Effect of the Nature of Elastomer and Plastomer Blocks from Styrene-diene Block-copolymers upon the Modification of Recovered Polypropylene

PAUL GHIOCA*, LORENA IANCU, RAMONA MARINA GRIGORESCU, BOGDAN SPURCACIU, IONETA-CODRINA BUJANCA
The National Research & Development Institute for Chemistry and Petrochemistry ICECHIM - Bucharest, 202 Splaiul Independentei, 060021 Bucharest, Romania

The study of modification by melt alloying of recovered polypropylene with styrene and α-methylstyrene-diene block-copolymers is presented in this paper. The block-copolymers were synthetized with the same composition and molecular weight in order to relieve more accurately the influence of the component block nature upon the modification degree of the polyolefin. It was found that only the nature of the diene block has a significant influence on the intensity of the modification degree for recovered polypropylene.

Keywords: recovered polypropylene, styrene-isoprene block-copolymers (SIS), styrene-butadiene block-copolymers (SBS), α-methylstyrene-butadiene block-copolymers (αMeSBαMeS)

Polypropylene (PP) is one of the most used polyolefin in the obtaining of containers and items for the majority of industries due to its low cost, good processability and high physico-mechanical properties, excepting the impact strength [1]. Following this preferential use, its share in recovered plastics is important, of about 18 % [2], and that led to a research development regarding the reintroduction of recovered polypropylene in the economic circuit [3-7].

It is well known that usually PP sorts present low impact strength, property more deficitary in case of recovered polypropylene. The most used process to improve the impact strength of pure and recovered PP is melt alloying with modifiers, especially elastomer and mineral fillers that sometimes need dynamic vulcanization, resulting in polypropylene composites with better properties for different applications [8-16]. PP modification by melt alloying aims mainly the improvement of the poor impact strength ever in case of pure PP sorts and the obtaining of a good balance between the tensile and impact strength. The maximum modification effect is given by the styrene-diene block-copolymers, as such or hydrogenated [17-22].

The biphasic morphology of both polymers and the different interphase compatibility make the polyolefin modification hard to be achieved, the recovered PP compounding requiring the establishment of nature influence of both elastomer and plastomer blocks, components of styrene-diene block-copolymers. The aim of this paper is to study this influence, determining correlations between the modification degree and the main physical-mechanical properties of the resulting composites.

Experimental part

The study was performed using three block-copolymers with different blocks: styrene-isoprene, styrene-butadiene, and α-methylstyrene-butadiene. Their synthesis was carried out by sequential anionic polymerization of monomers, in cyclohexane solution, initiated with n-butyl lithium, followed by the coupling of active blocks with silicone tetrachloride [23-25]. The block-copolymers were stabilized after polymerization with 1 % 2,6-di-tert-butyl-4-methylphenol (TOPANOL-OC), directly in the cyclohexane solution. The elastomers were separated from the synthesis solution by the desolvation process based on hot water and steam stripping of cyclohexane, the polymer final drying being accomplished in an oven under reduced pressure, at a temperature of 60 °C.

The molecular characterization of SIS elastomers and of the component blocks of final elastomers was determined by gel permeation chromatography (GPC) as being sequential synthesized. The polystyrene and α-methylstyrene content was determined using the melt flow index method and the density [26]. The dynamic-mechanical measurements were made on a Du Pont 983 apparatus at resonance frequency allowing the determination of glass transition temperature of polystyrene, poly-α-methylstyrene, polybutadiene, and polyisoprene constituent blocks, using the tgδ maximum value criterion. The tensile physical-mechanical properties were determined on polymer films of about 1 mm thickness obtained by centrifugal casting from toluene solution, using a Zwick 1454 dynamometer, with a stretching speed of 500 mm/min. The block-copolymers properties are presented in table 1.

