

Characterization of Virgin and Postconsumer Blended High-Impact Polystyrene Resins for Injection Molding

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ABSTRACT: This article focuses on the mechanical and rheological properties of virgin and recycled high-impact polystyrene (HIPS) materials and describes our progress in evaluating the viability of reusing postconsumer and virgin polymer blends of HIPS from electronics equipment housings. Plastics reuse challenges are briefly reviewed, and experimental results, such as the rheological properties, mechanical properties, molecular weight, and morphology of different blends, are summarized and discussed for reuse of HIPS from printer and monitor housings. It is found that all blends have similar molecular weight and polydispersity. Furthermore, the recycled resin and virgin resin consist of almost the same components. However, the morphology of the rubber phases is different. The mechanical properties are similar for the ASTM specimens molded with either set of blends. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 1–8, 2002; DOI 10.1002/app.2339

Key words: characterization; plastics recycling; mechanical properties; rheology; molecular weight; morphology

INTRODUCTION

The attention paid to polymer recycling has increased in the past decade. Plastics recycling is important because more efficient reuse of materials will reduce the quantities of plastics sent to

landfills, as well as reduce raw material extraction. Waste prevention practices are increasingly significant and increasingly encouraged with the advent of “take-back” legislation.^{1–3} It is accepted that direct use of postconsumer polymers is the most efficient and reliable way to treat plastic waste.⁴ However, how to characterize the postconsumer resin (PCR) and increase the percentage of the PCR are two of the problems in recycling plastic.

High-impact polystyrene (HIPS) occupies a large market share in computers, business machines, and other electronics.⁵ Furthermore, monitor housings and printers are two of the largest

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applications, but less than 1% is recovered from the total 19% market share of HIPS.⁶ Therefore, it is important to evaluate and develop viable options for discarded polymer products. However, the analysis of life cycle trade-offs between use of recycled plastics, recyclability, reduction of process wastes, energy consumption, yields, and product performance are complex.^{7–9} To date, many companies process either 100% virgin material or virgin material with small percentages of regrind. Sources of postindustrial regrind may be internal or from another industrial processor(s). Companies embracing product stewardship are struggling to develop viable approaches to process and recycle returned products economically. Postconsumer polymers may be contaminated by other materials;¹⁰ postconsumer products may contain polymer blends, as well as additives such as reinforcements, paint, or flame retardants.¹¹ Thus, postconsumer plastics introduce additional raw material uncertainties into the manufacturing process. In addition, incompatible polymer blends may be present in a product, requiring expensive disassembly procedures or less valuable mixtures. As a result, many plastics recyclers currently select between options such as incineration or downcycling, which is the formation of lower grade polymer materials.

Another complication is that returned polymers are exposed to various thermal and mechanical conditions. Therefore, our initial investigation began with characterization of the PCR. The viscosity is one of the basic properties for the reuse of the PCR. The melt viscosity of the PCR was measured and the virgin resins were identified with the same melt viscosity as the PCR. Next, the melt viscosities of postconsumer and virgin resin blends were measured. Then the mechanical properties of the blends were measured and the effect of different virgin resins and their weight percentages were discussed. This investigation helped us evaluate the viability of reusing the PCR in new injection molded products. Our goal was to characterize the relationship between the ratio of recycled content to virgin content and the mechanical properties. The mechanical properties, including tensile, flexural, and impact properties, of the blends with different percentages of reuse resin were analyzed through experiments. Moreover, we investigated the molecular weight and morphology of molded parts to help explain and predict the properties of recycled blends for injection molding. Understanding the relationship between rheological and design char-

acteristics provides suppliers (recyclers) and customers (molders) with valuable insights regarding viable uses for PCR.

EXPERIMENTAL

Characterization of Material

It is important to identify the postconsumer polymer properties. In general, it is nearly impossible to identify the original resin manufacturer for postconsumer polymers in electronics equipment. In our case, we only knew the polymer was labeled HIPS; we did not know the original resin manufacturer or product code. Therefore, we tested the rheological properties of the PCR to identify the most suitable “virgin resin” for the blends. The PCR material we used consisted of ground pieces of printer and monitor housings.

The fragments were larger than 100 mm. The incoming fragments were inspected manually for metal contamination and then were reshredded to reduce their size before mixing with the virgin resins. The maximum dimension of the shredded fragments was 1–10 mm, which was close to the size of the virgin resins.

