Influence of Styrene Block Copolymers on Thermal and Mechanical Properties of Recycled Polypropylene

MARIA RAPA[1], PAUL NICULAE GHIOCA[2*], ECATERINA MATEI[3], ELENA GROSU[1], LORENA IANCU[2], BOGDAN SPURCACIU[2], RAMONA MARINA GRIGORESCU[2], ALEXANDRA PICA[4], CONSTANTIN ANDREI BERBECARU[3], CORNELIU CINCU[4]

[1]S.C. ICPAO S.A., 8 Carpati Str., 551022, Medias, Sibiu, Romania
[2]INCDCP-ICECHIM, 202 Spl. Independentei, 060021 Bucharest, Romania
[3]Politehnica University of Bucharest, Center for Research and Eco - Metallurgical Expertise ECOMET, 313 Spl. Independentei, 060042, Bucharest, Romania
[4]S.C. ICAA S.A., 49 A Theodor Pallady Blvd, 032258, Bucharest, Romania

In this work, two commercial block copolymers namely, styrene–ethylene/butylene–styrene (SEBS) and styrene–butadiene–styrene (SBS) with the same amount of styrene were investigated to enhance the properties of recycled polypropylene (RPP) from post-consumer boxes. The amount of elastomer varied from 10 wt.% to 30 wt.% relative to RPP. The elastomer content influence on structural (MFI, DSC, VICAT, HDT, XRD) and mechanical properties (tensile properties, IZOD impact, hardness) of the RPP/SEBS and RPP/SBS blends was studied. The obtained resuls showed that the addition of both elastomers into recycled polypropylene had a similar effect on modification the RPP properties, but SEBS exhibited a higher increase of elongation at break and IZOD impact than SBS, due to a good compatibility with polymeric matrix.

Keywords: recycled polypropylene, block-copolymers, properties, waste management

The total production of plastics is higher than 230 million tons per year and is estimated to reach 400 million tons in 2020 based on the annual growth rate of about 5% [1]. Among all plastics, the polypropylene (PP) is a thermoplastic polymer widely used for auto components, textile, toys, and daily consumer goods. Nowadays, a major concern has been related to the treatment of solid wastes resulted from PP products after their use due to their negative effect on environment.

The use of recycled PP as raw materials for various industries has been known. For example, the recycled PP is widely used to form blends with polyethylene (PE) [2, 3], for lubricating greases [4], in construction industry [5-7], etc. Although the polypropylene recycling process is well established [1, 14, 15], the mechanical and thermal properties of recycled products are normally lower than those of virgin material. It was found that the recycling induced a reduction of PP molecular weight which was attributed to a chain scission mechanism [8] and a decrease in the thermal stability [9-11]. These phenomena are accompanied with the decrease of tensile strength with 15% [12], the elongation at break and melt viscosity and the increase of degree of crystallinity [13] with respect to the virgin PP. In other paper, it is shown that the presence of polyethylene and of many different qualities of polypropylene in the recycled material may have prevented any possible improvement in the mechanical properties [15]. In the previous papers [16, 17] our team modified the PP wastes resulted from textile cones and food packaging with poly (styrene-isoprene-styrene) (SIS) and the obtained blends were found suitable for industry field, e.g. automotive parts. Based on these findings, the objective of this study is to obtain and investigate the modified recycled polypropylene (RPP) coming from post-consumer boxes with two types of commercial styrene block-copolymers for possible applications.

Experimental part

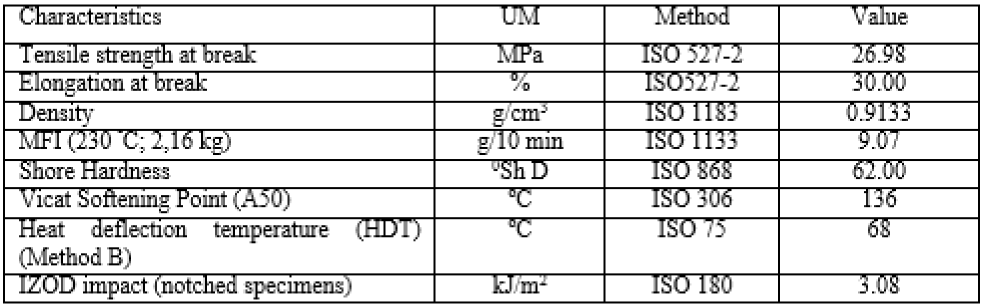
Materials

A recycled polypropylene (RPP), as grind material, obtained from post-consumer boxes was kindly supplied by a local recycler. Its physical-mechanical and thermal characteristics are presented in table 1.

