

Effect of Recycled Polypropylene on Polypropylene/High-Density Polyethylene Blends

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ABSTRACT: The effect of recycled PP on incompatible blends of virgin polypropylene (PP) and high-density polyethylene (HDPE) was studied. Recycled PP from urban solid waste was extracted with methyl ethyl ketone and the compatibilizing action of the product before and after extraction was examined. The characterization of the recycled PP was performed by FTIR, NMR, and DSC analyses. Mechanical properties of the blends were evaluated. The results showed partial compatibility of the blend components, reflected in the improvement of the tensile strength and elongation. Best results were achieved by the addition of extracted recycled PP on the 50/50 PP/HDPE blends.
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Key words: polymer recycling; degraded PP; PP/HDPE compatibilization

INTRODUCTION

About half the weight of the total polymers produced in the world is composed of polyolefins. Those are the cheapest plastics and are largely used for short-term packaging. Because of the low density and the hollow shape of the items, they emerge both in waters and landfills, provoking considerable environmental impact.^{1,2} Two different routes are frequently used for postconsumer plastic recycling: a single-step process, based on processing the mixture of plastic residues in heavy-duty machinery, or a multistep process, involving plastics fractionation before the final processing. The simple reprocessing of mixed

polyolefin waste usually leads to products with low mechanical properties because these polymer mixtures are frequently incompatible and contaminated by impurities.³

Polypropylene (PP) is gradually replacing some materials in commercial goods because of its favorable characteristics of price, density, and versatility. Although this polymer is highly susceptible to photodegradation, it is commonly used in artifacts that will be exposed to environmental degradation, such as packaging items and automobile bumpers. The radiation energy is absorbed by the polymer, causing the removal of the hydrogen atoms linked to tertiary carbon atom groups and the reduction of molecular weight, with modification of the chemical structure.^{4–6}

It is well known that the incompatibility of PP with both low-density polyethylene (LDPE) and high-density polyethylene (HDPE) causes loss of the mechanical properties of the blend. Recycled LDPE and HDPE are difficult to completely separate from the other polyolefins because of their close densities and similarity of physical proper-

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ties. So, the recycled product may contain fragments of PP as contaminant.^{4,7} The compatibilization of the multiple composition mixtures may overcome this problem to a certain extent.⁸ This may be attained either by melt-processing techniques, using *in situ*-formed copolymers, or adding copolymers, or else incorporating low molecular weight compatibilizing compounds.⁹ The present study reports the investigation of the compatibilizing effect of environmentally degraded PP on the mechanical properties of PP/HDPE blends.

EXPERIMENTAL

Materials

Polypropylene (PP) was supplied by PPH Companhia Industrial de Polipropileno (Rio Grande do Sul, Brazil): type H503; specific gravity (sp. gr.), 0.90 g/cm³; melt flow index (MFI), 2.9 g/10 min.

High-density polyethylene (HDPE) was supplied by Polialden Petroquímica (Bahia, Brazil): type BT 003; sp. gr., 0.95 g/cm³; MFI, 0.3 g/10 min.

Postconsumer rigid plastic waste was supplied by the Municipal Company of Urban Solid Waste (COMLURB, Rio de Janeiro, Brazil).

Methods

The pretreatment of postconsumer raw material consisted of industrial grinding, washing with water, and drying. A representative sample of the resulting flakes was taken for use in the present work. About 50 kg of PP fragments were separated from other polymers by floating successively in water and hydroalcoholic solution (sp. gr., 0.91 g/cm³) in 200-L tanks and dried at room temperature (30°C).^{2,3} Recycled PP (PPr1) and the blends were prepared in a Brabender single-screw extruder (Model GN F106/2), with L/D 25 and screw diameter 19 mm; screw rotation speed, 100 rpm at 190, 200, 210, and 215°C. The extrudates were cooled at 25–30°C and reduced to particles less than 2.7 mm in length. PPr1 was ground and extracted by methyl ethyl ketone (MEK) for 60 h. The extracted PP (PPr2) was also used in the mixtures. For the ternary blends, up to 5% of either PPr1 or PPr2 was incorporated onto a basic 50/50 PP/HDPE mixture.

