies showed four main problems 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^{4, 11} 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. In other cases^{11, 13}, the extrusion system was fit with a static mixer to further disperse the TLCP throughout the thermoplastic matrix prior

Table 4.1 The Composition and Commercial Names for Some TLCPs¹².

Article Name	Commercial Name	Supplier	Composition
PET / 60% HBA	--	Unica	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 / IA / HQ / BP
--	Granular	Granmont	TA / PhHQ / StHQ
HX1000	--	DuPont	Based on HQ and TA*
HX4000	--	DuPont	Based on HQ and TA*

PET, polyethylene 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.

* Other molar constituents are proprietary.

to injection molding. 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 overlapping processing temperatures.

However, there is one blending method that is different from the typical processing methods used to make TLCP / TP composites. This method alleviates the processing condition problem and it indirectly reduces the problem of anisotropy. This method is the dual extrusion technique patented by Baird and Sukhadia¹³. 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 samples¹⁵.

There are numerous advantages to this system: 1) because the two composite components are plasticated separately, a TLCP and a thermoplastic, whose processing temperature ranges do not ordinarily overlap, may still be processed into a composite, 2) composite strands containing 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 matrix¹⁴. The resulting compression molded parts have higher mechanical properties and a lower amount of anisotropy than injection molded in situ composites¹⁵. 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 previous work, a novel process¹⁶ was developed for the reclamation of a thermotropic liquid crystalline polymer (DuPont HX8000) from a polypropylene (Montell 6523) matrix. This process combined elements of reactive extrusion¹⁷ and selective dissolution^{18, 19} to dissolve the polypropylene (PP) matrix away from the HX8000. Reactive extrusion was used to lower the molecular weight of the PP and to increase phase separation between the HX8000 and the PP, because the PP component would not completely dissolve into the mineral oil due to molecular weight and phase constraint problems. From this work, it was determined that greater than 70 wt% of the HX8000 could be reclaimed from the PP matrix at a purity of greater than 96 wt%. Furthermore, it was seen that the reclaimed HX8000 demonstrated a loss in complex viscosity as a

function of angular frequency as compared to the pure HX8000 resin. A similar decline in shear viscosity, as function of shear rate, was also seen in the steady shear tests. However, when the neat HX8000 was partially replaced with reclaimed HX8000, injection molded in situ TLCP/PP composites showed no discernible difference in mechanical properties.

In this work, the purity of the reclaimed thermotropic liquid crystalline polymer (DuPont HX8000) is investigated in order to determine the effect this separation process had on the recovered material. The purity of the reclaimed HX8000 was determined by using thermogravimetric analysis (TGA) and pycnometry (density). The melt viscosity of the reclaimed HX8000 and of an injection molded blend of the reclaimed material with the pure HX8000 were examined using parallel-plate rheometry. Scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) was utilized to determine the presence of degraded PP within the reclaimed HX8000 and within the injection molded blends. Tensile and flexural testing of injection molded specimens was performed to determine any losses in mechanical properties due to the reclamation process.

4.2 EXPERIMENTAL

4.2.1 Materials

The thermotropic liquid crystalline polymer (DuPont HX8000) used in this study is a semi-crystalline TLCP which has two melting endotherms (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 derivatives²⁰. To process this TLCP, a melt temperature of at least 290°C is required.

The reclaimed HX8000, obtained using the novel reclamation process¹⁷, was recovered from composite which consisted of 40 wt% HX8000 and 60 wt% Montell PP 6523.

4.2.2 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 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. Thermogravimetric analysis (TGA) of the materials was also used to calculate the purity of the reclaimed HX8000. A Seiko SSC/5200 was used to calculate the weight percent of material that thermally degraded when a test sample was subjected to a constant temperature of 300°C for 25 minutes. It was assumed that any material that thermally degraded within the reclaimed HX8000 was residual polypropylene.

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 a shear rate of 1.0 sec⁻¹ and at a temperature of 290°C. Each sample was sheared steadily at each rate for 3 minutes before increasing the shear rate. A test sample

of the reclaimed HX8000 was cut from a compression molded plaque, while test samples of the pure HX8000 and of the reclaimed blends were cut from injection molded plaques.

4.2.3 Injection Molding

Blends of pure HX8000 and reclaimed HX8000 were injection molded in an Arburg Allrounder (Model 221-55-250). The screw diameter was 22.0 mm, with a fluted tip, and contained 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 plaques were: Zone 1 = 270°C, Zone 2 = 310°C, Zone 3 = 300°C, and the Nozzle = 290°C. The same processing conditions were used throughout with a screw speed of 200 rpm, a mold temperature of approximately 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 resins were dried in a vacuum oven at 120°C and for 18 hours prior to injection molding. The injection molded blends produced in this study were prepared by dry mixing the pure and reclaimed resin in two concentrations prior to injection molding:

- 1) 20 wt% reclaimed / 80 wt% pure HX8000
- 2) 40 wt% reclaimed / 60 wt% pure HX8000.

4.2.4 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.

4.2.5 Scanning Electron Microscopy

The morphology of the reclaimed HX8000 and the injection molded blends was examined using a Stereoscan S200 scanning electron microscope with an acceleration voltage of 15 kV. To prepare the samples, they were immersed in liquid nitrogen for at least two minutes, then fractured. They were subsequently attached to mounting stubs and coated with a layer of gold using an SPI sputter coater to enhance conductivity.