The block-copolymers were used for the modification by melt alloying of a recovered, without additives, polypropylene sort, mainly from food transport shuttles out of use due to their fragmentation during handling. PP has the following properties:

Molecular weight (Mv): 88 600 g/mole
Density: 0.8975 g/cm^3
Tensile strength: 20.8 MPa
Elongation at break: 75 %
Hardness: 74 ° ShD
Crystallinity: 76 %
Impact strength at 20°C: 7.1 kJ/m^2
Impact strength at -20°C: 4.6 kJ/m^2
Melt flow index at 190 °C, 5 kg: 1.6 g/10 min.

The compounding of recovered polypropylene with synthesized block-copolymers was performed using a roller with a friction coefficient of 1.18-1.20, at a temperature of 180-190 °C. The block-copolymers were added to the mixture after the PP film was formed, the elastomer dosage

---

* *email: pghioca@yahoo.com*

Crt. no.	Property	SIS	SBS	αMeSBαMeS
1	Polystyrene content, %	30.1	30.2	-
2	Poly-α-methylstyrene content, %	-	-	29.8
3	Total molecular weight, g/mole	168800	167100	170300
4	Polystyrene block molecular weight, g/mole	12100	12600	-
5	Poly-α-methylstyrene block molecular weight, g/mole	-	-	12700
6	Polyisoprene block molecular weight, g/mole	112400	-	-
7	Polybutadiene block molecular weight, g/mole	-	116700	119500
8	Tensile strength, MPa	17.8	20.1	22.6
9	Elongation at break, %	760	620	540
10	Hardness, ° Sh A	65	69	71
11	Melt flow index, 190 °C, 5 kg, g/10min.	1.5	1.45	1.2
12	Tg of the polystyrene phase, °C	91	90	-
13	Tg of the poly-α-methylstyrene phase, °C	-	-	126
14	Tg of the polyisoprene phase, °C	- 64	-	-
15	Tg of the polybutadiene phase, °C	-	- 78	-

Table 1
PROPERTIES OF THE STAR BLOCK-COPOLYMERS

ranging from 5 to 30 %. The resulting compounds were used to obtain pressed sheets at a temperature of 185-190 °C for 15 min, under a 198 N/m^2 pressure, being performed 2-3 short decompressions in order to eliminate any air bubbles embedded in the material during the melt alloying. In these conditions, two types of sheets were made: one with 1 mm thickness for the determination of physico-mechanical indicators when the composite is subject to a tensile stress, and one with 4 mm thickness for the stamping of hardness notched specimens used for Izod impact strength measurement of composites.

Tensile properties were determined using a FPZ 100 dynamometer, with an elongation rate of 50 mm/min, on type 5A specimens stamped from the 1 mm plates, according to SR EN ISO 527-96. Shore hardness in D scale was measured on the 4 mm pressed plates. Izod impact strength was determined on notched specimens at +20°C and -20°C, according to SR EN ISO 180-2009, using a Ceast instrument. The melt flow index was according to SR EN ISO 1133-93, at 190°C, under 5 kg loading. The crystallinity degree was determined from DSC measurements using a DSC Q2000 (TA Instruments) calorimeter.

Results and discussions

The studies regarding the melt alloying of PP with styrene-diene block-copolymers demonstrated that the modification degree of the polyolefin is influenced both by the molecular weight and the composition of block-copolymers [2, 17, 27-30]. In order to avoid these influences that may overlap with the effect of the nature of elastomer constituent block's, all the styrene-diene block-copolymers were synthetized with similar molecular weight and composition, as can be seen in table 1.

The 30 % polystyrene content and the molecular weight of 170000 g/mole give high physico-mechanical indicators to block-copolymers. The elastomers present melt flow indexes at 190°C closed to the one of recovered PP, being thus respected the optimal modification criterion of incompatible polymers or polymers with low compatibility [31-33].

The block-copolymers presence in the polypropylene matrix has as its first effect the uniform decreasing of polyolefin crystallinity with increasing the thermoplastic elastomers dosage in the system, as can be seen in figure 1. Comparing the composites and the initial PP, it can be observed a more pronounced decrease of the crystallinity degree than the one evidenced taking into account only the share of the block-copolymers in the system. This indicates that the elastomers are not dispersed only in the amorphous phase of recovered PP, they entering into the crystalline network and disturbing the lattice, the phenomenon being evidenced also by small angle X ray diffraction (SAXD) measurements in the modification of other polyolefins [34-35].

