Composite of Waste Polypropylene by Styrene-Isoprene Block-copolymers Blending

PAUL GHIOCA[1]*, BOGDAN SPURCACIU[1], LORENA IANCU[1], RAMONA GRIGORESCU[1], MARIA RAPA[2], ELENA GROSU[2], ECATERINA MATEI[3], CONSTANTIN BERBECARU[3], ALEXANDRA PICA[4], RADITA GARDU[4], CORNEL CINCU[4]

[1] National Institute for Research & Development in Chemistry and Petrochemistry - ICECHIM, 202 Splaiul Independentei, 060021, Bucharest, Romania

[2] S.C. ICPAO S.A., 8 Carpati Str., 551022, Medias, Sibiu, Romania

[3] Politehnica University of Bucharest, Center for Research and Eco - Metallurgical Expertise, 313 Spl. Independentei, 060042, Bucharest, Romania

[4] S.C. ICAA S.A., 49A Theodor Pallady Blv, 032258, Bucharest, Romania

This study aims to reintroduce the economic circuit of recovered uncontaminated with organic impurities polypropylene sorts, the melt alloying of polyolefin with styrene-isoprene block copolymers.

Keywords: styrene-isoprene block-copolymers, recycling waste polypropylene, melt alloying

The polypropylene is one of the most balanced polyolefin properties: excellent processability on all plastics processing machinery, stiffness and high strength, good chemical resistance [1-3]. These excellent properties have led to the preferential use of polypropylene in various areas: packaging, industrial parts, containers, etc., so that in 2013 the production of various types of polypropylene ranks first in Europe, 8.8 million t [4]. Consequently, the amount of polypropylene products out of use owns the largest share of about 18% of the recovered plastics [5], which has led to increased researches of recovery polypropylene reintroduction into the economic circuit.

The easiest economically recycling of recovered polypropylene is blending with maxim proportion 50% with virgin polypropylene, applicable for not organic products contaminated of the collected polypropylene [6-9]. Application of this method is limited because it can only be used in the manufacture of industrial parts which are not imposed special performance properties.

Modification by alloy melting the styrene-diene block copolymers are the most appropriate technology for recovery polypropylene reintroduction into the economic circuit, as it leads to obtain composite with performance properties, particularly with high impact strength, correcting this property, deficient in especially at negative temperatures even compared to virgin polypropylene [10-13].

The efficiency modification by alloying the melt depends on the degree dispersion of styrene-diene block copolymers in polyolefin matrix and is influenced both by molecular weight and the nature and composition of block copolymers [10, 13-21].

This paper presents the effect of composition of styrene-isoprene block copolymers on the modification of the melt alloying recovered polypropylene.

Experimental part

The study of modification by melt alloying was achieved using a sort of recovered polypropylene mainly from food transport containers uncontaminated with organic and has submitted the following properties:

Density, Kg / cm ^{3}: 0.8966
Crystallinity, % :77
Impact strength at 20 ^{0}C, kJ / m 2: 6.4
Impact strength at -20 ^{0} C, kJ / m 2: 3.8
Tensile strength, MPa: 17.8
Elongation at break, %: 166
Hardness, °Sh D: 72
ICT 190 ^{0}C, 5 Kg, g / 10 min: 7.8 to 8.4.

For the modification of recovered polypropylene have been used four linear styrene-isoprene block-copolymers (SIS) synthesized by sequential anionic polymerization of monomers in a cyclohexane solution, initiated by n-butyl lithium (1.5 mol cyclohexane solution) [22-26].

The styrene-isoprene block -copolymers were stabilized directly in cyclohexane solution of synthesis polymerization with 2, 6- di-tert-butyl-4-methylphenol in a proportion of 1% based on the amount of polymer. SIS block copolymers were separated from the solution by damp stripping with hot water and water vapour, and finally dried in an oven at low pressure at 60 ^{0} C.

The final molecular weight of the elastomer and the blocks component collected during synthesis was determined by gel permeation chromatography (GPC). The physico-mechanical properties were determined on films 1 to 2 mm thickness obtained by centrifugal casting in toluene solution, in accordance with the specific requirements of characterization of block copolymers of styrene-diene.

The recovered polypropylene modification with styrene-isoprene block-copolymers was performed using a roller at optimum load capacity. The compounding recipes complied this load, the amount of styrene-isoprene block-copolymer being varied from 5 to 30%. The maximum weight of styrene-isoprene block copolymer indicated in literature does not exceed 40% [27-29].

The working temperature was 180-190 ^{0}C and a friction coefficient of 1.18 to 1.20 was used.

