The Effects of Reclamation on a Thermotropic Liquid Crystalline Polymer

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ABSTRACT: In previous work, a process was developed to reclaim a thermotropic liquid crystalline polymer (DuPont HX8000) from composites comprised of polypropylene (PP) reinforced with HX8000. The reclamation was accomplished by chemically degrading the PP and then dissolving the PP away in heated mineral oil. From this work, it was found that there were significant drops in dynamic and steady shear viscosity for the reclaimed HX8000, but that there were no losses in mechanical properties when the recovered HX8000 was used to generate PP–HX8000 injection-molded composites. In the present work, the reclaimed HX8000 was analyzed to understand the contradiction between rheological and mechanical properties. The effects of the reclamation process on the recovered HX8000 were investigated by using pycnometry (density), thermogravimetric analysis (TGA), parallel plate rheometry, mechanical testing, scanning electron microscopy (SEM), and differential scanning calorimetry (DSC). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2517–2524, 1999

Key words: thermotropic liquid crystalline polymer; HX8000; polypropylene; reclamation; purity

INTRODUCTION

In previous work,¹ a novel process 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 extrusion² and selective dissolution^{3,4} to separate the HX8000 from the polypropylene (PP) matrix. Reactive extrusion was used to reduce the molecular weight of the PP, and thereby increase phase separation between the HX8000 and the PP, and to enhance the solubility of PP in the mineral oil. From this work, it was determined that greater than 70 wt % of the HX8000 could be reclaimed from the PP

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matrix at a purity of greater than 96 wt %. Furthermore, it was seen that the reclaimed HX8000 demonstrated lower values in complex viscosity as a function of angular frequency relative to that of 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* composites of the thermotropic liquid crystalline polymer (TLCP) and PP showed no difference in mechanical properties. Part of the purpose of this article is to try to explain the origin of these phenomena.

In this work, the reclaimed TLCP (DuPont HX8000) is investigated in order to determine the effect the separation process had on the recovered material. The purity of the reclaimed HX8000 is determined by using thermogravimetric analysis (TGA) and pycnometry (density). The melt viscosity of the reclaimed HX8000 and of an injection-

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molded blend of reclaimed material with pure HX8000 is examined using parallel plate rheometry. Scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) are 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 are performed to determine any losses in mechanical properties due to the reclamation process.

EXPERIMENTAL

Materials

The thermotropic liquid crystalline polymer (Du-Pont HX8000) used in this study is a semicrystalline TLCP, which has two melting endotherms (one at 228°C and the second at 278°C) and a density of 1.38 g/cm³. HX8000 is believed to be composed of an unspecified ratio of terephthalic acid, 4-hydroxybenzoic acid, hydroquinone, and hydroquinone derivatives.⁵ To process this TLCP, a melt temperature of at least 290°C is required. The reclaimed HX8000, obtained using the novel reclamation process,¹ was recovered from a composite that consisted of 40 wt % HX8000 and 60 wt % Montell PP 6523.

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%
$$\left[\frac{\rho - \rho_{\rm PP}}{\rho_{\rm HX8000} - \rho_{\rm PP}}\right]$$
 (1)

where ρ is the density of the reclaimed pieces, $\rho_{\rm PP}$ is the density of the pure PP, and $\rho_{\rm HX8000}$ is the density of the pure HX8000. 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 was lost when a test sample was subjected to a constant temperature of 300°C for 30 min. It was assumed that any material that was driven off from the reclaimed HX8000 was residual PP.

A Rheometrics mechanical spectrometer (Model 800) was used to determine the viscoelastic proper-

ties 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 a shear rate of 0.003 s^{-1} to a shear rate of 1.0 s^{-1} and at a temperature of 290°C. Each sample was sheared steadily at each rate for 3 min 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.

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 nonreturn 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 as follows: Zone 1, 270°C; Zone 2, 310°C; Zone 3, 300°C; 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 s.

The pure and reclaimed HX8000 resins were dried in a vacuum oven at 120°C and for 18 h prior to injection molding. The injection molded blends produced in this study were prepared by dry mixing the pure and reclaimed resin in the following two concentrations prior to injection molding: (1) 20 wt % reclaimed/80 wt % pure HX8000 and (2) 40 wt % reclaimed/60 wt % pure HX8000.