Number-average molecular weight (\overline{M}_n) and weight-average molecular weight (\overline{M}_w) were determined by GPC in a Waters 150-CV+ (Waters Instruments, Rochester, MN), using as effluents trichlorobenzene for polymers and chloroform for residue extraction. FTIR spectra were taken in a Perkin–Elmer 1720 spectrometer (Perkin–Elmer, Foster City, CA). Solid-state NMR spectra were obtained in a Varian VXR 300 (Varian Associates, Palo Alto, CA), frequency 75.4 MHz, pulse 90°. DSC data were determined in a Perkin–Elmer model DSC-7, using 10°C/min for heating and 2°C/min for cooling. Melting temperature (T_m) and crystallization temperature (T_c) analyses were run from 30 to 200°C. TGA analyses were carried out in a Perkin–Elmer 7 Series Thermal Analysis System, using 10°C/min heating rate under nitrogen, from 100 to 550°C. MFI tests were performed in an Emic IFT-315, according to ASTM D1238 (procedure A, conditions E and L). Specific gravity measurements were taken according to ASTM D792. Mechanical tests were carried out in an Instron tensile tester (Model 4204), 1-kN cell, cross-head speed of 1 cm/min, gauge length of 2.225 cm, according to ASTM D1708. Samples were cut from 0.1 × 15.0 × 15.0-cm plates, molded in a Carver press at 200°C and 22.2 kN, for 5 min.

RESULTS AND DISCUSSION

The total loss in the pretreatment of the postconsumer plastic waste by industrial grinding, washing, and drying was about 10% in weight. From this material, the polyolefin fraction was removed by floating in water. The PP fraction obtained by the sink-float procedure represented 10% in weight of the polyolefin residues.

The molecular weight and the polydispersity of PPr1 ($\overline{M}_w = 38,500$; $\overline{M}_w/\overline{M}_n = 3.5$) were lower than those for a virgin typical PP sample ($\overline{M}_w = 172,500$; $\overline{M}_w/\overline{M}_n = 5.0$). This result indicates that the recycled material should have been exposed to environmental/thermal degradation, involving mainly macromolecular chain cleavage, probably with oxidation to some extent. There was a large increase in the melt flow index for PPr1 (14.8 g/10 min) compared to that for PP (2.9 g/10 min). On the other hand, PPr2 did not exhibit significant differences in the molecular weight and polydispersity ($\overline{M}_w = 45,500$; $\overline{M}_w/\overline{M}_n = 2.2$) compared to PPr1 values. This shows that the extensive extraction with solvent did not

Table I Thermal and Mechanical Analyses of Virgin and Recycled Polyolefins

Material Characterization	PP	HDPE	PPr1	PPr2
Melting temperature T_m (°C)	166	139	163	163
Crystallization temperature T_c (°C)	117	121	128	128
Degradation temperature T_{onset} (°C)	440	470	443	436
Tensile strength at yield				
Stress (MPa)	36	29	28	29
Elongation (%)	13	11	14	9
Tensile strength at rupture				
Stress (MPa)	35	21	27	29
Elongation (%)	640	630	523	601

cause any substantial damage in the polymer molecule.

The extraction of polar contaminants, originating from the unremoved food residues in PPr1, resulted in a small amount of a waxy extract (1.5%; $\overline{M}_w = 725$; $\overline{M}_w/\overline{M}_n = 1.2$), remaining as an apparently unaffected powder residue (PPr2). The extract showed monodispersity, which could be expected for a nonpolymeric material.

The results of the thermal and mechanical tests performed on virgin and recycled polyolefins are shown in Table I. The corresponding values for binary and ternary polyolefin mixtures are presented in Table II. T_m and T_c confirmed the expected composition of PPr1 as polypropylene. DSC measurements on the binary 50/50 PP/HDPE blend, which are incompatible within that range, showed two peaks for T_m as well as for T_c . HDPE, which has a much higher degree of crystallinity than that of PP, was more affected by the presence of the second polymer, which can be seen by the changes in both T_c and T_m values. The differences in T_c were greater than those in T_m .

When 1 wt % of recycled PP is added to a binary 50/50 PP/HDPE mixture, an unexpected decrease in the HDPE crystallization temperature was observed, whereas for PP, T_c was kept constant. The increase up to 5% of recycled PP as an additive to the 50/50 PP/HDPE blend did not show any further significant effect. This suggests that the presence of the added PPr1 or PPr2 influenced the morphology of HDPE much more than that of PP. As this effect is shown by both PPr1 and PPr2, independently of the proportion within the range 1 to 5%, a qualitative effect is suggested, probably as a result of the chemical modification of the degraded polymer molecule, without any participation of the waxy residues.