4.2.6 Differential Scanning Calorimetry Testing

A Seiko DSC 220C was used for the differential scanning calorimetry testing, with a constant purge of argon bathing the sample. The instrument was calibrated using indium and zinc standards. Samples were prepared by cutting thin pieces of each material from

compression molded plaques. The test samples were ranged in weight from 7-8 mg, as determined using a Mettler ME30 microbalance. This balance has a range of 0 to 30 mg, with an error of ± 0.030 mg. The pure and reclaimed HX8000 samples were heated from 40°C to 300°C, held at 300°C for 10 minutes, and then cooled from 300°C to 40°C. The PP 6523 test sample was heated at 10°C/min from 40°C to 200°C, held at 200°C for 10 minutes, and then cooled at 10°C/min from 200°C to 40°C. All DSC runs are normalized to 1.0 mg.

4.3 RESULTS AND DISCUSSION

4.3.1 The Reclamation Process

Before evaluating the reclaimed HX8000, the reclamation process needs to be explained in order to get a better understanding of the thermal, mechanical, and chemical history of the reclaimed HX8000. In previous work ¹⁷, the PP/TLCP composites were granulated into pieces small enough for extrusion. Next, the granulated composite was mixed with dicumyl peroxide and fed into the extruder. The melt was then extruded into a heated mineral oil bath. This solution was stirred vigorously for the length of the batch process, approximately 3 hours, after which the pieces of HX8000 were screened out. The recovered HX8000 was 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 HX8000 was washed with hexane to dissolve the kerosene. The liquid solution was decanted off and the pieces of HX8000 were dried in a convection oven.

4.3.2 Physical Properties of the Reclaimed HX8000

Having evaluated the reclamation process and having obtained material from this process, the purity of the recovered HX8000 was measured. Density tests run on the reclaimed pieces of HX8000 resulted in an average density of 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 37.92 wt% HX8000 and 62.08 wt% PP. Furthermore, thermogravimetric analysis (TGA) of these two samples resulted in similar values for the compositions. From Figure 4.1, it can be seen that there was a 3.0 wt% loss of material from the reclaimed HX8000 sample. This can be attributed to the thermal degradation of leftover polypropylene at this temperature. There was a 55 wt% loss of material from the control sample of 40 wt% HX8000 / 60 wt% PP 6523, which correlates with the density measurements of this blend. Based on these results, it seemed that these forms of purity determination were accurate methods.

4.3.3 Mechanical Properties of the Reclaimed and Pure HX8000 Plaques

In this work, only injection molded plaques of the reclaimed and pure HX8000 were investigated in order to determine the ability to reuse the recovered HX8000. The ability to use the reclaimed HX8000 as a blending resin with pure HX8000 to generate further in situ composites was determined by Collier and Baird¹⁷. The reclaimed HX8000 was

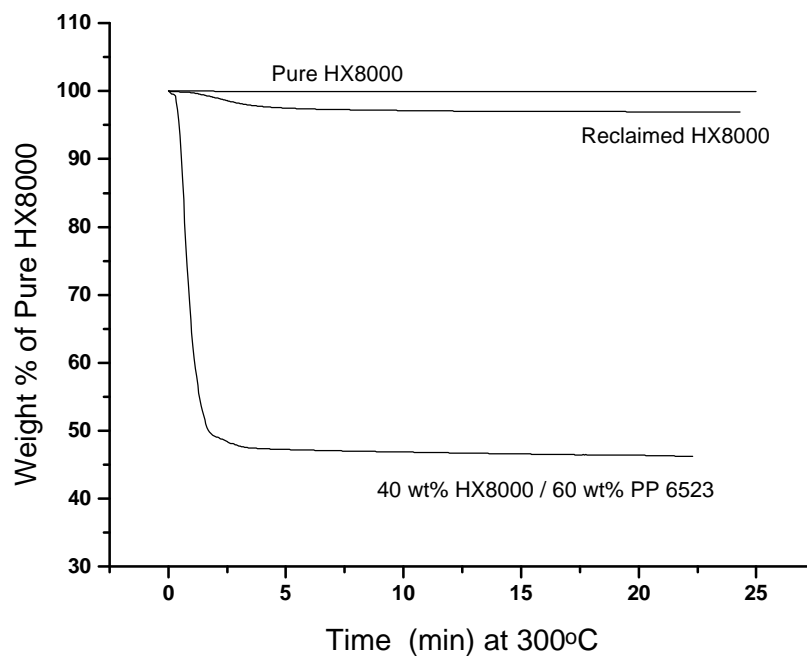


Figure 4.1 Thermogravimetric Analysis (TGA) of the Pure HX8000 = (—), Reclaimed HX8000 = (---), and of the Control Sample of 40 wt% HX8000 / 60 wt% PP 6523 = (—), which were held at 300°C for ~ 25 minutes.

blended with pure HX8000 and then injection molded to form plaques for mechanical testing.

The injection molded plaques were first tested for their tensile properties. From Figure 4.2, it can be seen that as the fraction of reclaimed HX8000 was increased, there was no loss, within error, in tensile modulus as compared to the pure HX8000. The average value for the pure HX8000 was 11.0 (1.1) GPa, while the average value for the 40 wt% reclaim / 60 wt% pure HX8000 was 10.5 (1.3) GPa. As for the tensile strength, even at a loading of 40 wt% reclaimed HX8000 there was no loss in strength compared to the pure HX8000.