A Rheometrics mechanical spectrometer (RMS 800) rheometer was used. The rheological properties of the blends, which consisted of different percentages of postconsumer HIPS and virgin resins, were also studied at 180, 200, and 220°C. Molded disks were used for the measurement of the viscosity for the blends.

Measurement of Molecular Weight

The molecular weight was measured by gel permeation chromatography. The samples used were molded blends with 0, 50, and 100% Huntsman PS 702, molded blends with 50 and 100% Nova PS 3350, and unmolded 100% virgin Nova PS 3350. The solution was prepared by dissolving blends in tetrahydrofuran. Each sample was analyzed twice with a running time of 45 min and an injection volume of 200 μ L. We report the average of the two runs in Table I.

Microscopy and Spectroscopy

For the morphological measurement, the aim was to observe the dispersion of the rubber phase in PS and the size of the rubber domains because the rubber particles can affect the mechanical properties. A Philips XL-30 FEG environmental scan-

Table I Number-Average (M_n) and Weight-Average (M_w) Molecular Weights and Polydispersity (M_w/M_n)

Materials	M_n	M_w	M_w/M_n
100% Huntsman 702	58198	180875	3.06
50% Huntsman 702	56730	171486	3.03
0% Huntsman 702	55262	162099	2.93
100% Nova 3350	54129	196963	3.64
50% Nova 3350	55724	181306	3.26
Virgin Nova 3350	57577	183095	3.18

ning electron microscope (ESEM) was used. The sample was stained by a 1% OsO₄ aqueous solution for 15 days and carbon coated for morphological measurements. The fracture surfaces were observed with 15 kV power. The original magnification in this study varied from 200 to 10,000 \times .

The purpose of the Raman spectroscopy tests was to determine if there was a detectable difference in the absorption spectra for the PCR and the virgin HIPS. The virgin resin Huntsman PS 702 was used in the experiment. The IR vibrational spectra were obtained using a Bruker Equinox 55 with an IR scope 1. The instrument was operated in reflectance mode using a 15 \times microscope objective and 4 cm⁻¹ resolution. OPUS software (version 2.2) was used for instrument control and data handling.

The Raman vibrational spectra were obtained using a Chromex Raman 2000 spectrometer with illumination by a 785-nm diode laser DSL and imaged on a Photometrics 1024 \times 256 pixel red enhanced CCD detector. The spectra were taken at a 180 $^\circ$ collection angle with a depth of focus of several millimeters. The laser power was typically 50 mW with a spot size of 80 μ m.

Processing Parameters for ASTM Specimens

To determine the initial processing parameters, a mold filling simulation was run on a C-MOLD 97.7. C-MOLD is a set of integrated computer aided engineering (CAE) simulations for plastics molding processes, including injection mold filling, postfilling, cooling, part shrinkage, and warpage. C-MOLD provides recommendations for processing parameters such as the fill time, inlet, and melt temperature. The CAE provides an easy to use data visualizer for viewing mesh information and analysis results.

The C-MOLD 97.7 was used to simulate the filling of our mold with one of the virgin resins (Huntsman PS 702), which had the same viscosity versus shear rate as our PCR. The ASTM mold consisted of six cavities, including two tensile specimens, two bending specimens, and two disks. From the results of the mold simulation and several experimental trials, the operating parameters, such as the inlet melt temperature, melt temperature, and cooling time, were selected to injection mold the ASTM specimens.

Physical Properties of ASTM Specimens

Six different weight percentages of blends were prepared, as shown in Table II. Two selected virgin resins, Huntsman PS 702 and Nova PS 3350, were used. These virgin resins were selected because they had close to the same viscosity versus shear rate curve as the PCR. The blends were mixed for 1 min in a Little Ford Lodge Precision Mixer.

The ASTM specimens were prepared with a 50-ton Sumitomo injection molding machine. The virgin material and PCR were mixed completely and then dried at 160 $^\circ$ F for 2 h prior to injection molding. According to the results of the mold simulation, the barrel temperature was set from 380 to 440 $^\circ$ F from the rear zone to front zone. The temperature of the cooling water at the outlet was kept at 77 $^\circ$ F.

For blends with Huntsman PS 702, the physical properties tested included the tensile strength and modulus (ASTM D638) at 23.3 $^\circ$ C and 21% humidity, the flexural strength and modulus (ASTM D790) at 18.4 $^\circ$ C and 12% humidity, and the notched Izod impact strength (ASTM D256) at 18.4 $^\circ$ C and 21% humidity. For blends with Nova PS 3350, all tests were performed at 27.3 $^\circ$ C and 30% humidity.

