Recycling of Poly(phenylene ether) Blends

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ABSTRACT: The effects of postindustry recycling of polymer blends composed of poly(phenylene ether) (PPE) on the properties of the PPE blends were investigated by simulated recycling with multiple molding cycles. Two compositions with different concentrations of PPE were reprocessed with an injection-molding machine. Mechanical, thermal, rheological, and morphological characterizations were carried out on as-produced and reprocessed samples to examine the influence of the number of molding cycles on the two specific PPE blends. Efforts were made to determine the effect of each molding cycle on the specific properties of the two PPE blends, including the Elastic (E), modulus, stress at break, strain at break, multiaxial impact, and melt viscosity. The results are discussed in detail. The retention of the properties correlated well with the unperturbed morphology of the compositions before and after recycling, as observed by transmission electron microscopy analyses on fractured tensile samples. However, more in-depth microanalyses are required to identify the effect of recycling on the individual components present in the studied compositions. In this study, we aimed to establish structure–property relations upon recycling using several characterization techniques. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2921–2927, 2011

Key words: molding; processing; polymer blends; poly(phenylene oxide); recycling

INTRODUCTION

Polymer recycling, postindustry and/or postconsumer, is a common practice in the plastics industry. The interest in recycling is mainly confined to commodity plastics, which enjoy high-volume consumption and, thus, render significant economic benefits. However, recycling and/or reprocessing either as a part in a pristine material or as a whole may prove to be economical in expensive high-performance polymers if the base polymer is judicially chosen, composed, and processed.[1–3]

Another driving force for the use of recycled material is ecological. There is a growing interest in waste minimization; this has led to an interest in the recycling of used material.[4–9]

The recycling of scrap from processing operations, which is defined as postindustry recycling (e.g., extrusion, injection molding, finishing) is widely used in the plastics industry. It involves the grinding of the scrap and its mixture with virgin material; this is followed by processing. This scrap can also be used alone or, more often, mixed with the virgin material at appropriate ratios according to the expected performance.[10,11]

A major potential disadvantage of the use of reprocessed material either as a part with the pristine material or as a whole is the significant deterioration of the polymer properties upon recycling/reprocessing. The successive temperature and shear stress and strain cycles due to reprocessing/recycling may lead to a decrease in useful combinations of the polymer properties, which are generally required for their intended applications.[12–14]

Poly(phenylene ether) (PPE), along with its blends, is a useful engineering thermoplastic because of its good rigidity, creep resistance, dimensional stability, high heat stability, and electrical, chemical, water, and flame resistance.[15]

Recently, there was a report on the recycling of PPE-based thermoplastic elastomer (TPE) through a twin-screw extrusion and injection-molding technique. PPE-based TPE showed a significant improvement in the mechanical properties upon recycling. The effect of recycling on the properties of polyolefin was explored in much detail.[16]

Few studies on the recycling of composite materials have been reported. A reduction in the mechanical properties was supported by a reduction in the aspect ratio of the reinforcement agents. It was also supported by detailed morphological studies.

TABLE I
Key Components of the Blends

Blend 1	Blend 2
PPE	PPE
High-impact polystyrene	High-impact polystyrene
Resorcinol diphosphate	
Antioxidant package	Antioxidant package
Styrene ethylene/butylene styrene	

However, no literature is available on PPE-based thermoplastic blends.[17–19]

The objective of this study was to study the retention of key properties of the studied blends after successive injection-molding cycles, which resembled recycling. This study could provide information on how many times the specific material could be recycled without any compromise in enabling properties. In this study, we aimed to establish structure–property relations with recycling using several characterization techniques. This article is of industrial application significance, particularly when recycling is of prime importance from the viewpoint of sustainability.

EXPERIMENTAL

Materials

Blends of PPE were used in this study: blend 1, composed of PPE and high-impact polystyrene with a PPE content of less than 50 wt %, and blend 2, composed of PPE and flame retardant (FR) additives with a PPE content of more than 50 wt %. The key compositions of the blends are shown in Table I.