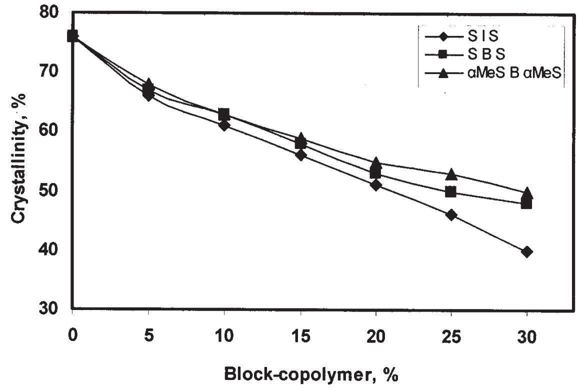

Fig. 1. Variation of the crystallinity degree of polypropylene composites depending on the block-copolymers content

The sharp decrease of composites crystallinity produced by the styrene-isoprene block copolymer compared to the effect of other elastomers, throughout the alloying domain, indicates a higher interpenetration degree of SIS elastomer mainly due to a better adherence of the continuous polyisoprene phase in contact with the PP microcrystalline phase [36-37]. Styrene and α-methylstyrene-butadiene block copolymers produce practically the same decrease of composites crystallinity at the first dosages because the contact with the polyolefin microcrystalline lattice is made in both cases by the elastomer butadiene continuous phase. At higher dosages, SBS elastomer produces a slightly more pronounced decrease in composites crystallinity compared to the αMeSBαMeS elastomer.

It is known that the elastomer melt viscosity largely controls the size of the dispersed particles in the

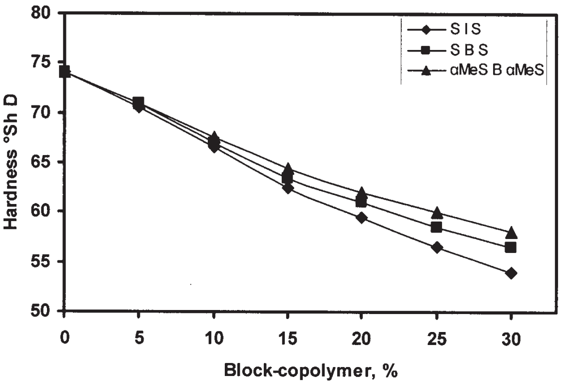

Fig. 2. Variation of the hardness of polypropylene composites depending on the block-copolymers content

polypropylene matrix in polyolefins alloying [31-33]. Lower melt viscosity (higher melt flow index at 190 ° C, table 1) of SBS block-copolymers as compared to that of the αMeSBαMeS block-copolymer leads to the formation of smaller elastomeric particles in the case of the first polymer. Consequently, they penetrate more easily into PP microcrystalline network, thus explaining the effect of a more pronounced decrease in the crystallinity degree of the composites mentioned above, given by the SBS block-copolymer.

The presence of the block-copolymers in PP compounds lowers the composites hardness, the effect being presented in figure 2. The decreasing of composites hardness is relatively uniform, respecting a rule of simple expansion of a hard material (PP) with an elastic one (block-copolymers). Since the block-copolymers hardness decreases in the order: αMeSBαMeS, SBS, SIS, the composites hardness shrinks in the same order, as expected.

The introducing of block-copolymers into the polyolefin matrix has as effect the decreasing of polypropylene composites tensile strength (fig. 3), a phenomenon characteristic for polymer alloys with incompatible components and where the Van der Waals forces play an important role in the interaction between components [38 - 39]. Since by definition the tensile strength represents the material behaviour until its destruction, then, in case of composites, it is the cumulative response of the two components: PP and the thermoplastic elastomer. Considering that the tensile strength of block-copolymers (table 1) decreases in the order: αMeSBαMeS, SBS, SIS, also the maximization of the decreasing effect in tensile strength of polypropylene composites occurs in the same order (fig. 3).

