Journal of Thermal Analysis and Calorimetry, Vol. 59 (2000) 425–432

Dedicated to Prof. Edith A. Turi in recognition of her leadership in eduction

THERMAL ANALYSIS APPLIED TO DISCARDED CAR BUMPERS

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Abstract

The thermal properties of discarded bumpers from standard grade automobiles were compared to the corresponding data obtained from binary and ternary blends of virgin polyolefins of composition similar to the recycled product. After grinding and separating by specific gravity, the recycled material was identified by DSC, DMTA, TGA and ^{13}C NMR. We found that it contains three polymers: polypropylyene (PP) as the major component, ethylene, propylene, diene methylene terpolymer (EPDM) and a small amount of high density polyethylene (HDPE).

Keywords: car bumpers, recovered plastic, recycled plastic, thermal properties

Introduction

The interest in the recycling of materials, particularly plastics, has increased continuously as concern on Nature preservation extends throughout the world. Two good reasons for this concern are the desire not to waste resources and the disposal of scrap materials which may otherwise pollute the environment [1]. The recyclability of car components has become as important as that of packaging waste. For many car makers, this is a requirement that needs to be met before they will consider using some materials [2]. Car manufacturers have increasingly turned to polymer materials as a mass reduction method. Among the plastics used in vehicles, PP bumpers have been targeted for recycling because of their large size [3]. PP has been used in increasing ratios in the molding compound for bumpers due to its capability for manufacture and recycling [4]. Thermoplastic polyolefin (TPO) compounds, which are blends of elastomeric ethylene-propylene (EP) or ethylene, propylene, diene methylene terpolymers (EPDM) with PP, are expanding their usage specially in bumpers, owing to their low cost and capability of recycling. Recycled plastics from bumpers are finding applications in several areas, even as new bumpers [2, 5].

In the present work, the identification of the recycled material from used car bumpers was carried out by DSC, DMTA, TGA and ^{13}C-6NMR, due to the similarity of the

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1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

polyolefin structures. The results were compared to the corresponding data obtained from binary and ternary blends of virgin polyolefins of similar composition.

Experimental

Materials

Polypropylene (PP), type H301, supplied by OPP Petroquimica S.A., Brazil; specific gravity, 0.91; MFI, 10 g 10 min^{-1};

Ethylene, propylene, diene methylene terpolymer (70/25/5) (EPDM), type Keltan 57C, supplied by DSM Elastomeros Brasil Ltda, Brazil; specific gravity, 0.86; Mooney viscosity, 61;

High density polyethylene (HDPE), type BT003, supplied by Polialden Petroquimica S.A., Brazil; specific gravity, 0.94; MFI, 0.3 g 10 min^{-1};

Plastic waste from used car bumpers from five different manufacturers, supplied by Gerauto Ltda, Rio de Janeiro, Brazil.

Methods

Plastic waste from used bumpers (about 60 kg) was submitted to cutting, washing with water, drying and grinding, resulting small fragments (under 2.0 cm larger dimension). A representative sample was taken according to ABNT NBR 10007 method [6]. The fragments were separated by floating successively in water and two ethanol solutions (specific gravity, 0.94 and 0.91, respectively) in 150-liter tanks. The fractions were dried over newspaper sheets on the floor at room temperature (30°C) [7]. The polyolefin compounds were prepared in a Haake Rheocord 9000 equipment with a Rheomix 600 roller rotor mixer at 60 rpm. The processing time and temperature were chosen according to the material. All blends were processed at 180°C for 5 min. The selected compositions were 90/10, 85/15, 80/20 and 75/25 PP/EPDM binary blends, and 85/5/10, 80/10/10 and 70/20/10 PP/HDPE/EPDM ternary blends.

DSC data were determined in a Perkin Elmer model DSC-7 equipment, using 10 K min^{-1} heating rate. T_m and T_c were run from 30 to 200°C. TGA analyses were carried out in a Perkin Elmer 7 Series Thermal System, using 10 K min^{-1} heating rate under N_2, from 30 to 700°C. DMTA data were determined in a Polymer Laboratories model PL MKIII equipment, using 2 K min^{-1} heating rate, frequency, 1 Hz, from –150 to 60°C. Specific gravity measurements were taken according to ASTM D792. Solid-state ^{13}C NMR spectra were obtained in a Varian VXR 300 equipment, frequency 75.4 MHz, pulse 90°.