The TGA results did not show significant differences in the degradation temperature (T_{onset}) for PPr1, PPr2, and virgin PP, which suggests that there was not a large modification in the molecular structure of the recycled polymer. On the other hand, for HDPE, T_{onset} is much higher (470°C); the higher degree of crystallinity is associated with regular polymethylene chains, with-

Table II Thermal and Mechanical Analyses of Polyolefin Blends

Material Characterization	PP/HDPE/PPr1				PP/HDPE/PPr2	
	50/50/0	50/50/1	50/50/2	50/50/5	50/50/2	50/50/5
Melting temperature T_m (°C)	165; 136	165; 135	164; 135	165; 135	163; 134	164; 135
Crystallization temperature T_c (°C)	122; 128	122; 125	122; 125	121; 125	122; 124	122; 124
Degradation temperature T_{onset} (°C)	451	452	444	456	454	450
Tensile strength at yield						
Stress (MPa)	—	—	—	—	28	28
Elongation (%)	—	—	—	—	14	11
Tensile strength at rupture						
Stress (MPa)	21	22	30	30	24	27
Elongation (%)	4	5	6	8	21	12

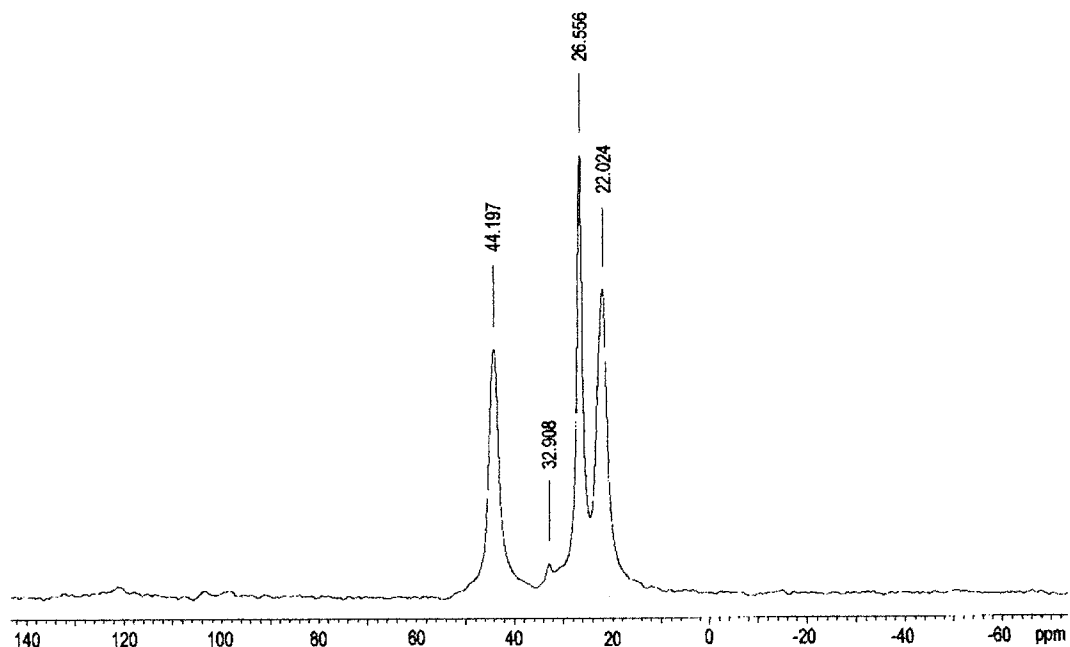


Figure 1 NMR spectrum of PPr1.

out branching. The binary mixture showed an intermediate temperature (451°C), and the same thermal behavior was observed for the ternary mixtures PP/HDPE/PPr1 and PP/HDPE/PPr2. This may be taken as an indication of preserved chain structures in the blends.

The NMR spectra of PPr1 and PPr2 are shown in Figures 1 and 2, respectively. Besides the PP characteristic signals, an additional signal at 33 ppm, associated with unsaturated ethylenic, probably vinyl terminal groups and/or vinylene units at the middle of the chain, were found. FTIR