TABLE II
Injection-Molding Temperature Profile

Barrel	Oil	Feed	Zone 1	Zone 2	Zone 3	Nozzle
Temperature (°C)	40	80	230	250	250	260

The injection molding of these blends was carried out on a LTM Demag, India 100-ton injection-molding machine. After each molding cycle, a required number of test specimen were taken out for testing, and then, the rest of the molded specimens were pelletized with a grinder and then molded again.

Ten such successive injection-molding cycles were carried out. The scheme of the experiment is shown in Figure 1. There are various methods for polymer recycling; however, the one we describe is practiced often in the molding industry.

The injection-molding conditions used to process the blend are shown in Table II. The mold temperature was maintained at 70°C with an oil-heated temperature controller. Before injection molding, the materials were dried for 4 h at 70°C.

The processing parameters used for injection molding are given in Table III. All of the parameters were kept constant for all of the molding cycles.

Mechanical properties

The tensile tests were conducted in accordance with ISO 527 with standard test specimens. The test was conducted on a Instron 5566, USA universal testing machine. The initial crosshead speed was 1 mm/min
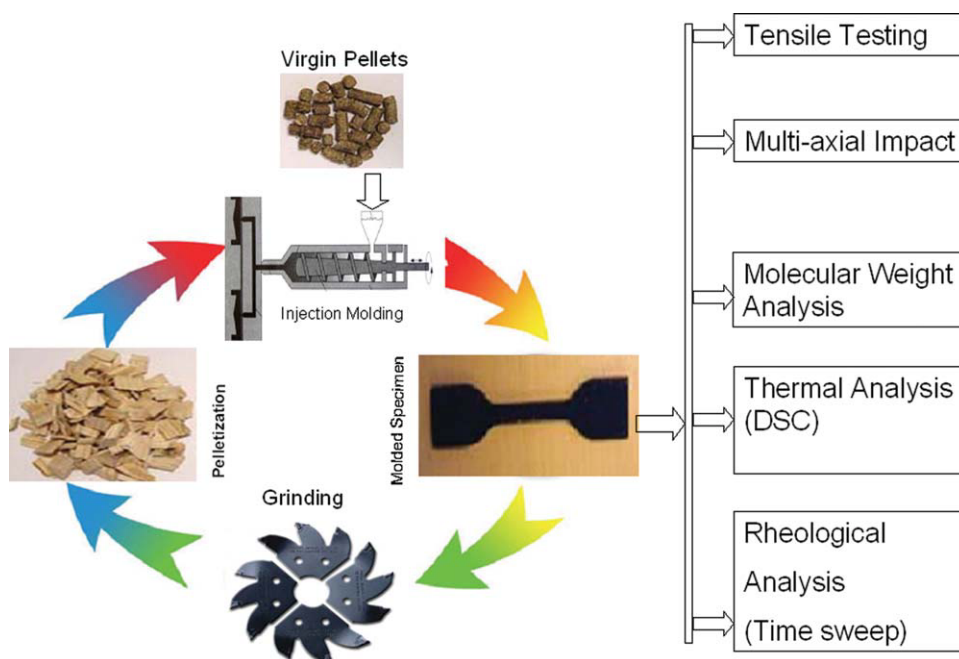

Figure 1 Schematic of the experiment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Injection-Molding Processing Parameters

Injection pressure bar	65 bar
Injection speed	25%
Holding pressure	55 bar
Holding time	10 s
Cooling time	10 s
Screw speed	25%
Backpressure	5 bar
Dosing stop	52 mm

to a strain of 1%, and then, a speed of 50 mm/min was used until the failure of the specimens occurred.

Multiaxial impact tests were carried out in accordance with ISO 6603. A close correlation with practical impact conditions was the main reason we chose multiaxial impact testing over notched or unnotched Izod impact testing. A Fractovis Plus instrument from CEAST, USA was used. The load was 10 kg, and the energy was 10 kN.

Transmission electron microscopy (TEM)

A Tecnai G2 transmission electron microscope, operated at 120 kV, was used to examine the morphologies of the representative samples. TEM micrographs were recorded for the control samples and for the samples after each recycling process. Thin sections of 150 nm were prepared with an ultramicrotome (Leica Ultracut UCT, USA) operated at $-90°C$; the sections were subsequently vapor-stained with a freshly prepared ($\sim 4\%$) aqueous solution of OsO_4 and RuO_4.

