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ABS/HIPS blends obtained from WEEE: Influence of processing conditions and composition

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ABSTRACT: The recycling of acrylonitrile–butadiene–styrene (ABS) and high-impact polystyrene (HIPS) from postconsumer electronic equipment housing was investigated. A preliminary study of shot size and particle size effects on the mechanical properties of ABS/HIPS (50/50) blends obtained directly via injection molding was conducted. Injection-molded specimens of ABS/HIPS blends, obtained at different compositions with or without previous extrusion, were subjected to mechanical, thermal, and morphological testing. Preliminary studies showed that a smaller particle size resulted in higher tensile and impact strength, regardless of the shot size used during injection molding. ABS/HIPS blends obtained using previous extrusion presented a slight increase in Young's modulus and a decrease in elongation at break and impact strength. The increase in glass-transition temperature related to the Polybutadiene (PB) phases of these blends indicated a possible increase in crosslinking structures during extrusion. In addition, these blends showed a coarse and heterogeneous morphology, suggesting that ABS did not completely mix with HIPS. Compared to processing conditions, the blend composition appeared to have a much stronger effect on the mechanical properties. The results obtained suggest the possibility of obtaining ABS/HIPS blends directly via injection molding as long as small ground particles are used. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43831.

KEYWORDS: blends; mechanical properties; recycling

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INTRODUCTION

The production of electrical and electronic equipment (EEE) is one of the fastest growing areas in the manufacturing industry. As a result, huge amounts of plastic waste from end-of-life electrical and electronic equipment (WEEE) are generated every year, creating serious environmental problems.[1] In Brazil, the average projected per capita WEEE generation for the period 2001–2030 is 3.4 kg, with a conservative estimate of 22.4 million tons of WEEE accumulated.[2]

Currently, some work has been carried out to develop different methods that add value to WEEE, and the recycling of polymeric materials can be an alternative.[3] In addition to reducing solid waste, recycling can also reduce the energy required for and the pollution generated in raw materials production.

Polymeric materials used in electronic equipment include PC (polycarbonate), HIPS (high-impact polystyrene), ABS (acrylonitrile–butadiene–styrene), PC/ABS, and PPO [poly(phenylene oxide)]/HIPS blends, as well as PVC [poly(vinyl chloride)] and PE (polyethylene) from cable insulation.[4] Some studies have shown that the two major components used for electronic equipment housing are HIPS (high-impact polystyrene) and ABS (acrylonitrile–butadiene–styrene).[5] The joint content of HIPS and ABS varied from 76 to 84 wt %, indicating the importance of adapting recycling processes particularly to styrene-based plastics.[6] HIPS can be defined as a multiphase system containing a continuous rigid phase (PS) in which rubber particles are dispersed.[7] ABS consists of styrene acrylonitrile (SAN) random copolymer mixed with and partially grafted to polybutadiene rubber.[8] The polybutadiene component tends to form particles within an SAN matrix.

The most common approaches to plastics recycling include incineration to produce energy and mechanical recycling where plastic waste is reused in manufacturing. During mechanical recycling, the plastic waste undergoes a sequence of processing steps that include grinding, washing, and separation of polymer type by density difference.[9] ABS and HIPS have similar densities. Therefore, blending these materials together can be an alternative to facilitate recycling, since separation processes of the different industrial wastes can be very complex and expensive.[10]

Few studies on ABS/HIPS blends have been conducted. Brennan *et al.*[11] studied recycled ABS/HIPS blends at different compositions obtained via batch mixing and observed that tensile

Table I. Compositions of ABS/HIPS Blends Obtained in This Study

Sample	ABS (wt %)	HIPS (wt %)
ABS	100	0
ABS/HIPS 75/25	75	25
ABS/HIPS 50/50	50	50
ABS/HIPS 25/75	25	75
HIPS	0	100

strength and stiffness are reasonably maintained across the composition range while impact strength and ductility decreased with increasing HIPS content. Similar results were observed by Tarantilli *et al.*[12] in ABS/HIPS blends at different compositions prepared using a twin-screw extruder. Arnold *et al.*[4] observed that there are significant effects of the processing route on the morphology of the ABS/HIPS 50/50 blend. The blend obtained via torque rheometer/compression molding presented a coarser morphology and phase separation than the blend obtained via extrusion/injection molding, suggesting that phase separation increases at longer mixing times.