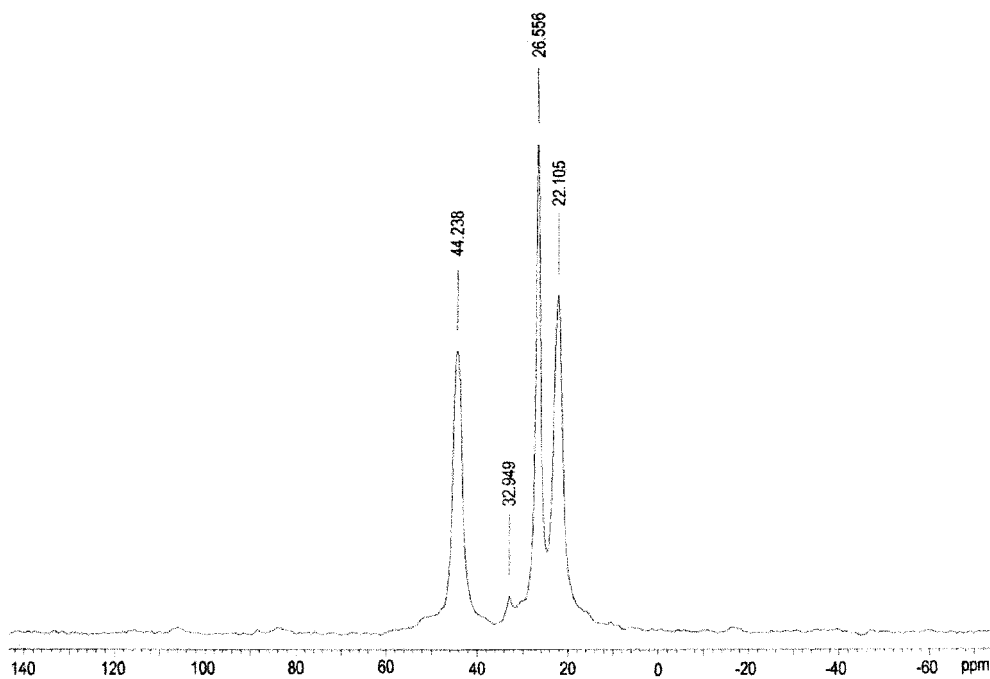


Figure 2 NMR spectrum of PPr2.

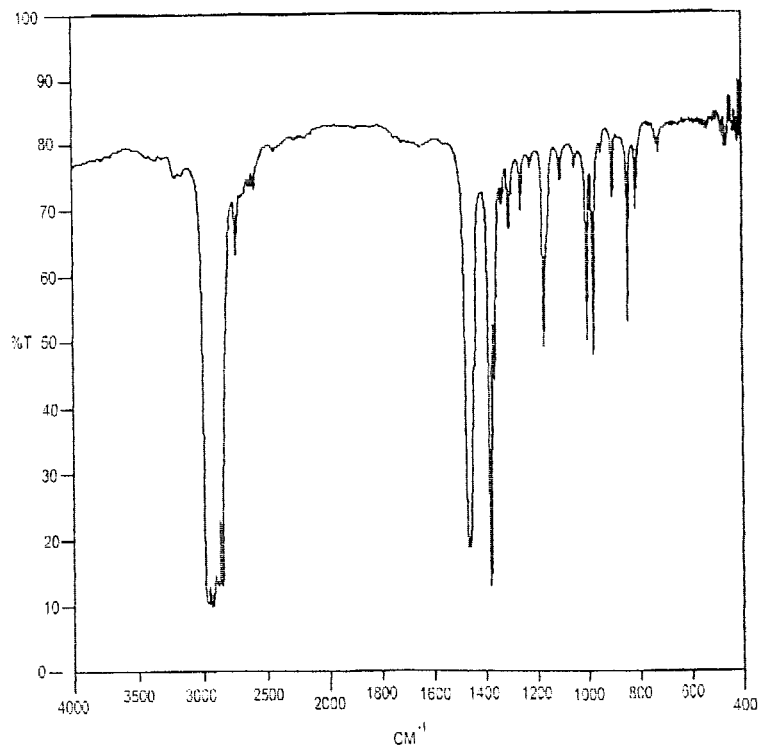


Figure 3 FTIR spectrum of PPr1.