Next, flexural testing was run on this set of injection molded plaques. From Figure 4.3, it can be seen that as the loading of reclaimed HX8000 was increased up to 40 wt% there was no loss in flexural modulus. The average value for the pure HX8000 was 13.6 (1.1) GPa, while the average value for the 40 wt% reclaimed HX8000 blend was 15.4 (0.7) GPa. The same result was true for the flexural strength. As the amount of reclaimed HX8000 was increased in the blend, there was no loss in flexural strength. The average value for the flexural strength of the pure HX8000 was 120.9 (14.8) MPa, while the average value for the 20 wt% reclaimed blend was 142.7 (3.7) MPa and the average value for the 40 wt% blend was 133.3 (3.5) MPa. Within error, the blend containing 20 wt% reclaimed HX8000 saw a distinct increase in flexural strength. Though the reason for this was not well understood, the most important point was that there were no losses (within error) in the mechanical properties with the reclaimed HX8000 material.

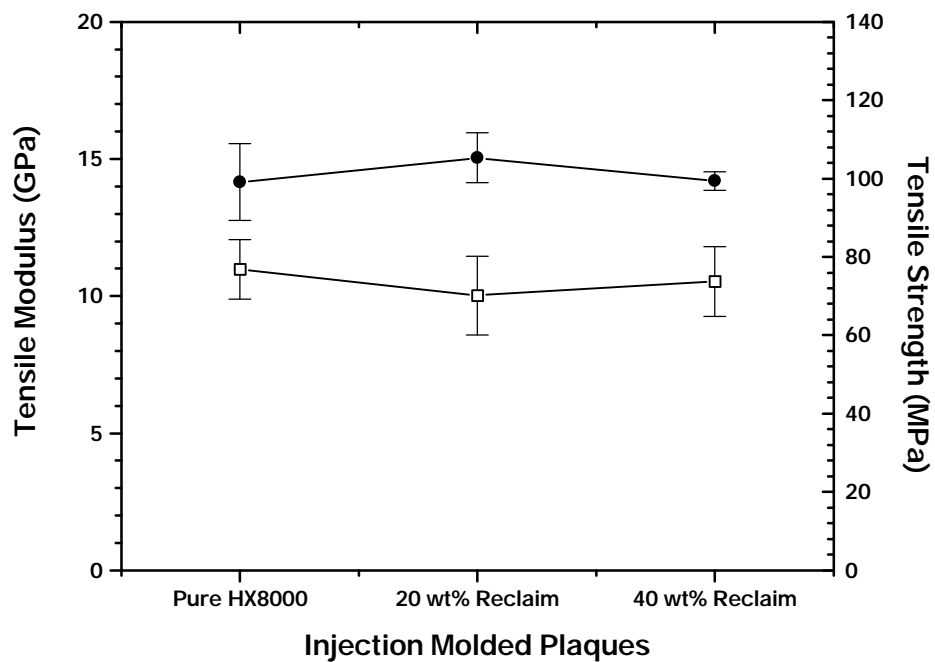


Figure 4.2 A Comparison of the Machine Direction Tensile Properties of Injection Molded Plaques of Pure HX8000 and Two Blends of Reclaimed HX8000 with Pure HX8000. (—●—) = Tensile Strength and (—□—) = Tensile Modulus.

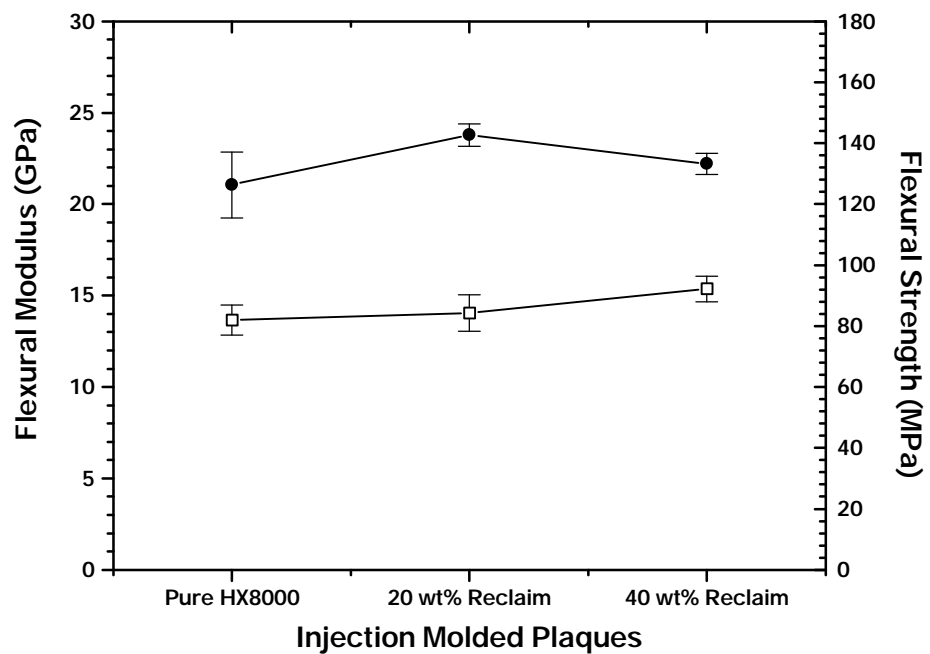


Figure 4.3 A Comparison of the Machine Direction Flexural Properties of Pure HX8000 and Two blends of Reclaimed HX8000 with Pure HX8000. (—●—) = Flexural Strength and (—□—) = Flexural Modulus.

4.3.4 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, a plaque of greater than 40 wt% reclaimed HX8000 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 pure HX8000, on the pure/reclaimed HX8000 blends, and on the reclaimed HX8000. 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 quantitative response of the reclaimed HX8000. From Figure 4.4, it can be seen that the pure HX8000 exhibited the highest complex viscosity. There was almost an order of magnitude drop in 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 demonstrated 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. Furthermore, the material response for the 40 wt% reclaimed / 60 wt% pure HX8000 blend seemed to represent a mathematical average of the other two response curves.