The present work aims to study the recycling of ABS and HIPS from postconsumer electronic equipment housing. A preliminary study of the effect of shot size and particle size on the mechanical properties of ABS/HIPS (50/50) blends obtained directly via injection molding was conducted. Subsequently, injection-molded specimens of ABS/HIPS blends were obtained at different compositions with or without previous extrusion. Mechanical properties were assessed by tensile and impact tests. Significant differences in mechanical properties were assessed by analysis of variance (ANOVA). Thermal properties and the morphology were assessed by means of differential scanning calorimetry and scanning electron microscopy analysis, respectively.

EXPERIMENTAL

Materials

The materials used in this work were ABS and HIPS from postconsumer electronic equipment housing (computers, printers, keyboards, and so on). These materials were kindly provided by CEDIR (Centro de Descarte e Reúso de Residuos de Informática) of São Paulo University (USP), Brazil.

Methods

The materials were identified using the ASTM International Resin Identification Coding System (ASTM D7611/D7611M) and Fourier transform infrared spectroscopy (FTIR) analysis. FTIR spectra were obtained using a Nicolet-560 FTIR spectrometer (Madison, WI, USA). Samples for FTIR analysis were thin films prepared by hot pressing. A resolution of 2 cm^{-1} and 32 scans were used. Subsequently, the materials were separated by polymer type (ABS or HIPS), washed, cut, and ground into two different particle sizes (approximately 3 and 8 mm).

In order to establish the best conditions for obtaining ABS/HIPS blends directly via injection molding, a preliminary study was conducted on the effect of shot size and ground material particle size on the mechanical properties of ABS/HIPS (50/50) blends obtained directly via injection molding.

Preliminary Study: Influence of Injection Molding Conditions. ABS/HIPS 50/50 blend specimens for tensile and impact tests were obtained directly via injection molding by varying shot size (50, 150, 300 mm/s) and particle size (3 and 8 mm), using a Battenfeld (Vienna, Austria) injection-molding machine HM 60/350 (heating cylinder temperature profile: 190–200 °C, injection pressure: 65 MPa, mold temperature: 50 °C). Prior to injection molding, the materials were dried in an air-circulating oven (at 80 °C for 4 h).

ABS/HIPS Blends Obtained at Different Compositions without Previous Extrusion. In order to check the effect of previous extrusion on blend properties, neat polymers (ABS and HIPS) and ABS/HIPS blend specimens for tensile and impact tests were obtained directly via injection molding (Battenfeld HM 60/350) using the same injection conditions (injection pressure: 65 MPa, heating cylinder temperature profile: 190–200 °C, mold temperature: 50 °C). The particle size of the ground material as well as the shot size were defined in the previously described preliminary study. Table I shows the compositions of the ABS/HIPS blends obtained in this study.

ABS/HIPS Blends Obtained at Different Compositions with Previous Extrusion. ABS/HIPS blends were prepared in a Haake PolyLab 900/Rheomix PTW16 twin-screw extruder Haake (Karlsruhe, Germany). The temperature profile ranged from 200 to 190 °C, and the screw speed was 150 rpm. Neat polymers (ABS and HIPS) were subjected to the same processing in order to undergo the same thermomechanical history. Specimens for

Table II. Tensile and Impact Properties of ABS/HIPS (50/50) Blends Obtained Directly via Injection Molding with Varying Shot Size (50, 150, 300 mm/s) and Particle Size (3 and 8 mm)

Particle size (mm)	Shot size (mm/s)	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m)
3	50	2.58 (± 0.06)	33.8 (± 0.9)	10.6 (± 3.0)	6.1 (± 0.0)
	150	2.65 (± 0.15)	34.0 (± 0.7)	16.7 (± 5.9)	6.2 (± 0.1)
	300	2.56 (± 0.04)	33.4 (± 1.1)	13.3 (± 3.0)	6.2 (± 0.2)
8	50	2.57 (± 0.07)	31.2 (± 0.6)	5.2 (± 2.2)	4.4 (± 0.3)
	150	2.54 (± 0.03)	31.3 (± 0.2)	9.6 (± 4.1)	4.6 (± 0.2)
	300	2.55 (± 0.04)	30.9 (± 0.5)	10.1 (± 6.2)	4.5 (± 0.1)