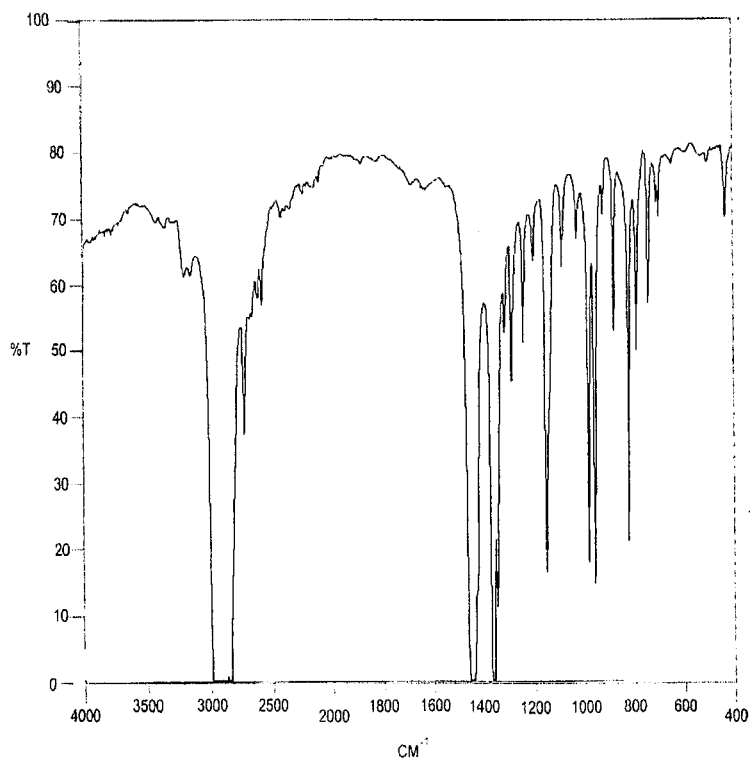


Figure 4 FTIR spectrum of PPr2.

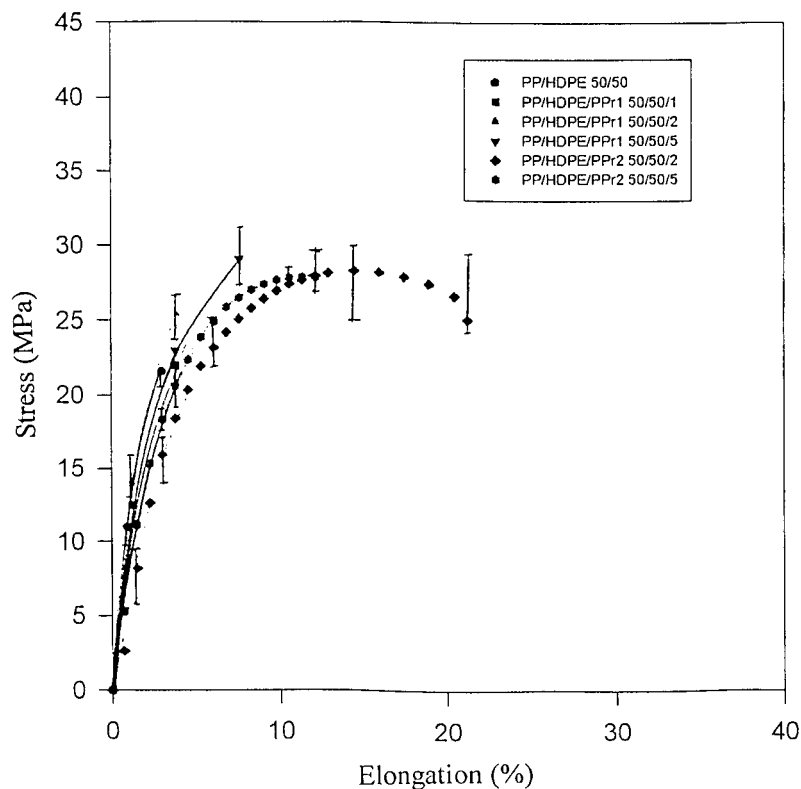


Figure 5 Tensile strength tests on polyolefin blends.

spectra of PPr1 and PPr2 are presented in Figures 3 and 4, respectively. The recycled materials did not show any carbonyl absorption, either before or after extraction with MEK, which indicates that the PP degradation was not oxidative; the degradation should have caused chain cleavage and unsaturation. As a consequence, the apolar character of the PP molecule was not changed, maintaining its affinity to other polyolefins, which is an essential condition for the compatibility action.

The mechanical properties of the polyolefin blends listed in Table II are plotted in Figure 5. Clearly shown is the incompatibility of the 50/50 PP/HDPE blend, causing the premature break of the test samples before reaching the yield point. The increase of tensile strength and elongation at rupture of ternary blends as compared to that of the binary blend indicated some compatibilizing action of PPr1 on the system components. The ternary blend samples broke before the yield point. Small quantities of PPr1 were enough to improve the mechanical properties of the blends under investigation. The addition of PPr2 on binary blends was more effective, as far as compatibilizing action was concerned, which could be ex-

plained by the absence of polar contamination in the extracted, recycled material. The ternary blend samples reached and surpassed the yield point before breaking, confirming the compatibilization action of the recycled PP on incompatible 50/50 PP/HDPE blends.

CONCLUSIONS

The experimental results suggest that the degradation that occurred in PP molded, postconsumer artifacts after exposition to natural, uncontrolled outdoor conditions provided spontaneous, nonoxidative chemical modifications on PP molecules, which brought a certain compatibilizing action toward 50/50 PP/HDPE incompatible blends. We did not find any report on this effect in the literature.

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