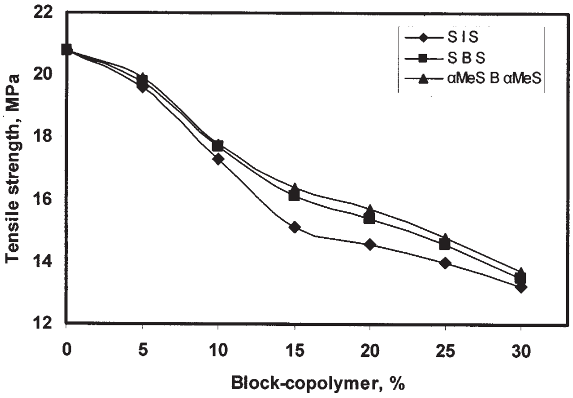

Fig. 3. Variation of the tensile strength of polypropylene composites depending on the block-copolymers content

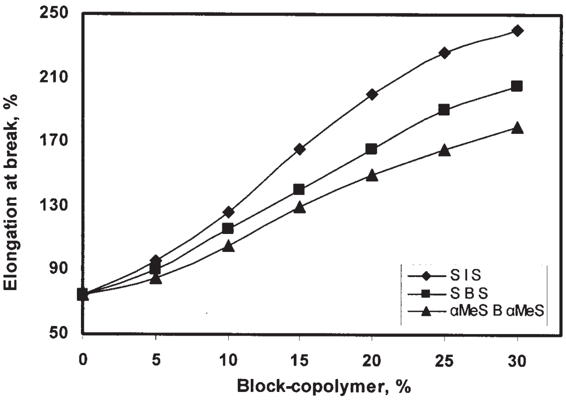

Fig. 4. Variation of the elongation at break of polypropylene composites depending on the block-copolymers content

The tensile properties measurement is performed at a stretching speed of 50mm / min, speed that allows a rearrangement of the crystalline phase in amorphous one. To mention that the crystalline phase is consisting in its turn of two components: PP continuous phase and elastomeric phase dispersed in it. In case of this complex morphology, the interphase contact plays a crucial role in ensuring the integrity of the material and the elongation at break is a measure of the adhesion and interpenetration degree of these multiple phases [40-42].

In figure 4 is shown the variation of the elongation at break depending on the block-copolymers dosage and it can be seen that the composites have higher elasticity in the order: αMeSBαMeS, SBS, SIS. The maximum effect produced by the SIS block-copolymer in the PP modification by melt alloying is more clearly laid out by the higher values of "real tensile strength" presented by these elastomer composites (fig. 5). The real tensile strength is calculated by dividing the tensile effort to the actual transverse surface presented by the specimen at break. This synthetic indicator is defined by the relation:

$$\sigma_t = 273/293\ \sigma_b . \lambda_b$$

where:
σt – real tensile strength;
σb – tensile strength;
λb – elongation at break.

As it can be seen from figures 3 and 5, the variation of both tensile strength and real tensile strength, depending on the content of the block copolymer in the polypropylene composites, shows an inflection around 15 % dosage of elastomers. This signals a beneficial change in particle size of dispersed elastomer in the PP matrix, a change that

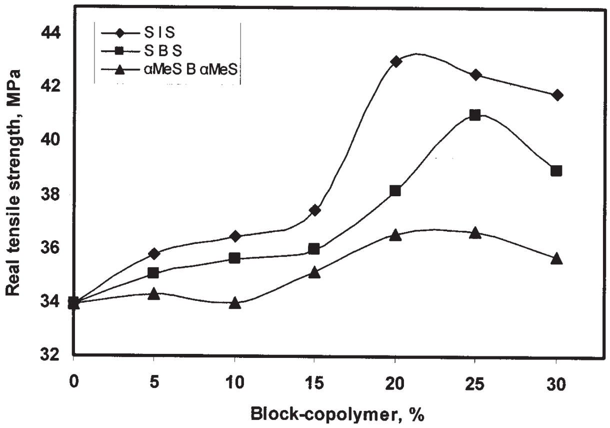

Fig. 5. Variation of the real tensile strength of polypropylene composites depending on the block-copolymers content