Table III. Analysis of Variance of Mechanical Properties of ABS/HIPS (50/50) Blends Obtained Directly via Injection Molding by Varying Shot Size (50, 150, 300 mm/s) and Particle Size (3 and 8 mm)

Property	Source of variation	Sum of squares	Degree of freedom	Mean square	*F*	*p* value
Tensile modulus	Particle size	13324.67	1	13324.67	2.06	0.16
	Shot size	8292.15	2	4146.08	0.64	0.54
	Interaction	14719.09	2	7359.54	1.14	0.34
Tensile strength	Particle size	49.56	1	49.56	77.68	0.00
	Shot size	1.26	2	0.63	0.99	0.39
	Interaction	0.07	2	0.04	0.06	0.94
Elongation at break	Particle size	206.09	1	206.09	8.75	0.00
	Shot size	146.97	2	73.48	3.12	0.06
	Interaction	19.32	2	9.66	0.41	0.67
Impact strength	Particle size	21.42	1	21.42	495.43	0.00
	Shot size	0.10	2	0.05	1.12	0.34
	Interaction	0.00	2	0.00	0.06	0.94

*F is the ratio of the Model Mean Square to the Error Mean Square

tensile and impact tests were obtained via injection molding using the same conditions as those used for the directly injected specimens. Prior to extrusion and injection molding, the materials were dried in an air-circulating oven at 80 °C for 4 h.

Mechanical and Thermal Characterization. Charpy impact tests were performed using notched specimens according to ASTM D256-D (5.4J pendulum). Tensile tests were performed at room temperature using an Instron 5567 universal tester (Norwood, MA, USA), according to standard conditions (ASTM D-638). Prior to testing, the specimens were conditioned for one week at 23 °C and 50% relative humidity. At least 10 specimens of each material were tested.

Differential scanning calorimetry (DSC) tests were carried out using a TA Instruments calorimeter DSC-Q20 (New Castle, DE, USA). All runs were conducted under nitrogen atmosphere. The samples were heated at a heating rate of 10 °C/min from −140 to 120 °C. DSC data from the first heating cycle were considered.

Morphology Characterization. Impact fracture surfaces of the blends were analyzed by scanning electron microscopy (SEM) using a CamScan model CS3200LV microscope (Cambridge, England). The specimens were coated with gold using an Edwards sputter coater (Crawley, England).

RESULTS AND DISCUSSION

Preliminary Study of the Effect of Shot Size and Particle Size on the Mechanical Properties of ABS/HIPS (50/50) Blends Obtained Directly via Injection Molding

Table II presents the tensile and impact properties of ABS/HIPS (50/50) blends obtained directly via injection molding by varying shot size (50, 150, 300 mm/s) and particle size (3 and 8 mm). The significant differences in the mechanical properties were assessed by analysis of variance (two-way ANOVA with replication), adopting a significance level (Student's *t*-test) of 0.05. Two variables were considered: shot size and particle size. Table III presents the results obtained.

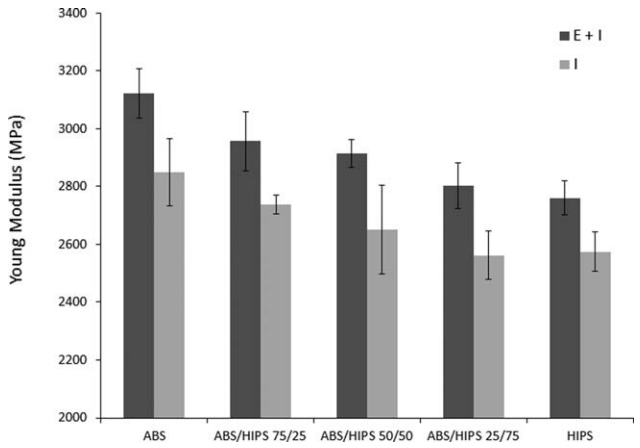

Figure 1. Young's modulus of ABS and HIPS polymers and ABS/HIPS blends.