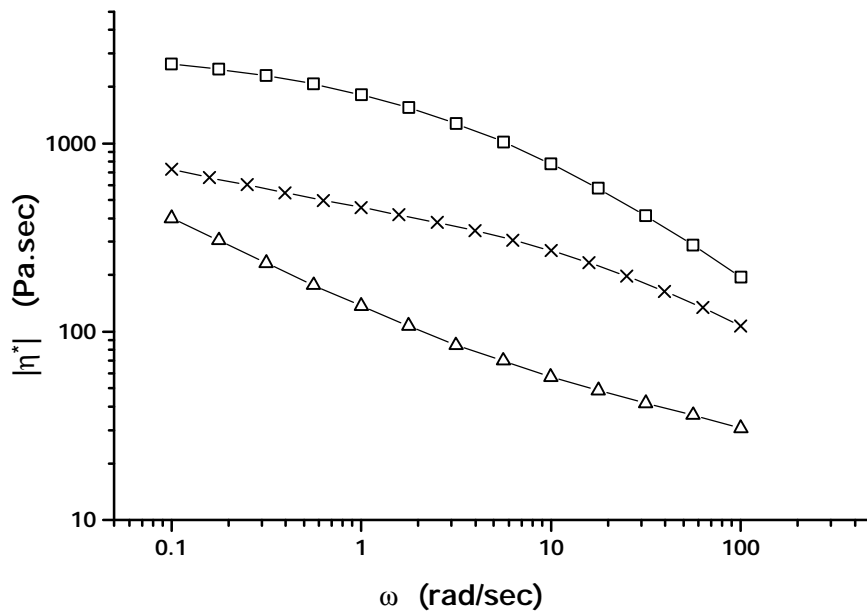


Figure 4.4 Complex Viscosity ($|\eta^*|$) vs. Angular Frequency (ω) Comparison among the Pure HX8000 = (—□—), the 40 wt% Reclaimed / 60 wt% Pure HX8000 = (—x—), and the 97 wt% Pure, Reclaimed HX8000 = (—△—). Run at 290°C.

The reduction in viscosity was also investigated by performing steady shear rate sweeps on the blended, pure, and reclaimed samples. From Figure 4.5, 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 were some differences in the response of the reclaimed HX8000 and the blended sample as compared to the dynamic tests. From Figure 4.5, it can be seen that the shear viscosity of the 40 wt% blend was much closer to the shear viscosity of the pure HX8000. Furthermore, the shear viscosity of the 40 wt% blend continued to rise at a shear rate of 0.001 sec^{-1} and failed to reach a Newtonian plateau as seen with the pure HX8000. This was different than what was seen in the dynamic oscillatory tests, which showed the blended material had a complex viscosity that was an average of the pure and reclaimed HX8000. Another difference between the dynamic and shear viscosity tests was that 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.

4.3.5 Proposed Explanations for the Differences in Rheological Properties

These differences in melt viscosity behavior could be explained by two opposing theories. The first theory was that the HX8000 underwent a reduction in molecular weight during the reactive extrusion step. This subsequent reduction in molecular weight could result in the order of magnitude drop in complex viscosity. Degradation of the HX8000, however, could not explain the unique behavior of the complex viscosity as a function of frequency.

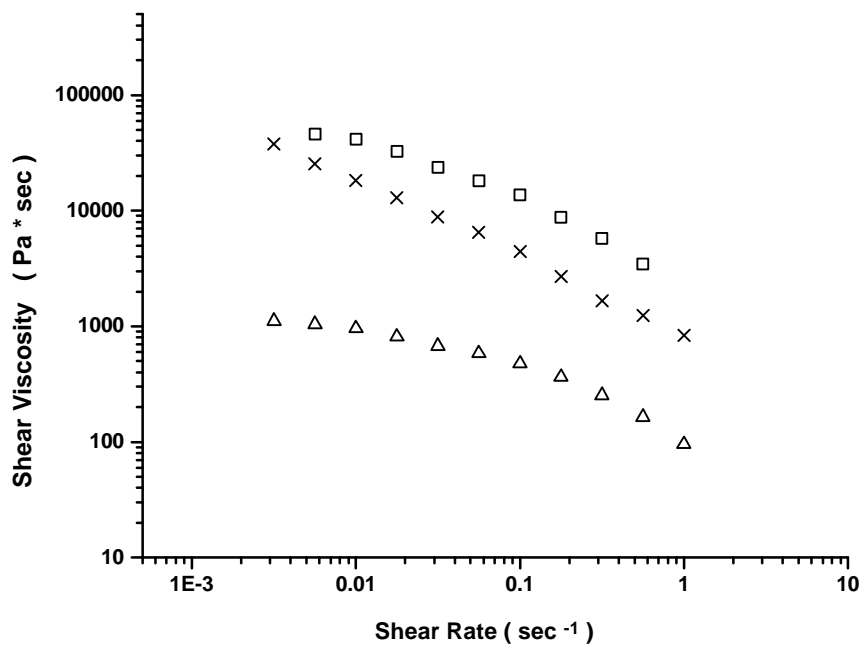


Figure 4.5 Shear Viscosity vs. Shear Rate Comparison among the Pure HX8000 = (—□—), the 40 wt% Reclaimed HX8000 / 60 wt% Pure HX8000 = (—x—), and the 97 wt% Pure, Reclaimed HX8000 = (—Δ—). Run at 290°C.