Molecular weight determination

The molecular weight was determined by gel permeation chromatography with a Shimadzu, USA model ACL-10AVP series instrument. Chloroform was used as the mobile phase with a flow rate of 1 mL/min during the gel permeation chromatography measurements. The molecular weight data reported in this study were based on narrow-molecular-weight-distribution polystyrene standards (MW XYZ-ABC).

Modulated differential scanning calorimetry (MDSC)

MDSC is a new extension of conventional differential scanning calorimetry (DSC) that provides information about the reversing and nonreversing characteristics of thermal events and the ability to directly measure the heat capacity. This additional information aids interpretation and allows unique insights into the structure and behavior of materials. Specifically, MDSC permits the separation of the total heat flow signal into its thermodynamic (heat capacity) and kinetic components. MDSC gives simultaneous improvements in sensitivity and resolution and can separate overlapping events that are difficult or impossible to do by standard DSC.

A Q1000 machine manufactured by TA Instruments, USA was used to analyze the thermal transitions of the studied material. The sample was heated at the rate of 5°C/min in an inert atmosphere (N_2 atmosphere). Aluminum pans were used to analyze the material. The heat flow rate difference between the sample and the reference pan was measured as a function of the temperature. The experiment was conducted from 50 to 250°C. Baseline and temperature calibrations were performed in the required temperature range according to ASTM E 967 and ASTM E 968.

MDSC was performed to segregated total heat flow into reversible and nonreversible heat flow. The glass-transition temperature (T_g) shift was accurately measured in reversible heat flow. The reversible heat flow was correlated with the specific heat component, and the nonreversible heat flow was correlated with the kinetic component. Processes, such as crosslinking, partial melting, and crystallization, were considered to be responsive in the irreversible heat flow. An additional sinusoidal heating rate was provided by MDSC to improve the resolution and sensitivity.

The general theory of MDSC is as follows:

$$dH/dt = C_p(dT/dt) + f(T, t) \quad (1)$$

T = Temperature, t = time, and $f(T,t)$ = function of Temperature and time.

$$\text{Total heat flow (DSC)} = \text{Heat capacity component} + \text{Kinetic component} \quad (2)$$

$$\text{Total heat flow (DSC)} = \text{Heating} - \text{rate dependence} + \text{Time dependence} \quad (3)$$

$$\text{Total heat flow} = \text{Reversing MDSC} + \text{Nonreversing heat flow} \quad (4)$$

where dH/dt is the heat flow signal, C_p is the sample heat capacity, dT/dt is the sample heating rate.

Dynamic mechanical analysis (DMA)

The DMA study was conducted in a RDA III strain controlled rheometer from Rheometric Scientific, USA. A parallel plate 25 mm in diameter was used for the rheological studies. The experiment was conducted at 260°C. A time-sweep experiment was conducted at a constant frequency of 1 Hz (6.28 rad/s) with strain amplitude of 3% for 1800 s. The data were analyzed with Orchestrater software, supplied by Rheometric Scientific.

Viscosity as a function of the shear rate

The change in viscosity as a function of the shear rate was monitored with a Capillary rheometer
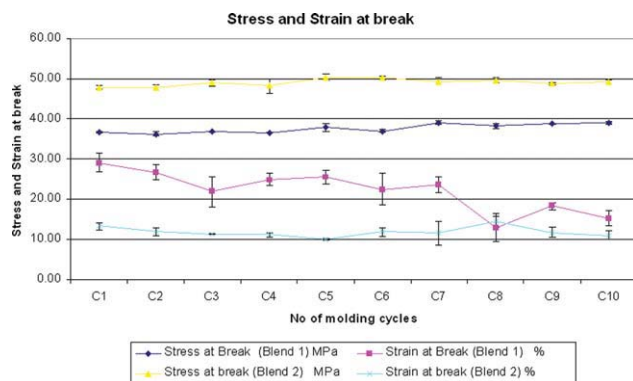
Figure 2 Stress and strain at break for blends 1 and 2 (C = cycle). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(Rheograph 6000) from Gottfeat Machine, USA. The experiment was carried out in accordance with ISO11443 with pelletized material. The temperature was maintained at 260°C. We used a diameter of 1 mm and a dwell time of 180 s.