Results and discussion

Pre-treatment of the plastic waste from used car bumpers by industrial grinding resulted in 5% loss in mass. Most of the resulting material was separated by floating in water, which was an indication of their polyolefin nature. There was no separation in 0.94 and 0.91 g cm^{-3} ethanol solutions; the only fraction obtained had specific gravity under 0.91. These results showed that the discarded car bumpers were mostly composed of PP.

Table 1 Thermal characteristics of polyolefins – DSC and TGA

PP/HDPE/EPDM blends/w/w/w	T_m/°C			T_c/°C	T_{onset}/°C
100/0/0	162; 166	–	–	111	438
0/0/100	–	–	–	–	438
0/100/0	–	135	–	116	471
90/0/10	166	–	–	115	454
85/0/15	165	–	–	113	454
80/0/20	163	–	–	113	456
75/0/25	162	–	–	112	456
85/5/10	166	129	–	114	452
80/10/10	166	130	–	114	455
70/20/10	168	134	–	115	453
Recycled material	159; 163	127	–	114	440

Table 2 Thermal characteristics of polyolefins – DMTA

PP/HDPE/EPDM blends/w/w/w	T_g/°C			tanδ		
100/0/0	8	–	–	0.0717	–	–
0/0/100	–	–	–39	–	–	0.5179
0/100/0	–	–115	–	–	0.0514	–
90/0/10	11	–	–49	0.0840	–	0.0411
85/0/15	8	–	–50	0.0843	–	0.0447
80/0/20	8	–	–51	0.0785	–	0.0576
75/0/25	8	–	–51	0.0778	–	0.0641
80/10/10	7	–126	–47	0.0801	0.0178	0.0454
70/20/10	8	–127	–48	0.0807	0.0207	0.0446
Recycled material	7	–126	–57	0.1022	0.0281	0.0746

We tried to correlate the expected composition of the recycled material to the known binary and ternary blends by thermal methods of analysis. The thermal characteristics of the polyolefin materials are shown in Tables 1 and 2. By DSC, there was a definite similarity in the T_m and T_c temperatures of the virgin PP (T_m: 162° and 166°C; T_c: 111°C) and the recycled material (T_m: 159° and 163°C; T_c: 114°C). It is interesting to notice that both materials, virgin PP and the complex blend from discarded car bumpers, showed two melt temperatures, which may be attributed to the monoclinic crystal α-form of PP [8]. The crystalline portion of the polymer may be considered as a multi-component system which contains a variety of lamellae of different thickness; each group of lamella melts at the same temperature [9]. These results confirm the specific gravity indication that PP was largely present in the car bumpers.

The DSC curves of the discarded material are presented in Fig. 1. An additional melt peak is shown at 127°C; it may be ascribed to HDPE as a component of the car bumpers recycled composition. As expected, DSC did not reveal the presence of EPDM, which is an amorphous, random terpolymer; however, this does not exclude the presence of EPDM in the recycled material. It will be investigated by ^{13}C NMR.