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 crosshead speed of 1.27 mm/min and an extensiometer (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.

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 2 min, then fractured. The samples were subsequently attached to mounting stubs and coated with a layer of gold using an SPI sputter coater to enhance conductivity.

Differential Scanning Calorimetry Testing

A Seiko DSC 220C was used for the DSC testing, while a constant purge of argon bathed 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 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 to 300°C, held at 300°C for 10 min, and then cooled from 300 to 40°C. The PP 6523 test sample was heated at 10°C/min from 40 to 200°C, held at 200°C for 10 min, and then cooled at 10°C/min from 200 to 40°C. All DSC runs are normalized to 1.0 mg.

RESULTS AND DISCUSSION

The Reclamation Process

In the other work,¹ 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 h, 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 min-



Figure 1 Thermogravimetric analysis of the (-) pure HX8000, (-) reclaimed HX8000, and (-) control sample of 40 wt % HX8000-60 wt % PP 6523 which were held at 300°C for 30 min.

eral 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.

Physical Properties of the Reclaimed HX8000

In the present work, the purity of the recovered HX8000 was analyzed by using density measurements and TGA. Density tests conducted on the reclaimed pieces of HX8000 resulted in an average density of 1.3630 (0.0003) g/cm³. Based on eq. (1), this density represented a material that was 96.80 (1.0) wt % HX8000 and 3.2 (1.0) wt % degraded PP. Because this calculation assumed that the reclaimed HX8000 only consisted of two phases (PP and HX8000), the possible presence of mineral oil was not accounted for in this equation. 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 (1.0) wt % HX8000 and 62.08 (1.0) wt % PP. The deviation of the calculated value from the control value was probably a function of the error associated with producing an injection-molded plaque of that exact composition. To further establish the presence of degraded PP within the recovered material, TGA of similar samples was performed. From Figure 1, it can be seen that there was a 5.0 (2.0) wt % loss of material from



Figure 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.

the reclaimed HX8000 sample. This can be attributed to the thermal degradation of leftover PP at this temperature, but it could also be attributed to leftover mineral oil. There was a 55.0(2.0) wt % loss of material from the control sample of 40 wt % HX8000-60 wt % PP 6523, which correlated with the density measurements of this blend. Based on these results, it seemed that both techniques were relatively accurate methods to utilize for the determination of purity. Although the exact identity of the material lost under TGA cannot be verified, it was established that 95 (2.0) wt % of the recovered material was pure HX8000.

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 Baird.¹ The reclaimed HX8000 was 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 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 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.

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 the mold to be filled without material escaping from



Figure 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.



Figure 4 Complex viscosity $(|\eta^*|)$ versus angular frequency (ω) comparison among $(-\Box)$ the pure HX8000, $(-\times)$ the 40 wt % reclaimed-60 wt % pure HX8000, and $(-\Delta)$ the 97 wt % pure, reclaimed HX8000 run at 290°C.

the sides. 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, the pure-reclaimed HX8000 blend, and 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, 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/s, but showed a loss in complex viscosity with increasing angular frequency after a frequency of 1.0 rad/s. 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. From Figure 4, the material response for the 40 wt % reclaimed-60 wt % pure HX8000 demonstrated some interesting behavior. At lower angular frequencies, the complex viscosity of the blend was closer to that of the reclaimed HX8000, while at higher angular frequencies, the blend's complex viscosity was closer to that of the pure HX8000.

The reduction in viscosity was also investigated by performing steady shear rate sweeps on the blended, pure, and reclaimed samples. From Figure 5, it can be seen that the reclaimed HX8000 showed almost a two-orders-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 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 s⁻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 s^{-1} in the steady shear test.



Figure 5 Shear viscosity versus shear rate comparison among $(-\Box)$ the pure HX8000, $(-\times)$ the 40 wt % Reclaimed HX8000-60 wt % Pure HX8000, and $(-\Delta)$ the 97 wt % Pure, reclaimed HX8000 run at 290°C.