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 seen in 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·sec²¹. 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 4.4, 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.

4.3.6 Scanning Electron Microscopy (SEM) of the Reclaimed HX8000 Samples

The presence of encapsulated droplets of degraded polypropylene was investigated by looking at cross-sections of the HX8000 plaques under scanning electron microscopy (SEM). In Figure 4.6, it can be seen that there were small inclusions of degraded polypropylene within the reclaimed HX8000. From the microscopy, it appeared that the size of the polypropylene drops were on the order of 200 μm in size. The presence of these droplets of degraded polypropylene would affect the rheological behavior of the reclaimed HX8000. However, it could also be concluded that the same droplets would lower the mechanical properties as well.

Because no losses in mechanical properties were seen, SEM micrographs were taken of a 20 wt% reclaimed / 80 wt% pure HX8000 injection molded plaque in order to investigate the morphology. From Figure 4.7, it can be seen that the droplets of degraded polypropylene were also found within the blended plaques. From Figure 4.8, it was seen that these degraded PP 6523 droplets were only on the order of 1-10 microns in size and were well encapsulated by the HX8000 matrix. Most likely, the size of these inclusions were reduced due to the dilution with the pure HX8000 and due to droplet deformation and break-up during processing. Therefore, it can be deduced that such small inclusions of degraded PP would not have affected the mechanical properties of the injection molded plaques.

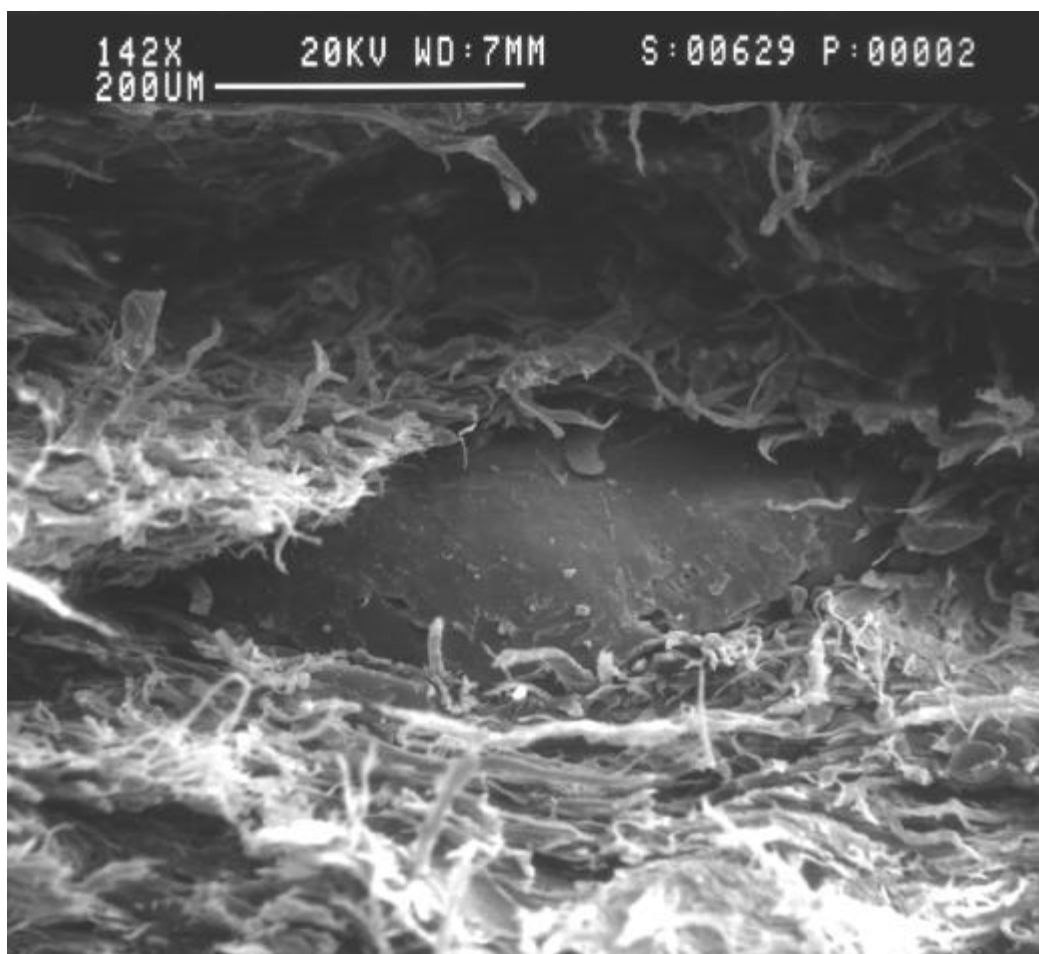


Figure 4.6 Scanning Electron Micrograph of the 96 wt% Pure HX8000 Compression Molded Plaque (cross-section) showing an Inclusion of Degraded PP 6523.