Two block-copolymers were used as impact modifiers: CALPRENE H6144 (SEBS) from Spain, a linear poly[styrene-b-(ethylene-co-butylene)-b-styrene] obtained by polymerization in solution and SOL T161 C (SBS) from Versalis, Italy, a poly(styrene-b-butadiene-b-styrene) star copolymer. Their properties are shown in table 2.

Preparation of RPP/SEBS and RPP/SBS blends

Binary RPP/SEBS and RPP/SBS blends with content ratios of 100/0, 90/10, 80/20 and 70/30 wt.% were prepared by melt blending on a laboratory twin rolls at processing



Characteristics	UM	Method	Value
Tensile strength at break	MPa	ISO 527-2	26.98
Elongation at break	%	ISO527-2	30.00
Density	g/cm^3	ISO 1183	0.9133
MFI (230 °C; 2,16 kg)	g/10 min	ISO 1133	9.07
Shore Hardness	^{0}Sh D	ISO 868	62.00
Vicat Softening Point (A50)	°C	ISO 306	136
Heat deflection temperature (HDT) (Method B)	°C	ISO 75	68
IZOD impact (notched specimens)	kJ/m^2	ISO 180	3.08

Table 1
THE CHARACTERISTICS OF RECYCLED PP

---

* *email: pghioca@yahoo.com; Tel.: (+40)213153299*

Table 2
THE CHARACTERISTICS OF INVESTIGATED BLOCK – COPOLYMERS

Characteristics	UM	SEBS	SBS
Total styrene (on polymer)	%	31	30
Viscosity (5.23 % sol. toluene)	cSt	30	
Volatile matter, max.	%	0.5	
Hardness Shore	°Shore A	75	69
Saturation	%	> 99	

Table 3
PROCESSING PARAMETERS FOR THE OBTAINING OF SHEETS

Parameter	U.M.	Value
Rolling		
Rolling temperature	°C	185 – 190
Rolling time	minutes	10
Friction ratio	-	1 :1,2
Pressing		
Preheating time	minutes	4
Pressing time	minutes	2
Pressing temperature	°C	185
Pressure	atm.	125
Cooling time	minute	45

temperature of 185-190°C. 1% 2,6-di-tert-butyl-4-methylphenol (TOPANOL-OC) was used as antioxidant for RPP/SBS blends. Square sheets with (150 x 150 x 4) mm and (150 x150 x 1) mm dimensions were prepared from the melted blends by rolling and pressing at the processing parameters stated in table 3. The specimens for characterization were taken out from these sheets.

Characterization

Differential Scanning Calorimetry Measurements (DSC)

Thermal analysis of RPP blends was performed using a DSC 823^e from Mettler Toledo calibrated with indium standard. The samples weighing between 12 and 14 mg were packed in aluminum pans and placed in the DSC cell. The samples were first heated from ambient temperature to 200 at a rate of 10°C/min, kept 2 min at 200°C in order to erase any previous thermal history, then cooled to ambient temperature and reheated as before to 200°C. The degree of crystallinity (χ_c) was calculated from DSC curves as follows:

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^0} x100,\% \qquad (1)$$

where:

ΔH_m is the heat of fusion for blend (J/g);

ΔH_m^o is the heat of fusion for 100 % crystalline isotactic PP (190 J/g).

X-Ray diffraction

The X-ray diffractograms of blends were investigated by X'Pert PRO MPD diffractometer (Cu K_α-Ni filtered irradiation, λ= 1.54065 nm). All curves were recorded in plane perpendicular to the film surface with the scan interval of 2θ ranging from 10 to 90°C at a scan rate of 5°C/min, using a Pixcel detector with 256 canals. The diameter of crystallite of RPP/Blends was calculated from the Debye-Scherrer equation [18]:

$$D = \frac{K x \lambda_{Cu\text{-}K\alpha}}{\cos\theta x FWHM} \qquad (2)$$

where:

D is the average crystallite size, nm;

K is the crystallite shape factor (0.89);

$\lambda_{Cu\text{-}K\alpha}$ is the X-ray wavelength;

FWHM is peak width at half-maximum intensity;

θ is the diffraction angle.