Table II Weight Percentage of Blends

No.	Virgin Resin (wt %)	Recycled Material (wt %)
1	100	0
2	85	15
3	75	25
4	50	50
5	25	75
6	0	100

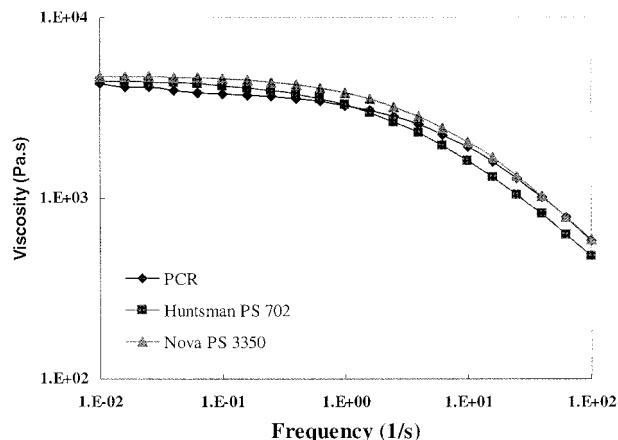


Figure 1 A comparison of the viscosity curves for postconsumer HIPS and virgin HIPS at 220°C.

RESULTS AND DISCUSSION

Characterization of Material

The rheological properties of the ground postconsumer HIPS were studied at 180, 200, and 220°C. Figure 1 shows the viscosity versus the frequency curve of the postconsumer material at 220°C. We identified two virgin resin candidates, Huntsman PS 702 and Nova PS 3350, in the C-MOLD resin databases by comparing the viscosity curves.

The viscosity of blends with different percentages of recycled resins was also investigated at 180, 200, and 220°C. Figures 2 and 3 show the viscosity of the blends with Huntsman PS 702 or Nova PS 3350, respectively, versus the frequency at approximately 200°C. It was found that all blends were shear thinning. It was also shown

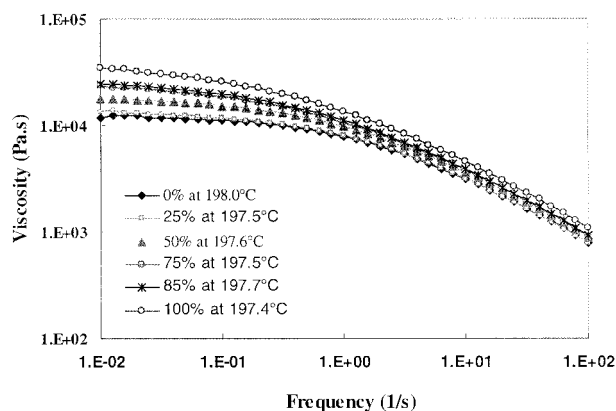


Figure 2 The viscosity of Huntsman PS 702 blends with different percentages of postconsumer resin at about 200°C.

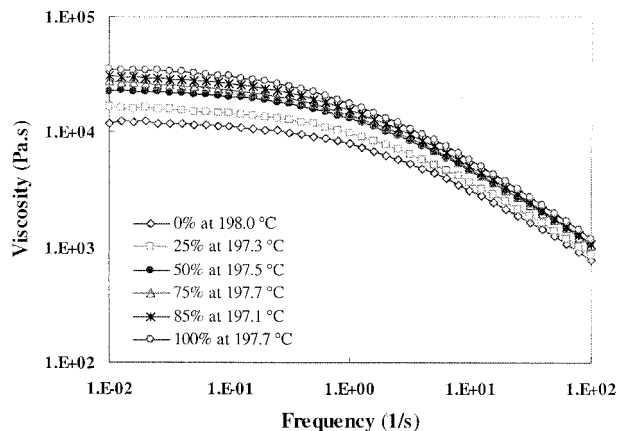


Figure 3 The viscosity of Nova PS 3350 blends with different percentages of postconsumer resin at about 200°C.

that the viscosity increased with the increase of the percentage of PCR.

Molecular Weight

The molecular weights are listed in Table I. The molecular weight and polydispersity of the blends with Huntsman PS 702 increased with the increase of the percentage of Huntsman PS 702. However, for blends with Nova PS 3350, the molecular weight decreased with the increase of the percentage of Nova PS 3350, although the polydispersity increased as the percentage of Nova PS 3350 increased. All blends, including recycled resin, had similar molecular weights and polydispersity, which would lead us to predict similar mechanical properties.