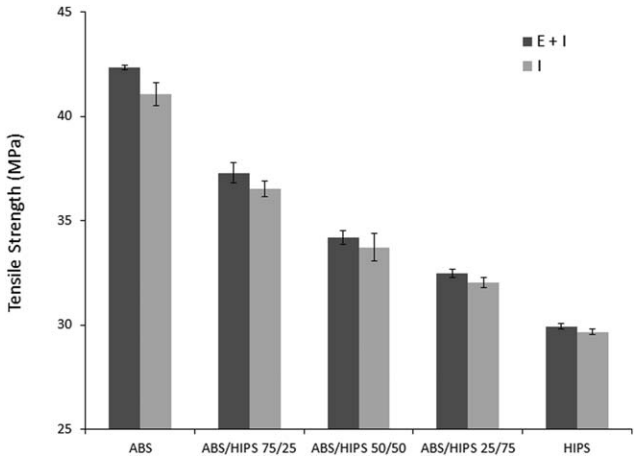

Figure 2. Tensile strength of ABS and HIPS polymers and ABS/HIPS blends.

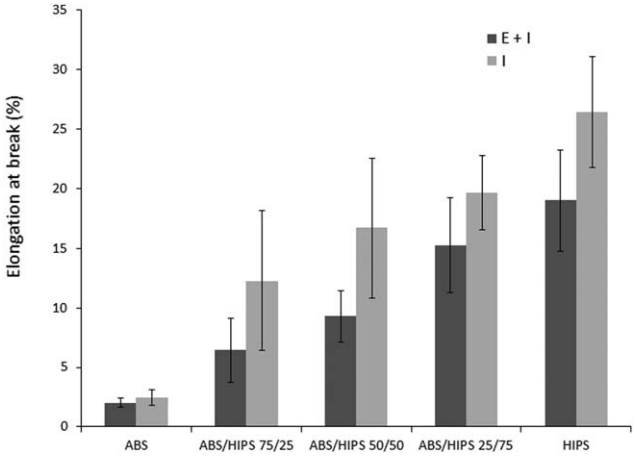

Figure 3. Elongation at break of ABS and HIPS polymers and ABS/HIPS blends.

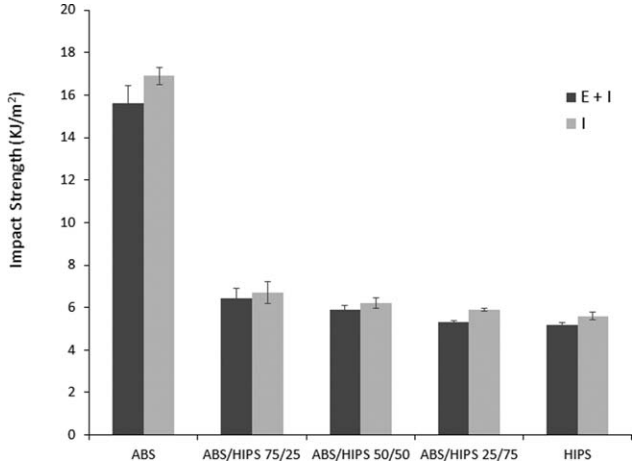

Figure 4. Impact strength of ABS and HIPS polymers and ABS/HIPS blends.

Tensile modulus values did not present significant differences when shot size or particle size were the source of variation ($p > 0.05$). For elongation at break and tensile and impact strength values, p appeared to be less than 0.05 when particle size was the source of variation, indicating that a smaller particle size resulted in a slight but significant increase in elongation at break and tensile and impact strength, regardless of the shot size used during the injection process. The interaction between the variables was statistically not significant. The smaller particles probably promoted more effective mixing during injection molding, resulting in a more homogeneous material.

In the next step of this investigation, all blends were obtained (with or without previous extrusion) using a shot size of 150 mm/s and 3-mm ground particles.

ABS/HIPS Blends Obtained with or without Previous Extrusion

Mechanical Properties and Morphology. Figures 1 to 4 present the tensile and impact properties of ABS and HIPS polymers and ABS/HIPS blends obtained directly via injection molding (I) and obtained via extrusion with subsequent injection molding (E + I).

The significant differences in the mechanical properties were assessed by analysis of variance considering two variables: blend composition and processing method (direct injection molding or previous extrusion with subsequent injection molding). Table IV presents the results obtained.