Density

The density of blends was measured in ethanol by Archimedes' principle with a density kit of AS 220/X RADWAG balance. Three measurements were performed for each sample.

Tensile properties

The tensile strength at break and elongation at break were carried out on a FP 10/1 machine according to standard ISO 527. Test specimens of 1 mm thickness and a crosshead speed of 50 mm/min were used. At least five samples were tested for each composition, and the average value was reported.

Hardness

The Shore hardness was measured on a Durometer with Shore D scale, according to ISO 868. Test specimens of 4 mm thickness were used and at least five points were tested for each blend, and the average value was reported.

Impact strength

The impact test was determined with an IZOD Pendulum (CEAST, Italy) in accordance with standard ISO 180 on rectangular shaped specimens with (80 x 10 x 4) mm dimensions. Notching of 8 mm depth on the sample was done by using a notching apparatus by CEAST, Italy. The test was performed with a hammer of 2 J. 10 specimens of each blend were tested to obtain the impact strength. IZOD Impact strength (a_{IN}), expressed as kJ/m^2 is calculated by dividing the impact energy (J) to the area under notch, according to formula (3):

$$a_{IN} = \frac{E_c}{hxb} x10^3, kJ/m^2 \qquad (3)$$

where:

E_C is energy used for breaking of specimen; J; h is thickness of specimen, mm;

b is width of specimen under notch, mm.

VST&HDT measurements

The VICAT softening temperature (VST) and heat deflection temperature (HDT) measurements were conducted using a HDT/VICAT SOFTENING POINT Apparatus (CEAST Test Equipment). Determination of VST was performed according to ISO 306 (Method A50), at a heating rate 50°C/h ± 5°C/h. Three test speciments with thickness of 4 mm were measured and the average value was reported. HDT measurements were carried out by using specimens with (80 x 10 x 4) mm dimensions according to EN ISO 75. The test was conducted at a heating rate of 120°C/h ± 10°C/h and a load of 1.8 MPa. Two test speciments were performed and the average value was reported.

MFI

The melt flow index (*MFI*) measurement of blends was performed according to standard ISO 1133 at 190°C, with a load of 2.16 kg. The test was performed in triplicate on about 10 g material and the average value was reported. A preheating time of 6 min is given before each experiment.

Table 4
DSC PARAMETERS ASSESSED FROM DSC CURVES FOR RPP BLENDS, SECOND HEATING RUN

Code sample	$\Delta H_{m\,PE}$, J/g	$T_{m\,PE}$, °C	$\Delta H_{m\,PP}$, J/g	$T_{m\,PP}$, °C	χ_c PE, %	χ_c PP, %
RPP	12.9	127.4	42.6	158.7	4.4	22.4
RPP/SEBS10	18.0	128.1	37.8	160.2	6.2	19.9
RPP/SEBS20	12.5	128.6	29.8	162.4	4.3	15.7
RPP/SEBS30	8.1	128.4	26.3	163.7	2.8	13.8
RPP/SBS10	14.0	129.3	26.9	162.3	4.8	14.1
RPP/SBS20	17.7	129.5	37.6	161.8	6.1	19.8
RPP/SBS30	13.6	129.8	22.7	163.5	4.7	11.9