RESULTS AND DISCUSSION

Two compositions with different concentrations of PPE upon recycling were studied in detail with mechanical, thermal, rheological, and morphological characterizations. Our major findings are elaborated next under the different subheadings.

Mechanical properties

The stress at break, strain at break, Elastic (E) modulus, and multiaxial impact properties were measured as a function of the number of molding cycles.[20] Figure 2 summarizes the stress at break and strain at break properties of blends 1 and 2. In the case of blend 1, the stress at break ranged from 36.7 to 39.03 MPa, and the strain at break ranged from 29.16 to 15.3%. In the case of blend 2, the stress at break ranged from 47.87 to 50.33 MPa, and the strain at break ranged from 10.01 to 14.43%.

Figure 3 presents the E modulus and multiaxial impact energy for blends 1 and 2. Through 10 molding cycles, the E modulus of blend 1 varied from 2320 to 2587 MPa. The multiaxial impact energy varied from 24.42 to 9.59 J. In the case of blend 2, the E modulus and multiaxial impact energy were in the ranges 23.76–24.54 MPa and 97.64–65.83 J, respectively.

On the basis of the results, we noted that there was no significant change in most of the mechanical properties, except the strain at break and multiaxial impact energy measured. A two-sample t test was performed to determine whether these values were the same statistically. A P value higher than 0.05

confirmed that statistically these values were same, and hence, recycling had no significant effect on the studied blends. However, in the cases of the strain at break and the multiaxial impact energy, the P value was less than 0.05; that is, statistically they were different. The drops in the strain at break and multiaxial impact energy could have been due to limited aging of the rubber present in high-impact polystyrene; however, further investigation is required to confirm it. Even after 10 molding cycles, the tensile strength and modulus remained in the same range. The retention of properties was justified by the unperturbed morphology; this is discussed in the next section.

Morphology

It is known that the morphology of a blend affects the properties, including the thermal, electrical, and mechanical properties. TEM studies were done on the samples chosen from each blend after the first, second, fifth, and tenth cycles of reprocessing. The samples were characterized for the morphological development upon recycling with TEM. Figure 4(a,b) shows the TEM images of blends 1 and 2, respectively. For both cases, images are marked as control (before processing, that is, cycle 0), cycle 1, cycle 2, cycle 5, and cycle 10, respectively. All images were recorded in the bright-field mode and at a magnification of 23,500×. In blend 1, PPE was in a discrete phase with a domain size of 1.5 μm, whereas in blend 2, PPE was in a continuous phase. As depicted in Figure 4, recycling did not significantly affect the morphology of the blends, even after 10 cycles. The stable morphology led to the retention of most of the mechanical properties.

Molecular weight determination

Figure 5 summarizes the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) data measured for
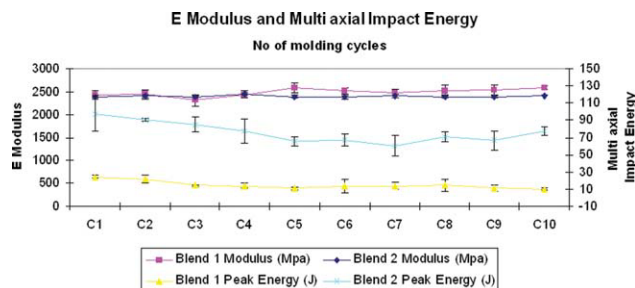