The ABS samples presented higher Young's modulus and tensile strength than the HIPS samples. However, ABS presented a smaller elongation at break. ABS/HIPS blends presented values intermediate between ABS and HIPS properties.

The increase in HIPS concentration in ABS/HIPS blends resulted in a decrease in Young's modulus and tensile strength and an increase in elongation at break, regardless of the processing method used. The impact strength was the most affected property. Even at the lowest HIPS concentration (25 wt %),

Table IV. Analysis of Variance of Mechanical Properties of ABS/HIPS Blends Obtained Directly via Injection Molding and Obtained via Extrusion with Subsequent Injection Molding

Property	Source of variation	Sum of squares	Degree of freedom	Mean square	*F*	*p* value
Tensile modulus	Processing method	557786.31	1	557786.3	52.60	0.00
	Blend composition	547749.21	4	136937.3	12.91	0.00
	Interaction	9872.35	4	2468.09	0.23	0.92
Tensile strength	Processing method	0.14	1	0.14	0.80	0.38
	Blend composition	196.73	4	65.58	375.62	0.00
	Interaction	0.87	4	0.29	1.67	0.20
Elongation at break	Processing method	323.90	1	323.90	17.73	0.00
	Blend composition	2435.01	4	608.75	33.33	0.00
	Interaction	84.17	4	21.04	1.15	0.35
Impact strength	Processing method	3.93	1	3.93	16.10	0.00
	Blend composition	864.90	4	216.22	885.31	0.00
	Interaction	1.64	4	0.41	1.68	0.17

*F is the ratio of the Model Mean Square to the Error Mean Square.