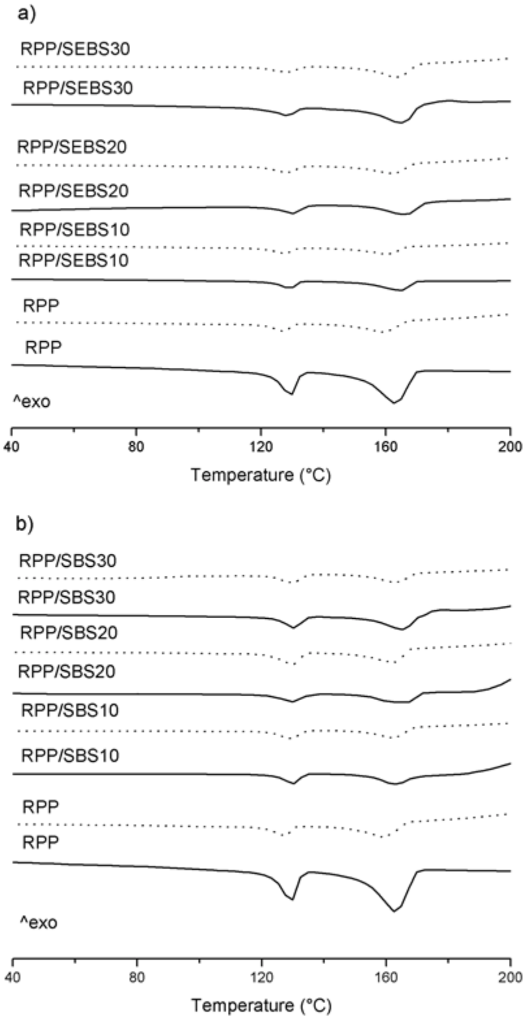


Fig. 1. DSC curves for the RPP blends (as first heating run – continuous line and second heating run – dotted line)
a) RPP/SEBS blends; b) RPP/SBS blends

Results and discussions

DSC spectra

DSC curves for the modified RPP with thermoplastic elastomers could be observed from figure 1 (a, b).

The melting temperature (T_m) of PE and PP and degree of crystallinity (χ_c) were evaluated from DSC curves and reported in table 4.

DSC data (fig. 1) show similar thermograms for all blends showing two peaks, one occurring around 130°C and other at 160°C, giving evidence that the recycled polypropylene is a mixture of polypropylene (PP) and polyethylene (PE). The melting point taking place at 160°C corresponds to the melting point of polypropylene (homopolymer), while the melting point taking place at 130°C is characteristic for polyethylene. It is known that PE is usually blended with PP to improve its stability and, during the recycling process these types of plastic are not easy to separate [19].

From the melting enthalpy (ΔH_m) of the PE (reported in table 4) it was determined the degree of crystallinity for the PE fraction in the recycled PP material by using the heat of fusion of crystalline polyethylene of 290 J/g. By assuming that the amount of crystalline regions of PE is probably the same as the amount of PE amorphous [15], we estimated the total content of PE (amorphous and crystalline) as being 9% in recycled blends.

From table 4 it is also observed that the degree of crystallinity for PP decreased with the increase of elastomer content indicating a preferential partition of elastomers in polyolefin amorphous phase [20]. The decrease of degree of crystallinity of RPP blends than the unmodified recycled polypropylene is expected to lead to a decrease of hardness and an increase of IZOD impact strength for RPP blends. Among two types of blends, those with SEBS exhibited a higher degree of crystallinity in comparison with those containing SBS. This can be explained by the presence of ethylene-butadiene block in SEBS structure having a higher affinity or compatibility with PP and does not disturb the crystalline lattice [21].

Regarding the melting temperature (T_m) of blends it can be observed a slowly increase with addition of elastomer. This can be explained by the balanced dispersion of elastomer domains in both crystalline and amorphous polypropylene phases.