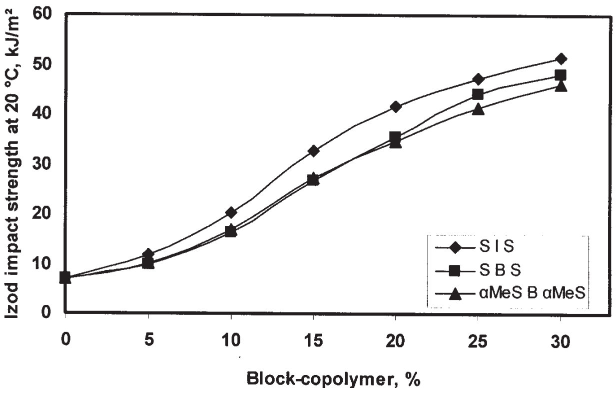

Fig. 6. Izod impact strength variation of polypropylene composites at +20 °C depending on styrene-isoprene block-copolymers content

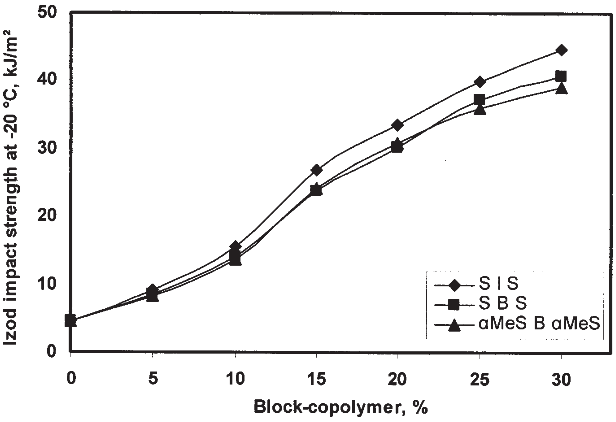

Fig. 7. Izod impact strength variation of polypropylene composites at - 20 °C depending on styrene-isoprene block-copolymers content

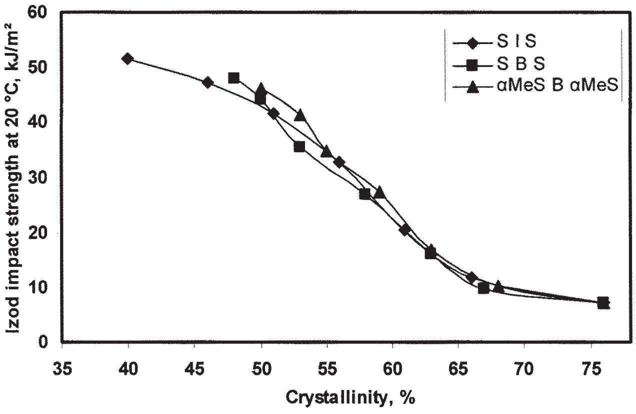

Fig. 8. Izod impact strength variation of polypropylene composites at +20 °C depending on the crystallinity degree

leads to a better allocation of the destruction effort of the composite material [43-44].

The most important consequence of melt alloying the recovered PP with styrene-diene block-copolymers is the appreciably increasing of the composites impact strength both at positive (fig. 6) and negative temperatures (fig. 7). The phenomenon is mainly correlated with the decreasing of the alloys crystallinity degree (figs. 8 and 9). The maximal increase of the impact strength is produced by the SIS block-copolymer that provides the higher elasticity of the composite material as a result of the stronger interpenetration into the microcrystalline network of PP (the sharp decrease in the crystallinity degree, fig. 1) and due to the higher adherence to its amorphous phase (the highest values of real tensile strength, fig. 5).