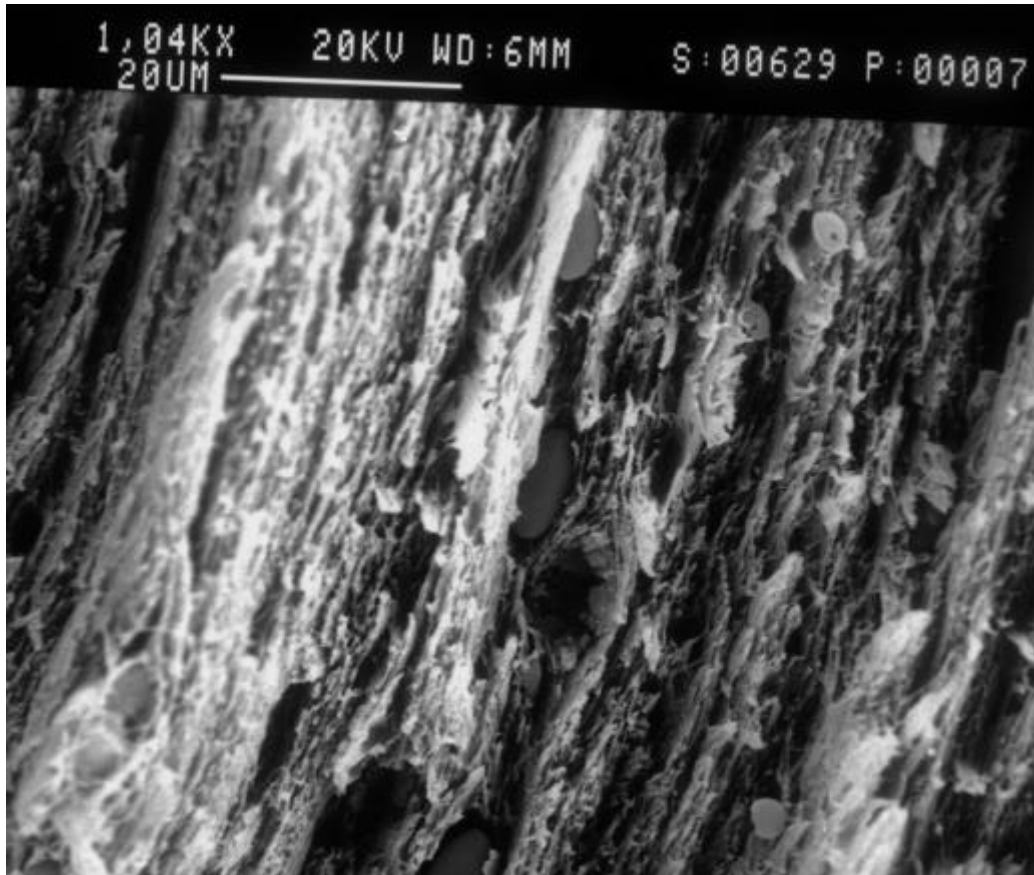


Figure 4.8 Scanning Electron Micrograph of the Same 20 wt% Reclaimed HX8000 / 80 wt% Pure HX8000 Plaque showing a Closer View of the Scale of the Degraded PP 6523 Inclusions.

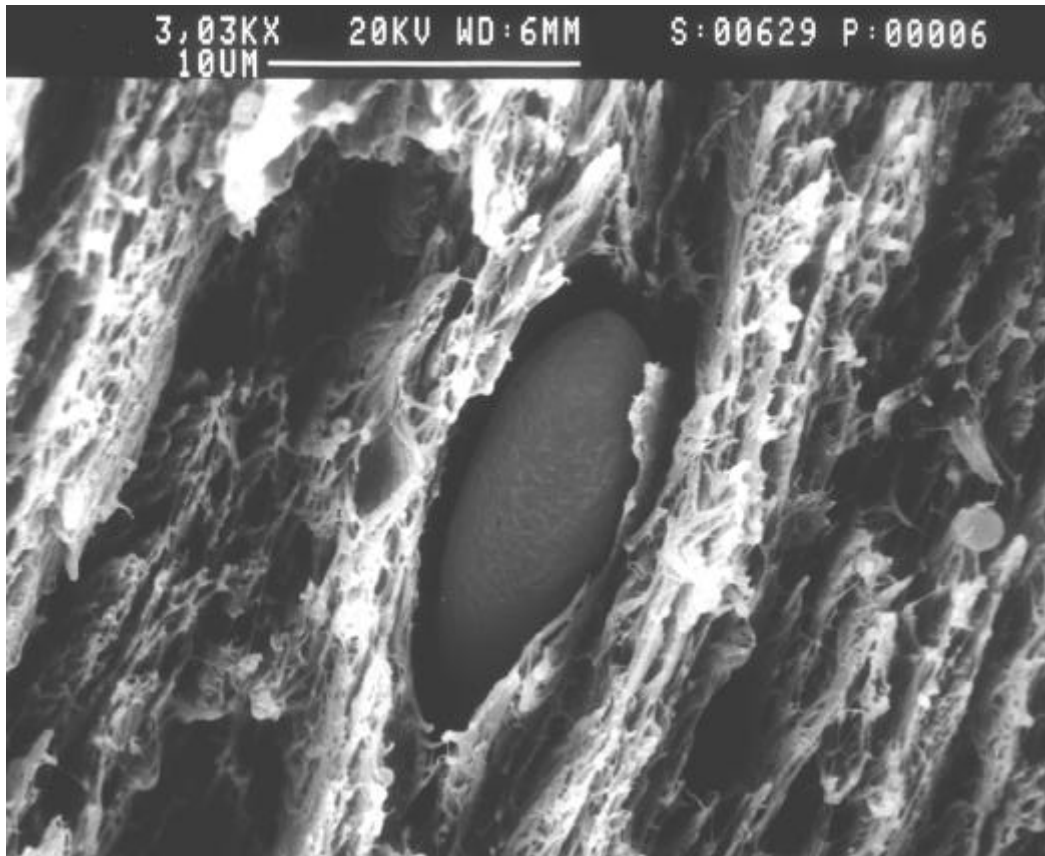


Figure 4.7 Scanning Electron Micrograph of an Injection Molded Plaque (cross-section / transverse) of the 20 wt% Reclaimed HX8000 / 80 wt% Pure HX8000 showing the Small Inclusions of Degraded PP 6523.