XRD analysis

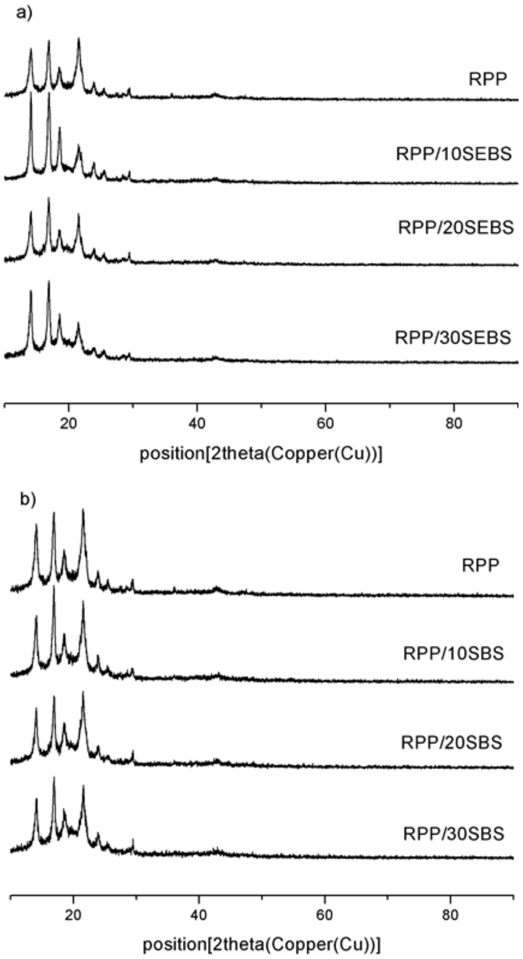


Fig. 2. XRD difractograms for the RPP blends
a) RPP/SEBS blend; b) RPP/SBS blend

Table 5
AVERAGE CRYSTALLITE SIZES (NM) OF PPR/SEBS AND PPR/SBS BLENDS

Elastomer content (wt. %)	Average crystallite size (nm)	
	PPR/SEBS	PPR/SBS
0	29.18	29.18
10	33.66	24.17
20	32.62	28.77
30	25.33	22.55

Figure 2 shows the X-ray diffraction patterns of the RPP reference and RPP/SEBS (fig. 2 (a)) and RPP/SBS blends (fig. 2 (b)). The average of crystallite sizes of RPP blends are presented in table 5.

The elastomers influence on the crystallite sizes of RPP blends is different depending on the content and type of elastomer used. Thus, blends with 30% SEBS and respectively 10, 20 and 30% SBS exhibit a decrease of the crystallite sizes compared with RPP, maybe due to the small dispersed particles of elastomers [22]. On the other hand, 10% SEBS and 20% SEBS lead to increase of the crystallite sizes causing disturbance of microcrystalline network formation. The effect exhibited by SEBS on the increase of the crystallite sizes of blends in comparison with SBS is due to the presence of ethylene-butadiene block making a high compatibility of SEBS with the RPP matrix.

Density

Figure 3 shows the effect of elastomer content on the density of RPP blends.

The addition of elastomer resulted in an increase of density of blends: thus from a density of 0.9133 ± 0.0018 g/cm^3 for the recycled polypropylene is obtained 0.9205 ± 0.0014 g/cm^3 for the RPP/SEBS 30 blend and 0.9176 ± 0.0018 g/cm^3 for the RPP/SBS 30 blend. It is observed from figure 3 that SEBS leads to higher values of density in comparison with SBS, due to its molecular weight.

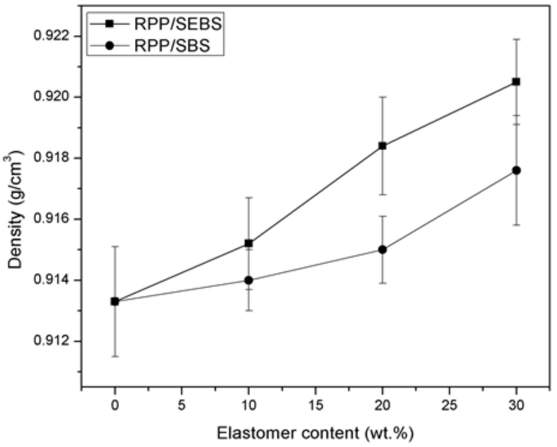


Fig. 3. Influence of elastomer content on the density of RPP blends

Tensile Properties

The tensile strength at break and elongation at break for investigated blends are depicted in figure 4 (a, b).

As can be seen from figure 4 a the tensile strength at break decreased as the percentage of elastomer increased, for example from 26.98 ± 1.8 MPa for RPP to 20.8 ± 1 MPa for RPP/SEBS30 blend and respectively to 18.7 ± 1.2 MPa for RPP/SBS30 blend. This decrease can be explained by the poor interface interaction between the elastomer phase and the polymeric matrix and as a consequence, the blend rigidity decreased [23]. It is assumed that the elastomeric domains are predominantly dispersed in the form of well-defined areas in the amorphous phase of RPP inducing an increase of brittleness and a decrease in the tensile strength of blends [17].