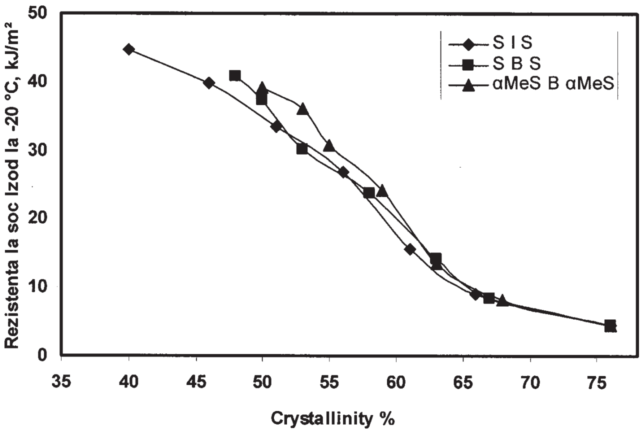

Fig. 9. Izod impact strength variation of polypropylene composites at -20 °C depending on the crystallinity degree

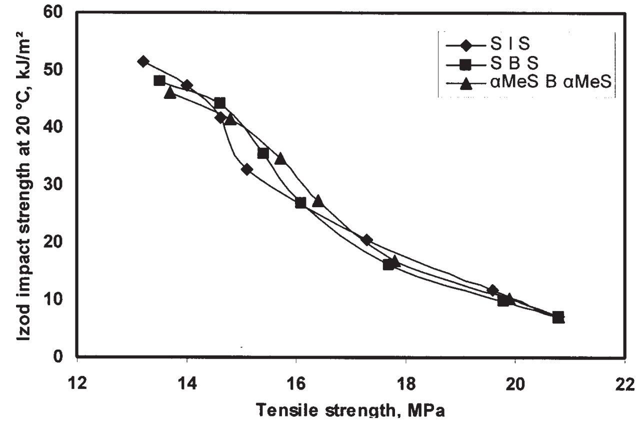

Fig.e 10. Izod impact strength variation of polypropylene composites at +20 °C depending on the tensile strength

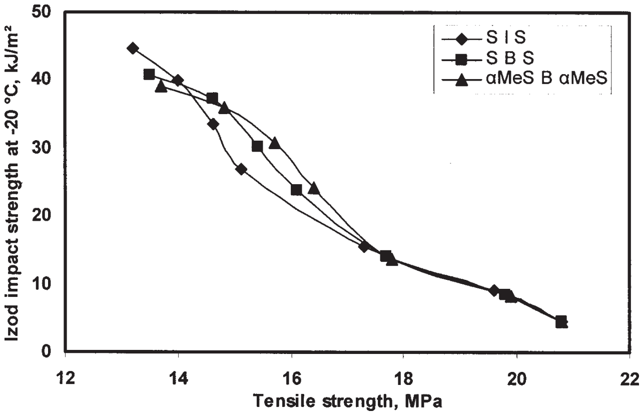

Fig. 11. Izod impact strength variation of polypropylene composites at -20 °C depending on the tensile strength

The SIS block-copolymer shows also the nearest melt viscosity to recovered PP, ensuring its optimal dispersion in the polymer matrix, forming elastomeric particles with the most appropriate dimensions that are able to absorb the energy better and to uniform redistribute the internal tensions and thus to effectively prevent the microcracks propagation that occur when the material is subject to mechanical stress [10, 16, 45, 46]. No significant differences between the values of the impact strength for the polypropylene alloys that contains SBS and αMeSBαMeS block-copolymers. The explanation is the fact that the polystyrene and poly α-methylstyrene blocks do not come in direct contact with the polyolefin matrix, being dispersed in the polybutadiene continuous phase. In this situation, the modification effect is given mainly by the poly-butadiene phase of the two block-copolymers and due to the fact that the polybutadiene blocks show very similar molecular weights and the alloying degree resembles, the polypropylene composites have basically the same impact strength at identical dosages of elastomers.

Patrick diagrams, charts that make correlations between the most important physico-mechanical properties of composites: impact and tensile, are presented in figures 10 and 11, the dosage of the styrene-isoprene block-copolymers being increased gradually with 5 % from right to left. These diagrams allow an easy selection of the block-copolymer dosage which provides an optimal balance between these two properties depending of the application domain requirements.