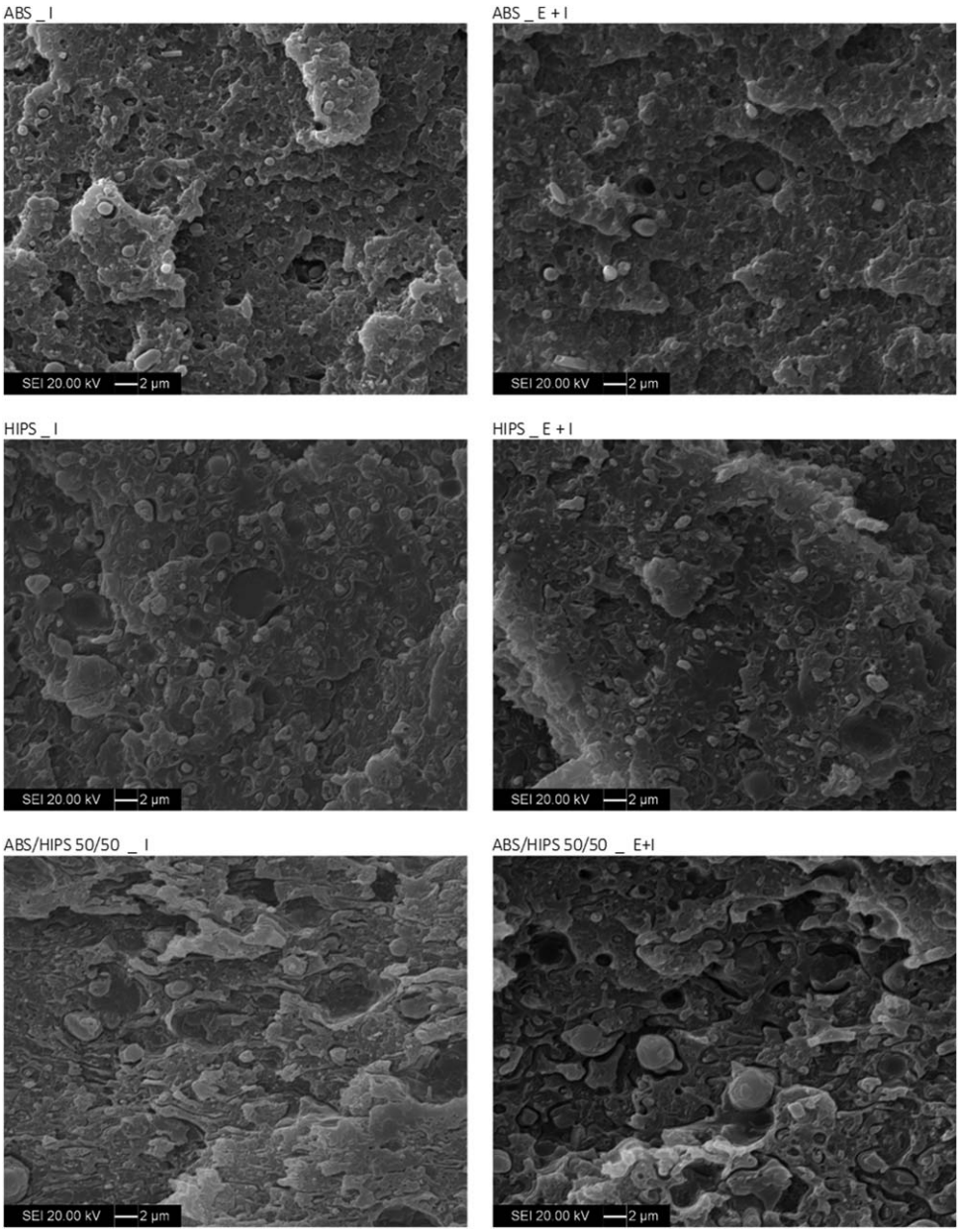

Figure 5. Micrographs of impact fracture surfaces of ABS, HIPS, and ABS/HIPS 50/50 blends obtained with (E + I) or without (I) previous extrusion.

ABS/HIPS blends exhibited a significant decrease in impact strength as compared to ABS. These differences appeared to be statistically significant ($p < 0.05$ for source of variation: blend composition), as can be seen in Table IV. These results are in agreement with studies on ABS/HIPS blends at different compositions obtained via batch mixer[11] and prepared using a twin-screw extruder.[12]

Injection-molded samples of ABS and HIPS polymers and ABS/HIPS blends obtained using previous extrusion presented an increase in Young's modulus as compared to the samples obtained without previous extrusion. However, these samples showed a decrease in elongation at break and impact strength. The differences in the mechanical properties observed were small but statistically significant according to the ANOVA results shown in Table IV ($p < 0.05$ for source of variation: processing method). Tensile strength values did not present significant differences when the processing method was the source of variation. The interaction between the variables processing method and blend composition appeared to be statistically not significant.

Figure 5 presents micrographs of impact fracture surfaces of ABS, HIPS, and ABS/HIPS 50/50 blends obtained with (E + I) or without previous extrusion (I). ABS and HIPS show the typical double phase morphology with PB granules dispersed in an SAN or PS matrix. In HIPS obtained using previous extrusion, the PB granules presented heterogeneous shapes because of possible degradation. ABS/HIPS 50/50 blends presented a coarse morphology mainly for the blend obtained using previous extrusion. This suggested that the ABS did not completely mix

Table V. Glass-Transition Temperatures

	Glass-transition temperature (°C)			
	PB		Matrix	
	E + I	I	E + I	I
ABS	−75.8	−76.9	90.5	90.8
ABS/HIPS 75/25	−76.0	−77.7	91.2	91.5
ABS/HIPS 50/50	−80.9	−82.9	92.8	92.8
ABS/HIPS 25/75	−81.9	−83.9	94.2	94.8
HIPS	−82.4	−84.8	95.0	95.7

with HIPS and the processing method considerably affected the blend structure. Arnold *et al.*[4] observed that ABS/HIPS 50/50 blends obtained by torque rheometer and compression molding presented coarser structures than those obtained by extrusion and injection molding. The authors also observed that the finest structure resulted from injection molding without previous extrusion, indicating that longer processing time leads to more phase separation. Chaudhry *et al.*[13] concluded that the phase morphology of PC/ABS blends prepared in a mixing chamber can be significantly affected by its processing conditions. The blend morphology changes from a well-dispersed PC phase to a cocontinuous morphology with increasing mixing time.