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. Although the decrease in complex viscosity could be as much as an order of magnitude, the degraded HX8000 would probably still have the same frequency behavior and would probably still reach a Newtonian plateau at the lower rates as with the pure HX8000. This type of shift in the viscosity response curves was seen in the degradation of PP 6523 during the initial work on the development of the reclamation process.⁶ 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 amount of degraded PP, 3.0 wt % or 5.0 vol %, according to the densities, still left in the reclaimed HX8000. One empirical method for evaluating the viscosity of heterogeneous blends is to use the following rule of mixtures⁶ (parallel arrangement):

$$\frac{1}{\eta_{\text{blend}}} = \frac{\phi_{d-\text{PP}}}{\eta_{d-\text{PP}}} + \frac{\phi_{\text{HX8000}}}{\eta_{\text{HX8000}}}$$
(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 PP could drop the overall viscosity of the blend an order of magnitude. The complex viscosity of degraded PP, at 290°C and 1.0 rad/s, was around 12.0 (0.3) Pa s.⁷ 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 s. From Figure 4, the measured dynamic viscosity for the reclaimed HX8000 was around 200 Pa s, which was in very good agreement with the predicted value. Although there was no justification for using this particular empiricism, this rule seemed to be able to account for the drop in dynamic viscosity.



Figure 6 Differential scanning calorimetry heating scans run at a heating rate of 10.0°C/min and normalized to 1.0 mg: (a) samples of Pure HX8000 and reclaimed HX8000 and (b) a sample of pure PP 6523.

There were other rules of mixtures, which utilize series, logarithmic, exponential, and other arrangements that did not account for this decrease in complex viscosity. Furthermore, no empiricism was able to account for the almost two-orders-ofmagnitude drop observed in the steady shear viscosity.

Differential Scanning Calorimetry (DSC) Testing

In order to investigate the proposed presence of degraded PP, DSC 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 6, it can be seen that there



Figure 7 Differential scanning calorimetry cooling scans run at a cooling rate of 10.0°C/min and normalized to 1.0 mg: (a) samples of pure HX8000 and reclaimed HX8000 and (b) a sample of pure PP 6523.

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 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 7, it can be seen that there was an extra peak, at \sim 110°C, in the reclaimed HX8000 as compared to 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 presence of degraded PP leftover in the sample. From Figure 7, it can also be seen that the reclaimed HX8000 demonstrated the same crystallization exotherm around 240°C as the pure HX8000. From the DSC runs, it can be qualitatively concluded that the reclaimed material was comprised of pure HX8000 and some leftover degraded PP.

Scanning Electron Microscopy of the Reclaimed HX8000 Samples

Furthermore, the presence of degraded PP was investigated by looking at cross sections of a HX8000 injection-molded plague under SEM. Because no losses in mechanical properties were seen in these plaques, SEM micrographs were taken of a 20 wt % reclaimed-80 wt % pure HX8000 injection-molded sample in order to investigate the morphology. From Figure 8, it can be seen that drops of degraded polypropylene were found within this blended plaque. From Figure 9, it was seen that these degraded PP 6523 drops were only on the order of 1–10 μ m in size and were encapsulated well by the HX8000 matrix. Therefore, it can be proposed that small inclusions of degraded PP would not have affected the mechanical properties of the injection-molded plaques.



Figure 8 Scanning electron micrograph of an injection-molded plaque (cross section/transverse direction) of the 20 wt % reclaimed HX8000-80 wt % pure HX8000 showing the small inclusions of degraded PP 6523.



Figure 9 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.

CONCLUSIONS

From a previous work,¹ a dual extrusion process was used to generate composite strands of HX8000 (a TLCP) and 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 technique. 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 PP, proved to be an effective method for the reclamation of a TLCP. 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 PP 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 purity of the reclaimed HX8000 was investigated in order to account for a drop in viscosity but with no loss in mechanical properties. From density measurements and from

TGA, it was found that the recovered material was 95 to 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 from that of pure HX8000, it was probable that this difference was due to the presence of trace quantities of PP rather than the degradation of the TLCP. The presence of an extra endotherm in the DSC heating scan and an extra exotherm in the DSC cooling scan was attributed to degraded PP leftover in the reclaimed HX8000. The existence of polypropylene drops was verified in the morphological investigation of injection molded plaques of pure and reclaimed HX8000 by means of SEM. Based on this work, the drop in viscosity with no loss in mechanical properties can be attributed to the presence of a small amount of PP leftover in the reclaimed DuPont HX8000.

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