Conclusions

The study of the properties of recovered PP composites obtained by melt alloying with styrene and α-methylstyrene-diene block-copolymers emphasized that all block-copolymers have a good modification effect, manifesting his strength in the order: αMeSBαMeS, SBS, SIS. The maximal modification effect of the SIS block-copolymer can be explained by the superior adherence of the polyisoprene phase in contact with the polypropylene matrix, leading to increased strength of the composite material, especially when subject to mechanical stress.

Replacing polystyrene with poly-α-methylstyrene blocks does not greatly influence the modification effect of the polyolefin, as only the polybutadiene block, common of the two elastomers, is in direct contact with the polypropylene matrix, and having the same molecular mass, it is expected also that the modification degree to be very close.

In conclusion, one can say that the modification degree of recovered PP by melt alloying is significantly influenced by the nature of the diene block from the block-copolymers.

References

1.HERNANDEZ, M., ICHAZO, M.N., GONZALES, J., ALBANO, C., SANTANA, O., Acta Microscopica, **17**, No. 1, 2008, p. 66

2. SAITER, J.M., SREEKUMAR, P.A., YOUSSEF, B., Recent Developments in Polymer Recycling, edited by FAINLEIB, A., GRIGORYEVA, O., Kerala, 2011, p. 261

3.AL-SALEM, S.M., LETTIERI, P., BAEYENS, J., Waste Management, **29**, 2009, p. 47

4.AL-SALEM, S.M., LETTIERI, P., BAEYENS, J., Waste Management, **29**, 2009, p. 2625

5.GHIOCA, P., IANCU, L., SPURCACIU, B., COSEREA, R.M., CINCU, C., GARDU, R., Mat. Plast., **50**, No. 1, 2013, p. 32

6.PEGORARO, M., SEVERINI, F., DI-LANDRO, L., BRAGLIA, R., KOLARIK, J., Macrom. Mat. Eng., **280-281**, 2000, p. 14

7.FERNANDES, B.L., DOMINGUES, A.J., Polimeros: Ciencia e Tecnologia, **17**, No. 2, 2007, p. 85

8.SHASHIDHARA, G.M., KAMESHWAR, J., DEVI, S.H., Indian J. Eng. & Mater. Sci., **18**, 2011, p. 69

9.VULUGA, Z., PANAITESCU, D.M., RADOVICI, C., NICOLAE, C., IORGA, M.A., Polym. Bull., 2012, p. 289

10.ZHANG, X., LI, B., WANG, K., ZHANG, Q., FU, Q., Polymer, **50**, No. 19, 2009, p. 4737

11.LIU, W., MIAO, Q., CHEN, G.I., China Plastics Industry, 2006, p. 51

12.DENAC, M., MUSIL, V., SMIT, I., J. Polym. Sci., Polym. Phys., **42**, 2004, p. 1255

13.BALKAN, O., DEMIRER, H., SABRI-KAYALI, E., J. Achiev. Mater. Manuf. Eng., **47**, No. 1, 2011, p. 26

14.MINIF, N., MASSARDIER, V., KALLEL, T., ELLEUCH, B., Polym. Adv. Technol., **21**, No. 12, 2010, p. 896

15.GALLO, R., BRAMBILLA, L., CASTIGLIONI, C., Eur. Polym. J., **41**, No. 2, 2005, p. 359

16.LUDA, M.P., BRUNELLA, V., GUARATTO, D., J. Mater. Sci., **2013**, 2013, Article ID 531093

17.UTRACKI, L.A., Polymer Blends Handbook, Hauser Publishers, Munich, 2003, p. 37

18.LI, Y, WEI, G.X., HUNG, J.S., J. Mater. Sci., **37**, 2002, p. 2447

19.ALBA PEREZ, A., GALLEGO, F., GOMEZ RIBELLES, J.L., MENLEON PRADAS, M., VERDU SANCHEZ, E., J. Macromol. Sci., Pt. B, Phys., **40**, No. 3-4, 2001, p. 443