Figure 3 E modulus and multiaxial impact data for blends 1 and 2 (C = cycle). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
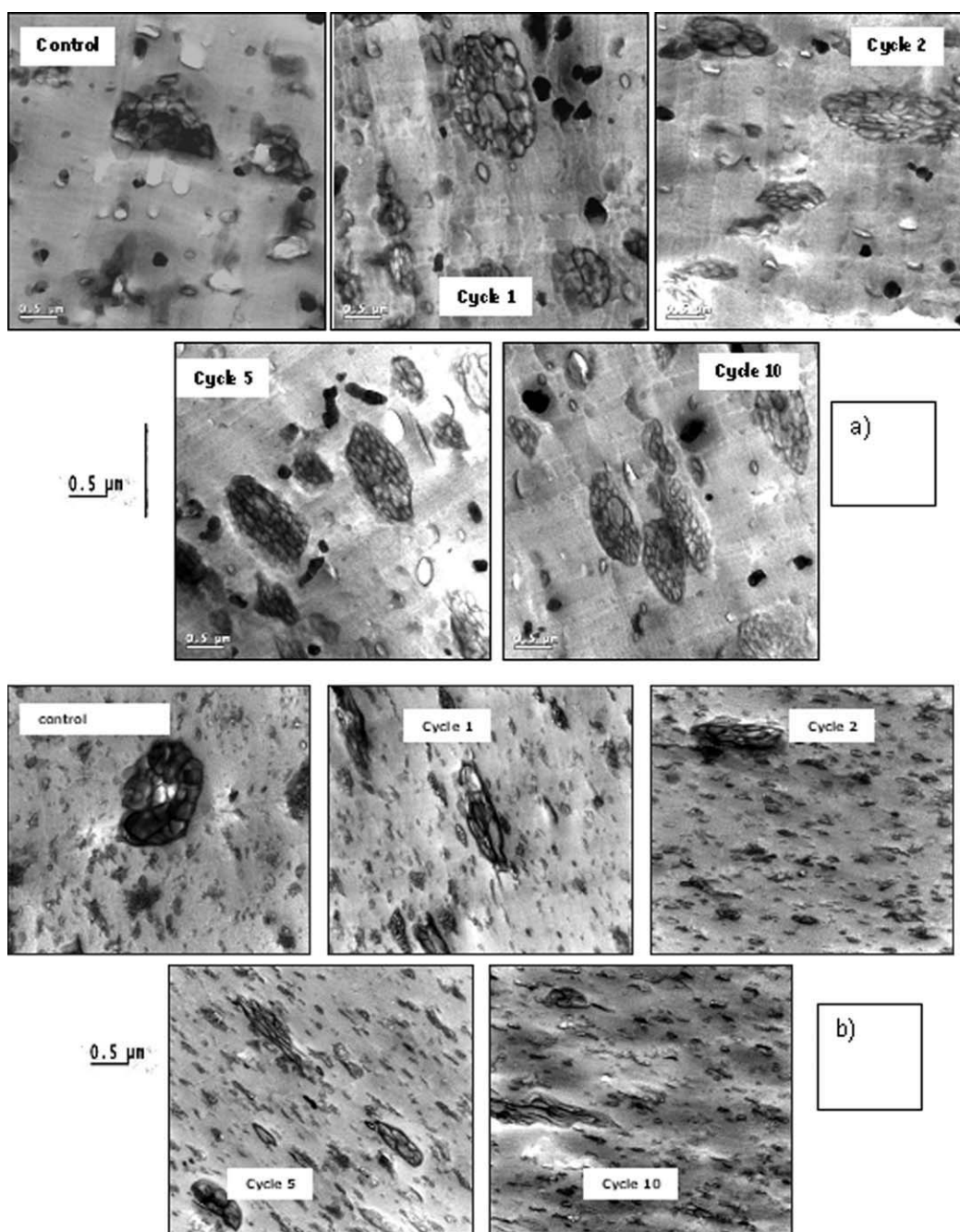
Figure 4 TEM micrographs of (a) blend 1 and (b) blend 2.

the control sample (before processing) and the recycled samples from cycles 1, 5, and 10. The data represent the molecular weight of blend as a whole, not for any individual component. In the case of blend 1, M_n and M_w were in the ranges 27,123–25,686 and 86,328–85002, respectively. PDI was in the range 3.14–3.33. In the case of blend 2, M_n and M_w were in the ranges 27,286–26,265 and 88,876–78,107, respectively. PDI was in the range 2.88–3.36. There was no significant change in the molecular weight data. The result was in line with the mechanical properties. The degradation was not enough to

deteriorate most of the mechanical properties of the blends.