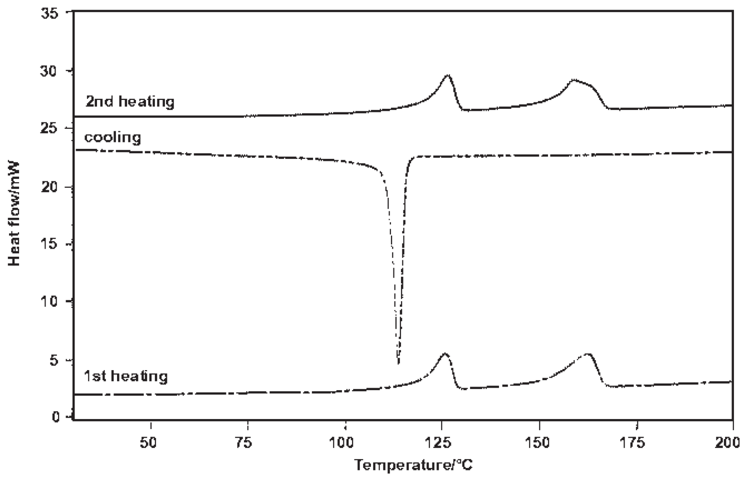

Fig. 1 DSC curves of the recycled material

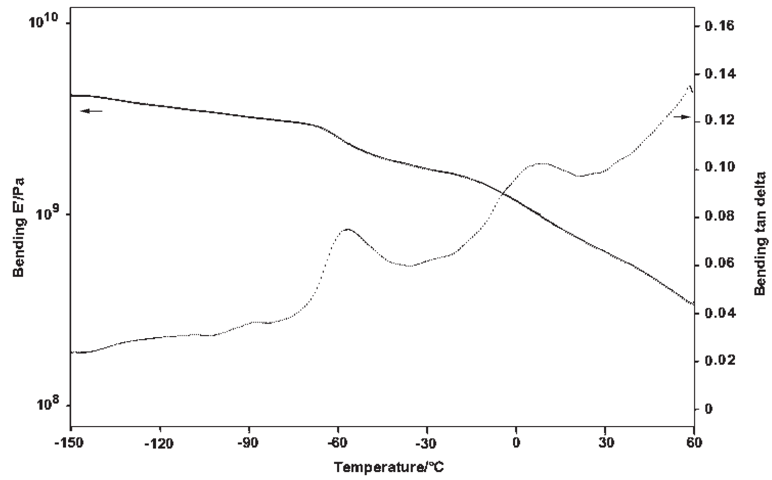

Fig. 2 Tanδ *vs*. temperature for the recycled material

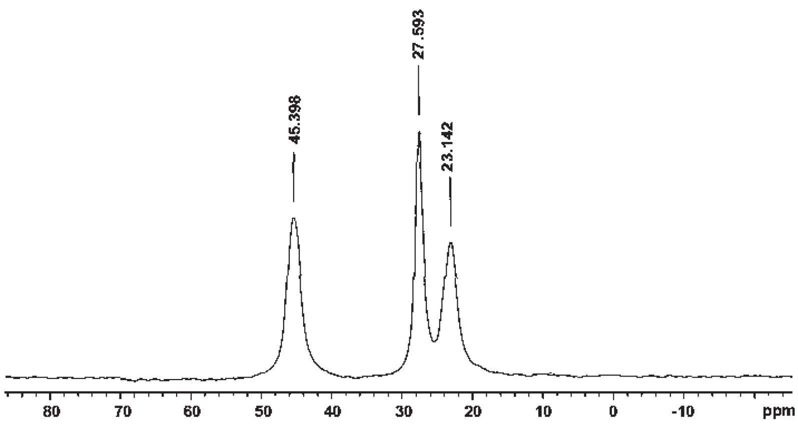

Fig. 3 ^{13}C NMR spectra of PP

Because of the possibility of HDPE being present in the car bumper compositions, the investigation on the behavior of PP/EPDM binary and PP/HDPE /EPDM ternary mixtures was undertaken. The binary blends showed crystalline peaks corresponding to PP (T_m: 162–166°C; T_c: 112–113°C). The ternary blends, however, besides the melt peaks corresponding to PP (T_m: 166–168°C) and HDPE (T_m: 129–134°C), presented also one crystallization peak (T_c: 114–115°C), which could not be ascribed to any of the polymer components. The presence of a small amount (10%) of EPDM changed the HDPE melt behavior, although did not apparently interfere on the PP results. This is reasonable because ethylene chemical units are dominant in EPDM constitution.

Thus, the experimental results suggest that the three main polymeric components of the discarded car bumpers are PP, EPDM and HDPE.

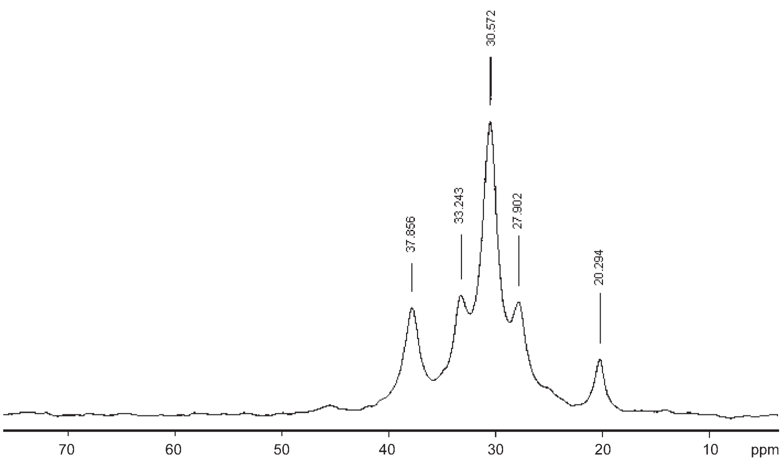

Fig. 4 ^{13}C NMR spectra of EPDM

An indication on structural modifications of the recycled material could be given by TGA. However, no marked difference was found in the TGA curves of virgin and recycled materials as well as in the binary and ternary mixtures. Table 1 shows that the degradation temperatures of PP, EPDM and recycled material were similar; HDPE showed higher values, as expected because of the regular polymethylene chains, without branches. The blends showed intermediate values. The inconclusive results may be due to a balance of scission and crosslinking of the macromolecular chains.