20.DA SILVA, P.A., JACOBI, M.M., SCHNEIDER, L.K., BARBOSA, R.V., COUTINHO, P.A., OLIVEIRA, R.V.B., MAULER, R.S., Polym. Bull., **64**, No. 3, 2010, p. 245

21.*** Patent SUA 6242532, 2001

22.AHMAD, Z., KUMAR. K.D., SAROOP, M., PRESCHILLA, N., BISWAS, A., BELLARE, J.R., BHOWMIC, A.K., Polym. Eng. Sci., 2010, p.331

23.HSIEH, H.L., QUIRK, R., Anionic Polymerization, Marcel DAEKKER, New York, 2008

24.CRAVER, C.D., CARRAHER, C.E., Appl. Polym. Sci., New York, 2010

25.HOLDEN, G., LEGGE, N.G., SCHRODER, E., Thermoplastic Elastomers, Hauser Publishers, Viena, 2006

26.BORDEIANU, R., CECHEZ, I., GHIOCA, P., STANCU, R., BUZDUGAN, E., Mat. Plast., **20**, 1983, p. 133

27.KARGER-KOCSIS, J., Polypropylene structure, blends and composites, Chapman & Hall, 1995

28.PUKANSZKY, B., in Polypropylene A-Z, Ed., J. KARGER-KOCSIS, Kulwer Publishers, Dordrecht, 1999

29.SMIT, I., DENAC, M., SVAB, I., RADONJIC, G., MUSIL, V., JURKIN, T., PUSTAC, A., Polimeri, **30**, 2009, 183

30.GHIOCA, P., BUZDUGAN, E., SERBAN, S., BRATES, G., SPURCACIU, B., Mat. Plast., **38**, 2001, p. 162

31.KARGER-KOCSIS, J., KALLO, A., SZAFNER, A., BODOR, G., Polymer, **20**, 1979, p. 37

32.JAYSREE, T.K., PRADEEP, P., THOMAS, S., MENON, R.P., Progr. Rubber Plast. Recycl. Technol., **19**, 2003, p. 288

33.PAUL, D.R., ROBESON, L.M., Polymer, **49**, 2008, p. 3187

34.STRIBECK, N., REIMERS, C., GHIOCA, P., BUZDUGAN, E., J. Polym. Sci., Part B, Polym. Phys. **36**, 1998, p. 1432

35.STRIBECK, N., GHIOCA, P., BUZDUGAN, E., J. Appl. Cryst., **30**, 1997, p. 708

36.*** SUA Patent H 1518, 1996

37.NANDI, S., GHOSH, A.K., J. Polym. Res. 2007, p. 387

38.KIE, H., NIES, E., STROEKS, A., SIMNA, R., Polym. Eng. Sci., **32**, 1992, p. 1654

39.YEUNG, R.C., DESAI, B.C., NOOLANDI , J., Macromolecules, **27**, 1994, p. 55

40.HONG JUN, C., XIAOLI, L., DESHU, M., JIANMIN, M., HONGSHENG, T., J. Appl. Polym. Sci., **71**, No. 1, 1999, p. 93

41.VAN der WAL, A., MULDER, J.J., ODERKERK, J., GAYMANS, R.J., Polymer, **39,** No. 26, 1998, p. 6781

42.VAN der WAL, A., VERHFUL, A.J., GAYMANS, R.J., Polymer, **40**, No. 22, 1999, p. 6057

43.ELIAS, H.G., An Introduction to Plastics, Wiley-VCH, Weinheim, 2003

44.DELHAYE, V., CLAUSEN, A.H., MOUSSY, F., HOPPERSTAD, O.S., OTHMAN, R., Polym. Test., **29**, No. 7, 2010, p. 793

45.FAN, Z.Q., ZHANG, Y.Q., XU, J.T., WANG, H.T., FENG, L.X., Polymer, **42**, no. 13, 2001, p. 5559

46.TAN, H., LI, I., CHEN, Z., SONG, Y., ZHENG, Q., Polymer, **46**, No. 10, 2005, p. 3522

Manuscript received: 19.07.2013