MDSC

In MDSC, T_g of the blends was monitored through the reversible heat flow of the blends. In the case of blend 1, cycles 1, 3, and 8 were analyzed, whereas in the case of blend 2, cycles 1, 3, and 9 were analyzed. The cycles are chosen on the basis of the change in properties observed. The T_g values of the chosen remolding cycles of blends 1 and 2 are shown in
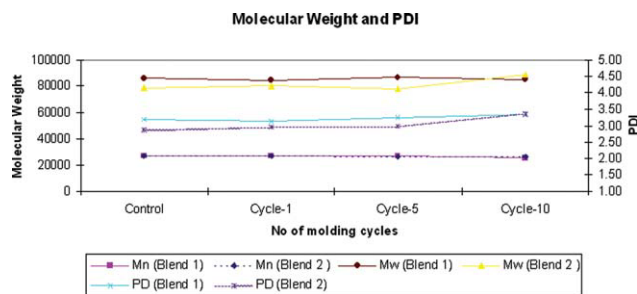
Figure 5 Molecular weight and PDI data for blends 1 and 2 (PD = polydispersity). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figures 6 and 7, respectively. T_g of blend 1 remained in the range 124.52–125.79°C. In the case of blend 2, T_g remains in the range 143.31–145.68°C. No significant change in T_g was observed through recycling. This confirmed that the thermoplastic matrix remained least affected throughout multiple molding cycles.

DMA

The stability of blends 1 and 2 was tested at 260°C. A time-sweep study was conducted at a constant frequency of 1 Hz (6.28 rad/s) with a strain amplitude of 3% for 1800 s. Figure 8 shows that viscosity of both blends remained fairly constant at 260°C throughout the test. This indicated that there was no significant degradation of the molecular weight in the blends.

Viscosity as a function of the shear rate

Viscosity as a function of shear rate was measured to determine the effect of multiple molding cycles on the flow properties of the blends. Both of the blends were sampled from cycles 1, 3, 5, 7, and 10. The experiment was done over wide range of shear rate, 115–2300 s^{-1}, and measurement was done at
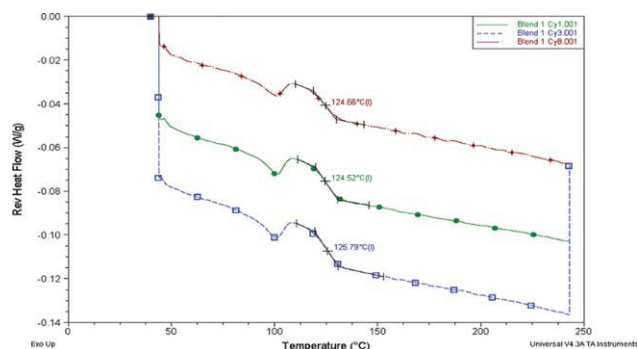

Figure 6 Thermogravimetric data for blend 1 (Cy = cycle). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
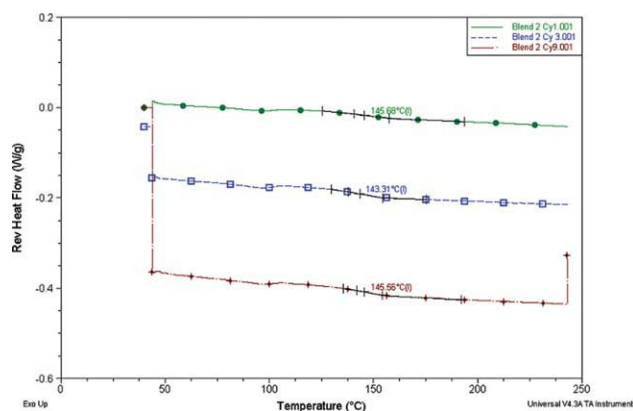
Figure 7 Thermogravimetric data for blend 2 (Cy = cycle). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

115, 230, 575, 1150, 1500, and 2300 s^{-1}. Table IV represents the viscosity data of both of the blends studied. In the case of blend 1, the viscosities were found in the ranges 794–869 and 121–126 Pa s at the lowest shear rate (115 s^{-1}) and the highest shear rate (2300 s^{-1}), respectively. In the case of blend 2, the viscosities were in the ranges 1993–2368 and 437–506 Pa s at the lowest shear rate (115 s^{-1}) and the highest shear rate (2300 s^{-1}), respectively.