4.3.7 Differential Scanning Calorimetry (DSC) Testing

To compliment the morphological results, and in order to get a further understanding of the quality of the reclaimed HX8000, differential scanning calorimetry tests were run. Heating and cooling scans were run on the pure HX8000 (control), the reclaimed HX8000, and on the pure PP 6523 (control) in order to make some comparative studies. From Figure 4.9, it can be seen that there was a difference in the heating scan for the reclaimed HX8000 as compared to the pure HX8000. A pronounced, melting endotherm was evident around 160°C in the reclaimed HX8000, which did not appear in the pure HX8000 scan. Upon looking at the heating scan of pure PP 6523, it was evident that this melting endotherm in the reclaimed HX8000 was the response from the leftover degraded PP. However, the rest of the heating scan for the reclaimed HX8000 was empirically the same as the pure HX8000. Subsequently, cooling scans were taken of the pure and reclaimed HX8000, as well as the pure PP 6523. From Figure 4.10, it can be seen that there was the same pronounced peak in the reclaimed HX8000 that did not appear in the pure HX8000. Upon looking at the cooling behavior of the pure PP 6523, it can be deduced that the extra exotherm in the reclaimed HX8000 was from the droplets of degraded PP leftover in the sample. From Figure 4.10, it can also be seen that the reclaimed HX8000 demonstrated the same crystallization exotherm around 240°C as the pure HX8000. However, from these scans it appeared that the response of the reclaimed HX8000 was not as large as the pure HX8000's response. Most likely, this was due to the presence of the degraded PP which probably limited the ability of the reclaimed HX8000 to arrange for crystallization.

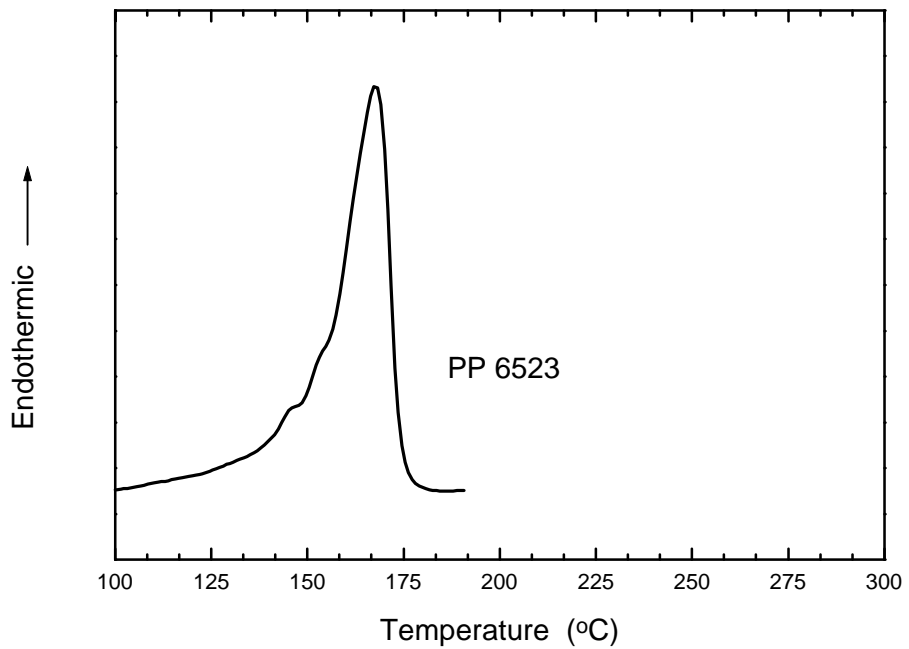
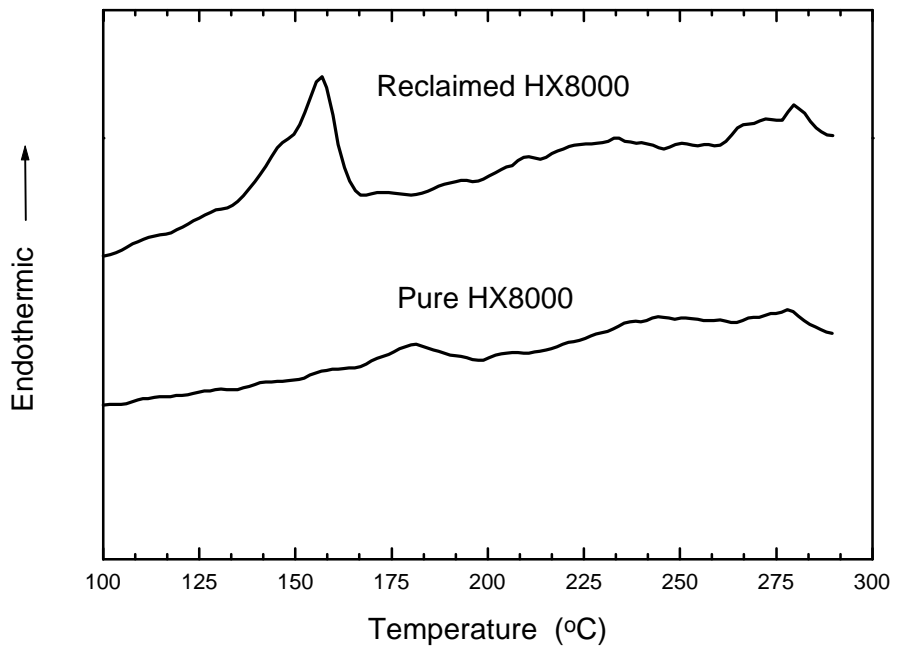


Figure 4.9 DSC Heating Scans of Pure HX8000, Reclaimed HX8000, and Pure PP 6523, using a Heating Rate of 10.0°C/min and Normalized to 1.0 mg.