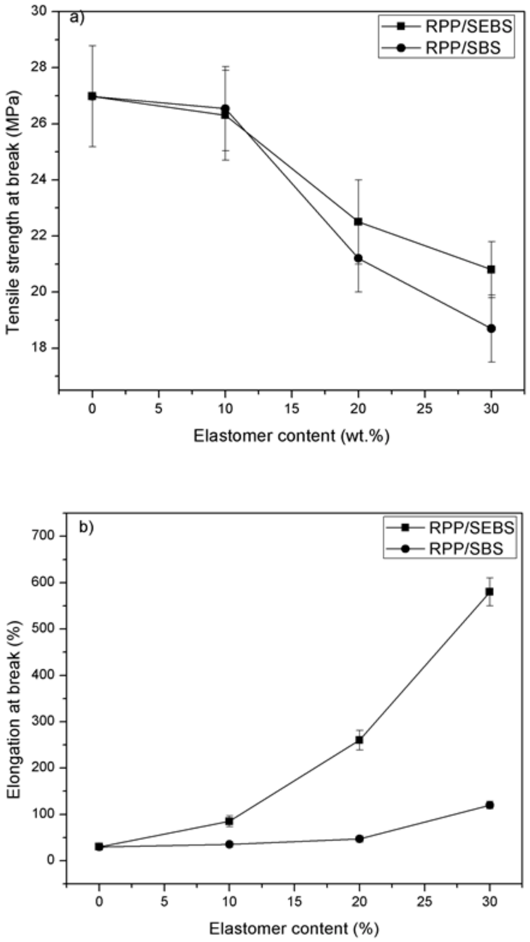


Fig. 4. Influence of elastomer content on the tensile properties of RPP blends a) Tensile strength at break; b) Elongation at break

The elongation at break (fig. 4 b) recorded a significant enhancement with increasing of the elastomer content which permits the flow and mobility of the RPP blends. Blends made with RPP and SEBS lead to a higher elongation at break than those based on RPP and SBS. Thus, RPP/SEBS30 blend is 19 times higher when compared with unmodified RPP while the RPP/SBS 30 blend increases up to 4 times. This is due to the low viscosity and phase adhesion of SEBS which has a higher adhesion with RPP than SBS, effects certified by the elongation growth while the tensile strength reduced.

Shore Hardness

The Shore hardness D values of RPP modified with two types of elastomers are presented in figure 5.

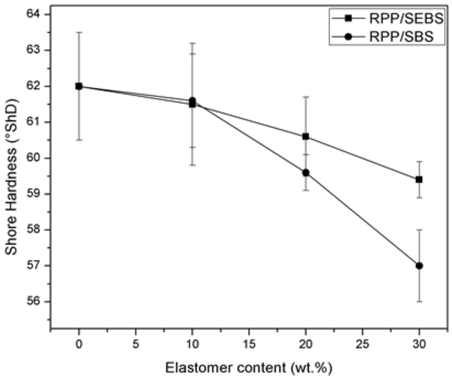


Fig. 5. Influence of elastomer content on the Shore D hardness of RPP blends

The addition of elastomer into the PPR matrix led to decrease of the Shore hardness values, and consequently of the resistance of material toward indentation (fig. 5). RPP/SBS blends recorded lower Shore D values than PPR/

SEBS blends because the percent of crystallinity is more reduced for these materials. It is well known that the Shore hardness depends on the viscoelastic properties of the material. These data are in aguement with elongation at break (fig. 4b) so we can state that the rubber elastomer can act as a plasticizer for the PP matrix [16].

IZOD Test

IZOD impact strength for the RPP/SEBS and RPP/SBS blends is shown in figure 6.