Effect on the color

No change in color was observed until six molding cycles had occurred. Visually, there was no difference in the molded part of the first six cycles. Aesthetically, the recycled material was as good as virgin material. However, the seventh cycle showed a lower gloss on the molded sample as compared to that of the first six cycles. The gloss gradually decreased until the tenth cycle. Although there was no significant change in color, the decreased
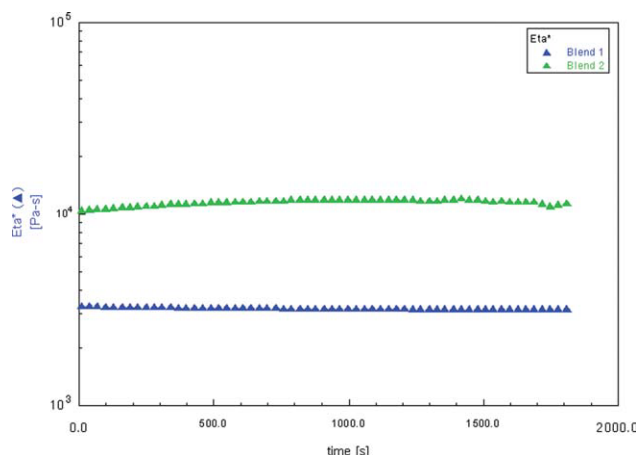

Figure 8 Time-sweep data for blends 1 and 2 (Eta* = Complex Viscosity). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
Viscosity as a Function of the Shear Rate

Shear rate (1/s)	Blend 1 viscosity (Pa s)					Blend 2 viscosity (Pa s)				
	Cycle 1	Cycle 3	Cycle 5	Cycle 7	Cycle 10	Cycle 1	Cycle 3	Cycle 5	Cycle 7	Cycle 10
115	794	812	869	831	850	2300	2106	2368	2018	1993
230	528	556	581	559	559	1681	1578	1712	1454	1440
575	305	320	325	319	326	1177	1149	1109	1050	861
1150	196	205	206	200	206	832	809	792	744	606
1500	164	171	171	166	169	701	690	682	634	560
2300	121	126	126	125	125	503	499	506	475	437

intensity of gloss gave poor aesthetics. These observations were true in both blends.

CONCLUSIONS

The effect of postindustry recycling on the properties of PPE blends was studied in detail with multiple simulated molding cycles.

Most of the mechanical properties were retained in essentially unaltered form, even after 10 molding cycles. We confirmed this by performing a two-sample t test, which proved that, statistically, the values were not different. This correlated well with the unperturbed morphology of the compositions before and after recycling, as observed by TEM analyses on the recycled samples. The molecular weight was found to be unaffected; this supported other findings. It showed that there was no significant drop in M_n or M_w of the blends after 10 molding cycles. Thermal analysis showed that there was no change in T_g of the compositions, even after 10 molding cycles. A capillary rheometer study showed no considerable change in the viscosity of the blends upon recycling. A similar observation was also made in the time-sweep experiment done on the parallel-plate rheometer.

Both of the blends showed similar behavior in the recycling study. The probable reason for drops in the multiaxial impact energy and strain at break was the limited aging of the rubber present in high-impact polystyrene. The matrix seemed to remain comparatively unaffected after 10 molding cycle, but aging of the dispersed rubber domain could have led to drops in the strain at break and multiaxial impact properties. Plausibly, the extent of degradation of rubber was not so severe as to affect the morphology; however, the extent of degradation was sufficient to affect those properties that were governed by the rubber domain, for example, the multiaxial impact. Further detailed study in this area is required to confirm the notion.

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