Microscopy and Spectroscopy

Figure 4 shows the ESEM images of different blends. The outer surfaces of the virgin resins, 100% Huntsman PS 702 and Nova PS 3350, were dotted with a broad range of rubber domains with many large rubber particles. The particle diameter was about 2 μm . However, for 50% Huntsman PS 702 and 50% Nova PS 3350, we only observed relatively smaller rubber particles. The particle diameter was about 1 μm . The surface structures for the 50% blends were less regular compared to those of virgin resins. We did not observe well-defined rubber domains for the PCR, and the surface was seemingly covered with a poorly defined dispersed rubber phase and some very small particles that may have been contaminants.

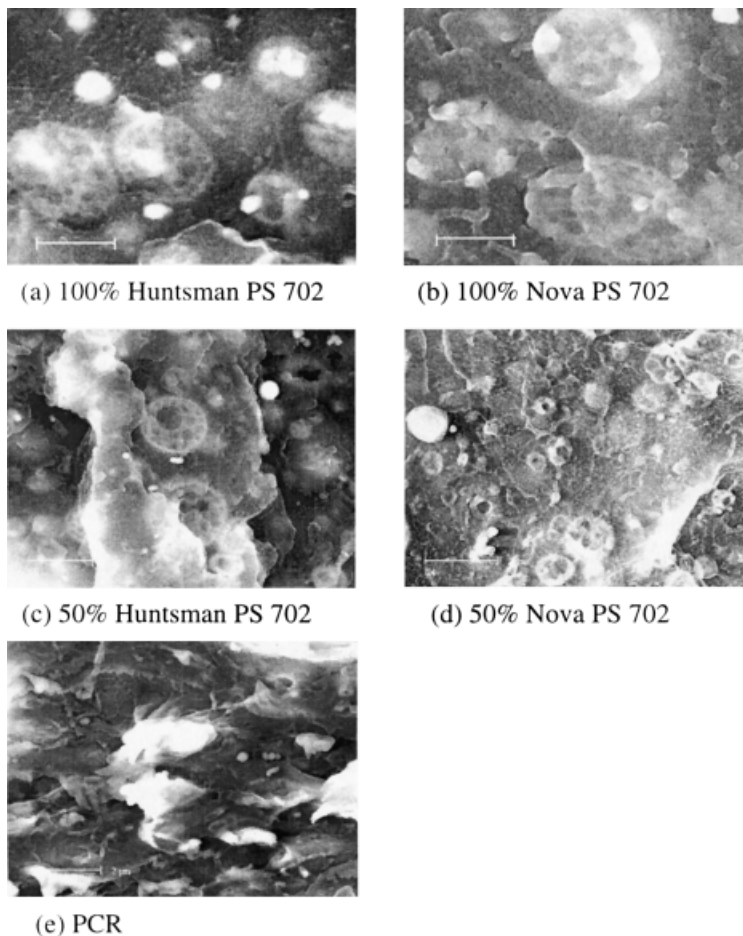


Figure 4 The images of different blends from ESEM; scale bar = 2 μm .

Figures 5 and 6 show the Raman spectroscopy and IR vibrational spectra of the recycled resin and virgin resin Huntsman PS 702, respectively. The figures show that the recycled resin and virgin resin consisted of almost the same compo-

nents. Combined with the results of the molecular weight measurements, we predicted that it was possible to mix the recycled resin and virgin resin for potential synergistic improvement of their properties.

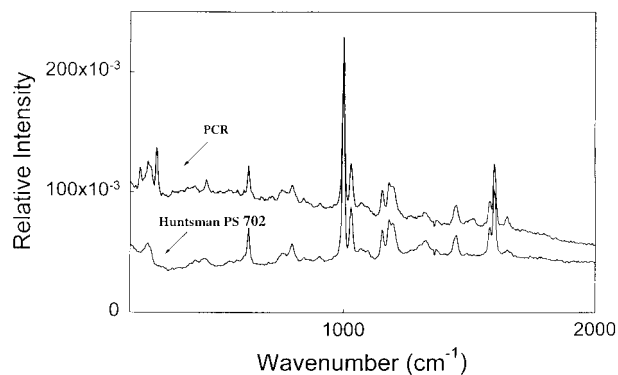


Figure 5 Raman spectroscopy of injection molded postconsumer resin and Huntsman PS 702.