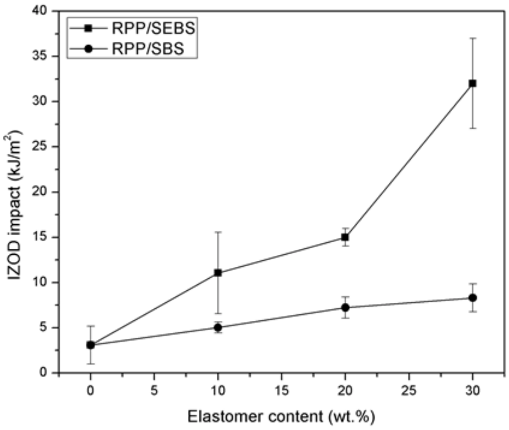


Fig. 6. Influence of elastomer content on the IZOD impact strength of RPP blends

As it can be seen from figure 6, the IZOD impact strength spectacular by increased with the addition of elastomers. Different effect of elastomers on Izod impact strength can be observed from figure 6. Thus, the addition of SBS causes an increase in the impact strength up to 3 times (8.30 ± 1.55 kJ/m^2) while for SEBS, the IZOD strength remarkably increased about 10 times (32 ± 4.97 kJ/m^2) when compared with unmodified RPP (3.08 ± 2.10 kJ/m^2). The appreciable increase of impact strength is the consequence of elasticity increase of the RPP blends, due to the styrene block-copolymers that absorb and transfer the impact force from the continuous phase of RPP. In addition, the flexible interface between elastomer and RPP prevents the development of cracks. Accordingly, the impact resistance of modified RPP blends is significantly improved and could be strictly correlated with the decrease of crystallinity degree. Also other authors [16, 17, 24] have noted a marked increase of IZOD strength when the styrene block-copolymers are used for compatibility of PP.

VST&HDT measurements

The influence of the used styrene block-copolymers on the VICAT softening temperature (VST) and heat deflection temperature (HDT) properties of the RPP blends are shown in figure 7 and 8.

VST and HDT values decreased as the elastomer content increased. The lowest VST value was recorded for the blend with 30 % SBS (106 ± 3°C). By comparison with unmodified RPP (68 ± 1°C) , the HDT results of prepared blends show the same trend to decrease as VST values.

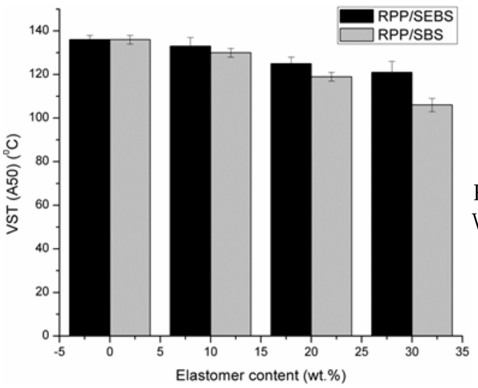


Fig. 7. Variation of VST properties for the unmodified RPP and RPP blends

The decrease in VST and HDT properties is due to the decrease in the crystallinity of the RPP blends with addition of elastomer (table 4).

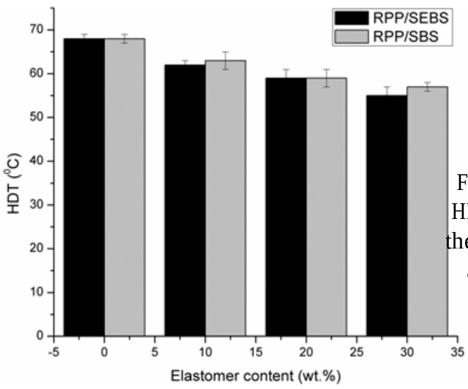


Fig. 8. Variation of HDT properties for the unmodified RPP and RPP blends

Melt flow index (MFI) measurement

The influence content of elastomer on MFI of RPP blends is shown in figure 9.

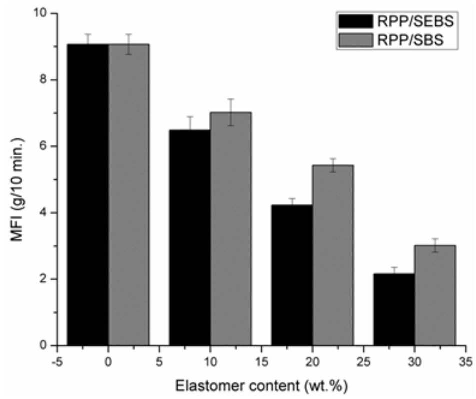


Fig. 9. MFI of the RPP blends versus unmodified RPP

According to the figure 9, the RPP blends presented lower values of MFI in comparison with recycled PP (9.07 ± 0.3 g/10 min), these decreasing being directly proportional with the content of elastomer from blends. That means an increase of viscosity and a decrease of fluidity. At the same content of elastomer, it is observed that the RPP/SBS blends showed higher MFI values (3 g/10 min - 7 g/10 min) compared with those based on RPP and SEBS (2 g/10 min - 6 g/10 min). These results can be explained by the fact that the SBS, due to its chemical structure, suffers undergoes thermo and photo-oxidative degradation during melt alloying.