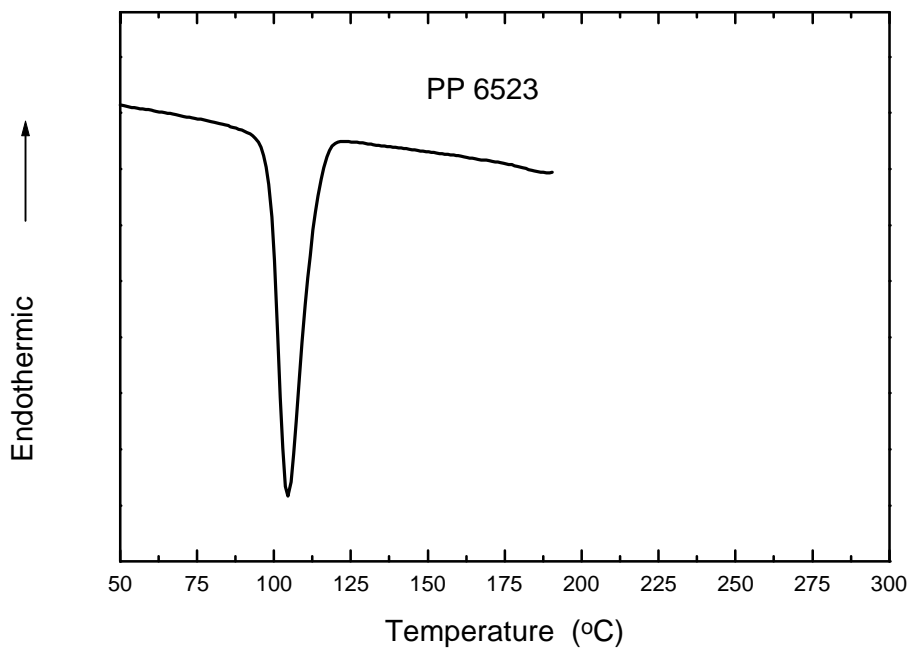
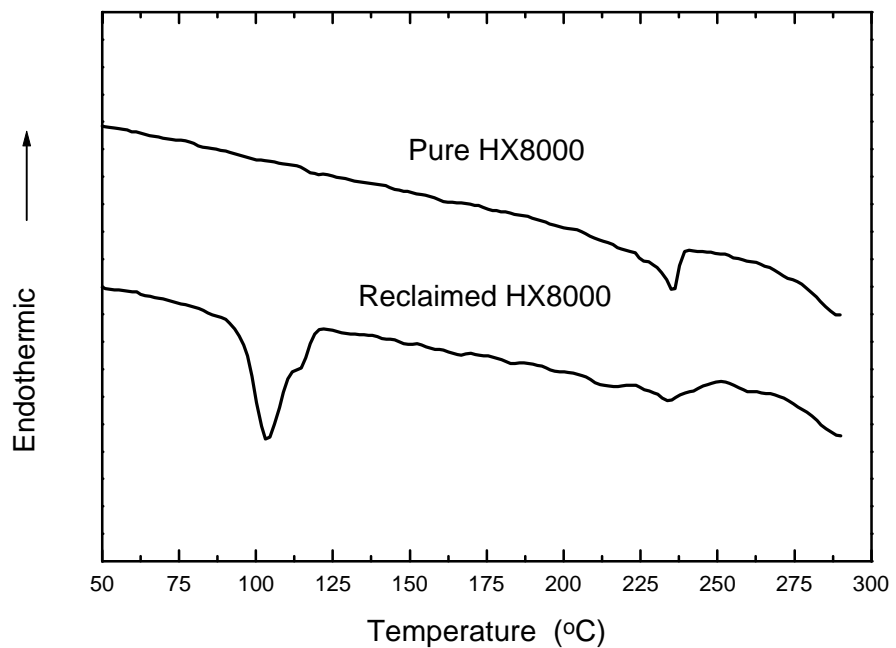


Figure 4.10 DSC Cooling Scans of Pure HX8000, Reclaimed HX8000, and Pure PP 6523, using a Cooling Rate of 10.0°C/min and Normalized to 1.0 mg.

4.4 CONCLUSIONS

From a previous work¹⁷, 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 novel recycling process was developed to facilitate the dual extrusion process. Furthermore, the development of the recycling process was concerned with using existing technologies and eliminating the use of expensive, toxic, and volatile organic solvents as much as possible. The recycling process, 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, proved to be a novel method for the separation of these two materials.

In this study, the quality of the reclaimed HX8000 was investigated in order to determine the effect that this process had on the thermotropic liquid crystalline polymer. From density measurements and from thermogravimetric analysis (TGA), it was found that this novel process resulted in a product that was 97 wt% pure HX8000. Furthermore, it was seen that the reclaimed material could be blended with pure HX8000 and then injection molded to form plaques 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.

The presence of degraded polypropylene drops was verified in the morphological investigation of these plaques using scanning electron microscopy (SEM). Based on the results from this study, it can be discerned that this process did not affect the inherent properties of the thermotropic liquid crystalline polymer (DuPont HX8000).

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