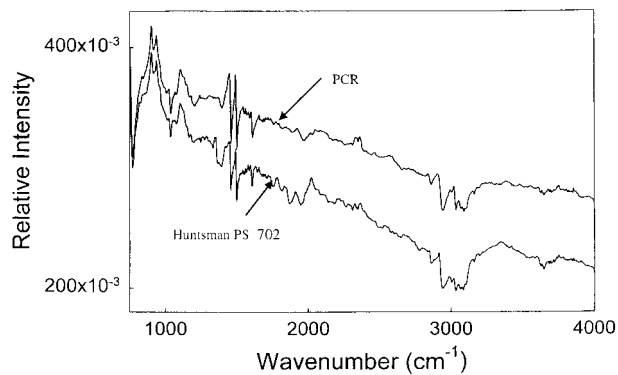


Figure 6 IR vibrational spectra of injection molded postconsumer resin and Huntsman PS 702.

Table III Processing Parameters from C-MOLD

Maximum machine	
Clamp force	4.90E+007 N
Injection volume	0.02 m ³
Injection pressure	1.8E+008 Pa
Injection rate	0.006667 m ³ /s
Fill time	2.00 s
Postfill time	12.08 s
Mold-open time	2 s
Temperature	
Ambient	298 K
Min/max melt	449.15/533.15 K
Transition	365.15 K
Inlet melt	522.09 K
Average coolant	298 K

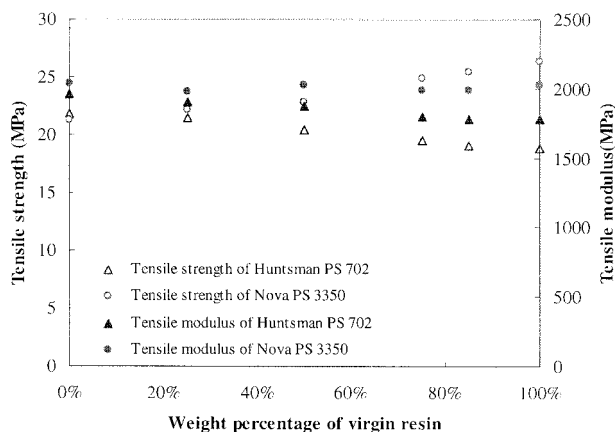
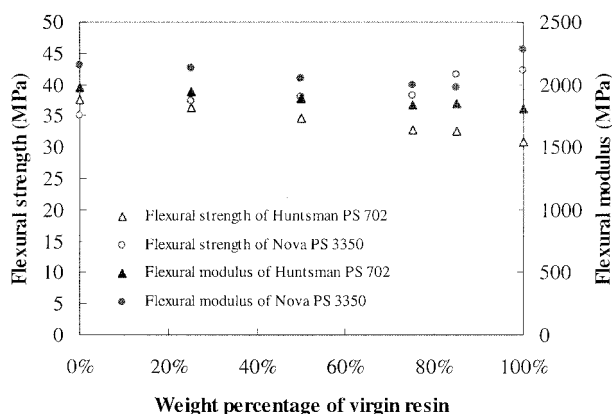
Processing Parameters for ASTM Specimens

The geometry was evaluated at first, and then the mesh for the C-MOLD simulation was created. The processing parameters for the ASTM specimens of Huntsman PS 702 from the C-MOLD simulation are given in Table III.

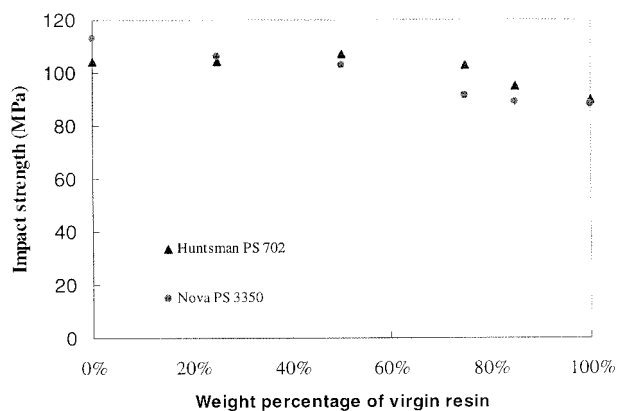
To compare the mechanical properties of the blends of Huntsman PS 702 to the properties of blends of Nova PS 3350, the same injection molding parameters were used to prepare the specimens of blends of Nova PS 3350.