Conclusions

The obtained results showed that melt blending of the recycled polypropylene from post-consumer boxes with styrene block copolymers represents both a good strategy for the waste management and a promising alternative of raw materials making composites with higher properties of elongation at break and impact strength.

Among two types of block-copolymer used in this study, SEBS was found more effective than SBS at the same content.

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, project number 67/2012.

References

1. ZARE, Y., Waste Manage. 33, 2013, p. 598.
2. TAI, C.M., LI, R. K.Y., NG, C.N., Polym. Test., 19, 2000 p.143.
3. BERTIN, S., ROBIN, J.J., Eur. Polym. J. 38, 2002 p. 2255.

4. MARTIN ALFONSO, J.E., VALENCIA, C., FRANCO, J.M., Polym. Test. 32, 2013, p. 516.
5. MURPHY, M., O'MAHONY, M., LYCETT, C., JAMIESON, I., Mater. Struct./Materiaux et Constructions 33, 2000, p. 438.
6. YIN, S., TULADHAR, R., COLLISTER, T., COMBE, M., SIVAKUGAN, N., DENG, Z., Constr. Build. Mater. 101, 2015, p. 1069.
7. VÄNTSI, O., KÄRKI, T., Resourc. Conserv. Recy. 104, 2015, p. 38.
8. WANG, K., ADDIEGO, F., BAHLOULI, N., AHZI, S., RÉMOND, Y., TONIAZZO, V., Compos. Sci. Technol. 95, 2014, p. 89.
9. CAMACHO, W., KARLSSON, S., Polym. Degrad. Stabil.78, 2002, p. 385.
10.JANSSON, A., MOLLER, K., GEVERT, T., Polym. Degrad. Stabil. 82, 2003, p. 37.
11. SAW, L.T., UY LAN, D.N. ABDUL RAHIM, N.A., MOHD KAHAR, A.W., XUAN VIET, C., Polym. Degrad. Stabil. 111 (2015) p. 32.
12. MERAN, C., OZTURK, O., YUKSEL, M., Mater. Design. 29, 2008, p. 701.
13. HAMAD, K., KASEEM, M., DERI, F., Polym. Degrad. Stabil. 98, 2013, p. 2801.
14. BAHLOULI, N., PESSEY, D., RAVEYRE, C., GUILLET, J., AHZI, S., DAHOUN, A., HIVER, J.M., Mater. Design. 33, 2012, p. 451.
15. BRACHET, P., HØYDAL, L.T., HINRICHSEN, E.L., MELUM, F., Waste Manage. 28, 2008, p. 2456.
16. RAPA, M. GHIOCA, P.N., GROSU, E., IANCU, L., SPURCACIU, B., GRIGORESCU, R., TRIFOI, A., CINCU, C., J. OPTOELECTRON. ADV. M. Vol. 15, No. 7- 8, 2013, p. 817.
17. GHIOCA, P., SPURCACIU, B., IANCU, L., GRIGORESCU, R., RAPA, M., GROSU, E., MATEI, E., BERBECARU, C., PICA, A., GARDU, R., CINCU, C., Mat. Plast., **52**, no. 3, 2015, p. 281.
18. MILEV, A., WILSON, M., KANNANGARA, G.S.K., TRAN, N., Mater. Chem. Phys.111, 2008, p. 346. doi:10.1016/j.matchemphys.2008.04.024.
19. MARTÍN-ALFONSO, J.E., ROMERO, A., VALENCIA, C., FRANCO, J.M., J. Ind Eng. Chem. 19, 2013, p. 580.
20. GHIOCA, P., IANCU, L., SPURCACIU, B., COSEREA, R.M., CINCU, C., GARDU, R., Mat. Plast. **50**, no. 1, 2013, p. 32.
21. ABREU, F.O.M.S, FORTE, M.M.C., LIBERMAN, S.A., J. Appl. Polym. Sci. 95, 2005, p. 254.
22. ŠMIT, I., DENAC, M., SVAB, I., RADONJIE, G., MUSIL, V., JURKIN, T., PUSTAK, A., Polimeri 30 (4), 2009, p.183.
23. ISMAIL, H., SURYADIANSYAH, Polym. Test. 21, 2002, p. 389.
24. ZHANG, X., LI, B., WANG, K., ZHANG, Q., FU, Q., Polymer 50, 2009, p. 4737.

Manuscript received: 3.02.2016