The dynamic mechanical thermal data of polyolefins are listed in Table 2. Virgin materials PP, EPDM and HDPE showed T_g at 8, –39 and –115°C, respectively. The binary blends PP/EPDM, as expected, showed two peaks; T_g of PP did not change, but T_g of EPDM shifted to lower temperatures. The addition of small amount of EPDM (10%) was sufficient to decrease its T_g in the blends to –49°C and remained constant above this percentual. These results suggest a certain degree of interaction between the polymer chains. Further studies by SEM and tensile/impact properties confirmed this compatibility. In the ternary blends, T_g of PP kept constant, but T_g's of HDPE and EPDM were lowered. In the 70/20/10 PP/HDPE/EPDM blend, T_g's shifted to –128 and –48°C, respectively. The recycled material showed the same behavior as the virgin ternary blends. Hence, the presence of HDPE interferes with the previously observed interaction of PP and EPDM, as shown by SEM and tensile results. Despite of it, impact behavior was markedly improved in the ternary blends, even in the presence of a minor proportion of HDPE (5%) [7, 10].

Figure 2 shows the variation of tanδ *vs*. temperature for the recycled material. As expected, tanδ values confirmed the crystalline nature of PP and HDPE, and the amorphous characteristic of EPDM (Table 2). In the PP/EPDM binary blends, the increase in EPDM content provoked, as expected, an increase in its tanδ. The higher values of tanδ observed in the recycled material when compared to the corresponding

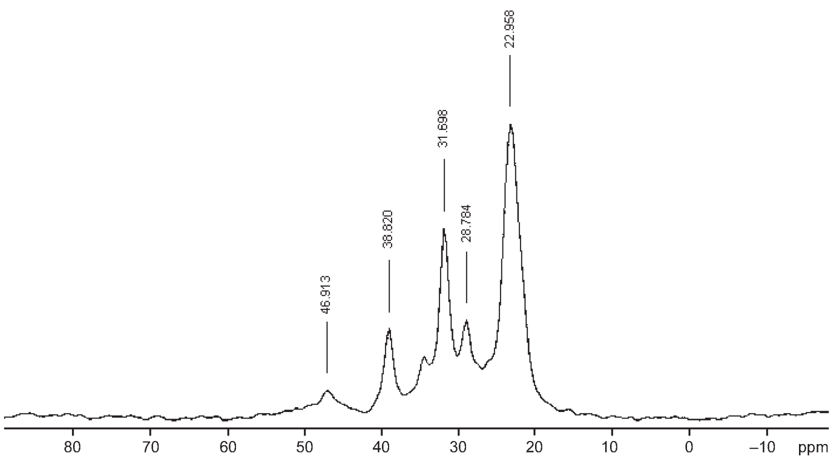

Fig. 5 ^{13}C NMR spectra of the recycled material

virgin composition, may be explained by the increase of the amorphous phase in the discarded bumpers, due to natural ageing of the polymer components.

Figures 3, 4 and 5 show ^{13}C NMR spectra of PP, EPDM and the recycled material, respectively. The assignments of the chemical shift are listed in Table 3 and confirm the presence of EPDM. HDPE cannot be confirmed by NMR. However, X-ray diffraction in the recycled material confirmed the presence of HDPE [7, 10].

Table 3 Chemical structure of polyolefins – ^{13}C NMR

Material	Chemical group	Chemical shift δ/ppm
PP	CH_2	45.4
	CH	27.6
	CH_3	23.1
EPDM	CH	37.9, 27.9
	CH_2	33.3, 30.6
	CH_3	20.3
Recycled material	CH_2	45.4, 33.3, 30.6
	CH	37.9, 27.9, 27.6
	CH_3	23.1, 20.3

In fact, the industrial use of PP/HDPE/EPDM compositions confirm its satisfactory performance in car bumpers and corroborate the need of EPDM as an adequate compatibilizer for the otherwise incompatible PP/HDPE blends.

Conclusions

Thermal analysis was applied to the material used in discarded car bumpers provenient from standard grade automobiles of different makes. It was found that the recycle polymer composition consists of PP, EDPM and HDPE polymer blend. DSC and DMTA analyses confirmed the presence of PP and indicated HDPE and EPDM. In addition, EPDM was characterized by ^{13}C NMR while HDPE was confirmed by wide-angle X-ray diffraction (WAXS).

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Authors acknowledge financial help of the Brazilian funding agencies CNPq (National Council of Scientific and Technological Development) and CAPES (Coordination of University Level Staff Development).

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