The observed mechanical properties may also be related to possible ABS or HIPS degradation during extrusion. Since ABS consists of PB and SAN phases and HIPS consists of PB and PS phases, the degradation mechanisms of these polymers are related to the degradation paths of their components. Vilaplana *et al.*[14] concluded that repeated extrusion of HIPS may induce physical changes (crosslinking) in the PB phase and chain scission in the PS matrix. In another study, Vilaplana *et al.*[7] observed that the repeated extrusion of HIPS also affected morphology; shrinkage and surface modification of PB granules were observed. According to Scaffaro *et al.*,[15] during ABS recycling the PB phase is attacked during the initial stages of degradation, leading to the progressive consumption of unsaturated groups and the formation of different products containing oxidized groups or further reactions that lead to the formation of stable crosslinked structures. At more severe degradation, breaking of butadiene/SAN grafts were observed. Rahimi *et al.*[16] observed that the most affected properties of ABS after being recycled for five times were impact strength and shrinkage.

The effect of previous extrusion on the degradation suffered by the PB phase or SAN or PS matrixes was evaluated by DSC analysis, as presented below.

Thermal Properties. The DSC thermograms of ABS and HIPS polymers and ABS/HIPS blends presented two glass-transition temperatures (T_g). One T_g was observed around −75 to −85 °C related to the T_g of the PB phase (present in ABS and HIPS). The second T_g was observed around 90 °C for ABS (related to the matrix SAN) and 96 °C for HIPS (related to the matrix PS). ABS/HIPS blends with different compositions display a single T_g, with intermediate values between the T_g values of SAN (ABS) and PS (HIPS), suggesting that the investigated blend compositions give fully miscible mixtures of PS and SAN matrix phases. This behavior does not corroborate the coarse morphology observed mainly for ABS/HIPS blends obtained using previous extrusion (Figure 5). It is likely that, because the T_g values of ABS and HIPS are very similar, T_g overlapping may occur.

Table V summarizes the DSC results obtained during the first heating scan of ABS and HIPS polymers and ABS/HIPS blends obtained with and without previous extrusion.

The T_g related to the ABS/HIPS blend matrix obtained with or without previous extrusion decreases with increasing HIPS concentration and remains practically unaltered when the processing conditions are changed. On the other hand, the T_g related to the PB phase of ABS, HIPS, and ABS/HIPS blends obtained using previous extrusion presented a slight increase, suggesting an increase in crosslinking structures.

This result suggests that the processing method affected the rubber phase structures. The increase in Young's modulus and the slight decrease in impact strength and ductility of samples obtained using previous extrusion may be related to the stiffness of the rubber phase, reducing deformation and also adhesion with the matrix. The coarse morphology observed for these samples also contributed to the behavior of the mechanical properties observed.

CONCLUSIONS

Injection-molded specimens of ABS and HIPS polymers (from WEEE) and their blends were obtained with and without previous extrusion and were investigated by means of morphology and mechanical and thermal properties. A preliminary study of the effect of shot size and ground material particle size on the mechanical properties of ABS/HIPS (50/50) blends showed that a smaller particle size resulted in an increase in elongation at break and tensile and impact strength, regardless of the shot size used during the injection process.

Increasing ABS content in ABS/HIPS blends resulted in an increase in Young's modulus and tensile strength and a decrease in elongation at break, regardless of processing method used. ABS/HIPS blends exhibited a significant decrease in impact strength as compared to ABS, even at the lowest HIPS content used.

Injection-molded samples obtained using previous extrusion presented a slight increase in Young's modulus and a slight decrease in elongation at break and impact strength as compared to those obtained directly via injection molding. The tensile strength values did not present significant differences.

The increase in T_g related to the PB phases of ABS, HIPS, and ABS/HIPS blends obtained using previous extrusion indicated a possible increase in crosslinking structures during extrusion.

The slight decrease in the impact strength and ductility for samples obtained using previous extrusion may be related to the increase in stiffness of the rubber phase, reducing its deformation and also the adhesion with the matrix. In addition, the morphology of these blends showed a coarser and more heterogeneous morphology, suggesting that the ABS did not completely mix with HIPS.

These results suggest that ABS/HIPS blends can be obtained directly via injection molding as long as small ground particles are used. This is a very interesting result for the recycling industries in terms of time and energy saving, resulting in a decrease in processing costs. Blend composition appeared to have a stronger effect on the mechanical properties in relation to processing conditions and should be taken into consideration according to the required mechanical properties.

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