Physical Properties of ASTM Specimens

The results of the physical properties tests for the blends of Huntsman PS 702 are shown in Figures 7–9. Figure 7 shows the tensile modulus and tensile strength of the blends for two different virgin resins versus the weight percentage of the virgin

**Figure 7** The tensile strength and tensile modulus versus the weight percentage of virgin resin.**Figure 8** The flexural strength and flexural modulus versus the weight percentage of virgin resin.

resin. It was found that the tensile strength and tensile modulus decreased slightly with the increase of the weight percentage of virgin resin for the blends with Huntsman PS 702, and the tensile strength and tensile modulus increased slightly with the increase of the weight percentage of virgin resin for the blends with Nova PS 3350. The standard deviations of the tensile strength and the tensile modulus were 0.63 and 67, respectively. Figure 8 illustrates the results of the flexural modulus and flexural strength. The flexural strength, like the tensile strength for the blends of Huntsman PS 702, decreased slightly. For the blends of Nova PS 3350 the flexural strength had the same trend as the tensile strength, increasing slightly. However, the flexural modulus had no specific changing trend for the blends of Huntsman PS 702 and Nova PS 3350. The standard deviations of the flexural

**Figure 9** The impact strength and tensile modulus versus the weight percentage of virgin resin.

strength and the flexural modulus were 0.60 and 46, respectively.

As shown in Figure 9, the impact strength of the blends of Huntsman PS 702 increased with the increase of the weight percentage of recycled HIPS when the percentage was small. At $\geq 75\%$ recycled HIPS, the strength reached a stable value. For impact strength of the blends of Nova PS 3350, it decreased with the increase of the weight percentage of virgin resin when the percentage was small. At $\geq 75\%$ virgin resin, the strength reached a stable value. The standard deviation of the impact strength was 2.6.

Although the Raman spectroscopy and IR vibrational spectra showed that the recycled resin and virgin resin consisted of almost the same components, and the blends had similar molecular weight and polydispersity, the ESEM showed that the different blends had very different microstructures and different rubber domain sizes. Thus, it was not surprising that the different blends had different mechanical properties because the mechanical properties of HIPS can be affected by the amount of rubber added, the type of rubber, the rubber size distribution, the phase volume, the degree of crosslinking, the level of adhesion, etc.^{12,13} The reason for the higher tensile modulus, tensile strength, flexural strength, and impact strength of the PCR compared to Huntsman PS 702 probably resulted from the higher tensile modulus and tensile strength of the original material or the addition of reinforcements in the pure resin when the printers and monitors were made. Also, the experiments demonstrated that the mechanical properties of recycled HIPS were slightly lower than those of Nova PS 3350. It was interesting to note that the mechanical properties of blends with Huntsman PS 702 and recycled resin were slightly better than the properties of the selected virgin material Huntsman PS 702. Our experiments demonstrated that it is possible to reuse the PCR. Relative to the selected virgin materials with the same viscosities as the PCR, reuse of PCR is an attractive option.

We compared our 100% PCR tensile and flexural properties with those published in a study comparing disassembled versus shredded HIPS from postconsumer television sets.¹⁰ We found that the tensile modulus of our blends was lower than that of the disassembled or shredded HIPS in Langerack's¹⁰ study; however, the tensile strength at yield of our blends was larger. It was also shown that the flexural modulus of our blend

was lower than that of disassembled or shredded HIPS in the other study,¹⁰ but the flexural strength was almost the same. The differences in the mechanical properties of the PCR in the two studies may have resulted from the different brands of original materials.

CONCLUSIONS

To determine the initial processing conditions for injection molding of virgin and postconsumer resin blends, a precharacterized resin must be designated for a C-MOLD simulation. To select a precharacterized resin for the C-MOLD simulation, virgin resin viscosity curves were matched with the PCR viscosity curve. Then the recommended C-MOLD simulation processing parameters were further refined for the blends for the ASTM test standard specimens by running several experimental runs.

All blends had similar molecular weight and polydispersity. Further, the recycled resin and virgin resin consisted of almost the same components, as shown in their Raman and IR spectra. The mechanical properties were similar for the ASTM specimens molded with either set of blends. The tensile modulus, tensile strength, and flexural strength increased slightly with the increase of the weight percentage of PCR for the blends of Huntsman PS 702. The impact strength increased with the increase of the weight percentage of PCR when the percentage was small and the strength finally reached a stable value. The physical properties of blends having recycled resin were better than the properties of the virgin resin Huntsman PS 702. On the other hand, the mechanical properties of PCR with Nova PS 3350 were slightly lower when compared to the pure virgin Nova PS 3350 resin.

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