In the first phase the polyolefin was introduced on the roller heated, after its melting and catching it in foil it was added additional TOPANOL OC at a rate of 1% on the total amount of the mixture for supplementary of composites for antioxidation protection. In the second phase it was introduced styrene-isoprene block-copolymer, and after

---

* *email: pghioca@yahoo.com*

Table 1
PROPERTIES OF STYRENE - ISOPRENE BLOCK COPOLYMERS WITH DIFFERENT POLYSTYRENE CONTENT

Crt. no.	Property	20 SIS	25 SIS	30 SIS A	30 SIS B
1	Polystyrene content, %	20	25.1	30.1	30.1
2	Total molecular weight, g/mol	101400	100600	101900	121000
3	Polystyrene block molecular weight, g/mol	10150	12600	15300	15000
4	Polyisoprene block molecular weight, g/mol	81100	75400	71300	91000
5	Tensile strength, MPa	7.20	7.40	7.70	7.60
6	Elongation at break, %	1533	1500	1440	1440
7	Hardness, ^{o}Sh A	34	36	38.5	38.5
8	Melt flow index (190 °C, Kg), g/10 min.	8.4	8.8	9.2	8.6
9	T_g of the polystyrene phase, ^{0}C	90	91	91	91
10	T_g of the polyisoprene phase, ^{0}C	-61	-61	-61	-60

embedding it in PP, were effectuated specific mixing operations (repeated cutting, rolling, etc.) in the blend was removed as a thick film of about 1 mm.

For all compounds the components placing order was as follows:

- Rolling catching a polyolefin: 5-6 min
- Incorporating TOPANOL OC + block copolymer: 3-4 min
- Homogenization: 3-5 min.

In order to avoid degradation of styrene-isoprene block-copolymer due to temperature and shear forces will be not exceeded for any blend the time of maintaining on the roller the maximum of 15 min.

Plates were made from the rolled sheets by pressing them at a temperature of 185-190 ^{0}C for 15 min, under a pressure of 196 N/m^2, followed by a sudden cooling of the mold under pressure. During pressing, 2-3 short depressurizations were made to eliminate air bubbles. In these conditions, plates of 1 mm thickness were obtained for dynamic physico-mechanical properties and thermal behavior (DSC), and plates of 4 mm thickness for hardness tests. From these 4 mm plates, were stamped unnotched specimens necessary for Izod impact strength determination.

Tensile properties were carried out 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 at +20 and -20 ^{0}C, on unnotched specimens stamped from the 4 mm plates, according to SR EN ISO 180-2009, using a Ceast instrument.

The melt flow index was determined on a laboratory plastometer, according to SR EN ISO 1133-93, at 190 ^{0}C, under 5 kg loading.

Results and discussions

Melt alloying recovered polypropylene by styrene-isoprene block copolymers produce significant changes in the morphology of polyolefin, the SIS elastomer modifying both its crystalline and amorphous phase [3, 5, 11, 17 - 20, 30].

The presence of SIS block copolymers in the amorphous polyolefin phase produces its "elasticizing", leading to significant increase impact strength of polypropylene composites. Significant increase composites impact strength depends on the dispersion and particle size of SIS elastomer dispersed in the amorphous matrix of polyolefin. In the case of polymers incompatible or low compatibility, the uniform dispersion of the adequate size is achieved when the minor component in the melt viscosity of the polymer is as close as possible [8, 28-34]. To meet this criterion melt alloying and considering the data presented in a previous paper [19], in a first stage were synthesized three styrene-isoprene block copolymers (SIS 20 25 SIS, SIS 30A) with molecular weight of 100.000 g/mol (table 1).

Polystyrene content was varied in the range of 20-30% in order to establish the effect of SIS elastomer composition on the properties of recovered polypropylene composites.

From table 1 it can be seen that the melt flow indices rise with increasing polystyrene content of styrene-isoprene block copolymers, indicating a decrease in melt viscosity thereof.

If maintaining constant total molecular weight (100.000 g/mol), increased weight polystyrene phase leads to raised molecular weight of polystyrene blocks while lower molecular weight polyisoprene blocks.

Considering that the melt viscosity of polyisoprene phase is higher than those of polystyrene phase, reduced molecular weight polyisoprene blocks leads to a more pronounced decrease in the melt viscosity of the styrene-isoprene block copolymers compared to its increase caused by raising mass molecular weight of the polyisoprene blocks. Thus from the game of these two contrary influences, with different weights, resulting in melt viscosity decrease explanation of styrene-isoprene block copolymers with increasing of their polystyrene content, emphasized by the increase in melt flow indices.

As the block copolymer SIS 30 A shows a state of relatively high melt flow (lower melt viscosity) was synthesizing a new block copolymer (SIS 30 B) with a molecular weight of 120.000 g / mol. Increasing molecular weight resulted in lower melt flow index, as can be seen from table 1. This change of the molecular weight aimed to that all the styrene izopropene blocks to present a melt viscosity closer to that of recovered polypropylene, to preserve their main criterion for melt alloying for incompatible or with low compatibility polymers.

The modification by melt alloying recovered polypropylene with styrene-isoprene block copolymers aims to balance the physical and mechanical properties by changing the biphasic morphology, crystalline and amorphous polyolefin.

A first effect of these styrene-isoprene block copolymers in polyolefin matrix consists in decreasing the degree of crystallinity of polypropylene composites, the effect amplifying with increasing their share in the system as can be seen from figure 1.

The decreased crystallinity polypropylene composites do not follow simple two-component mixture (theoretical

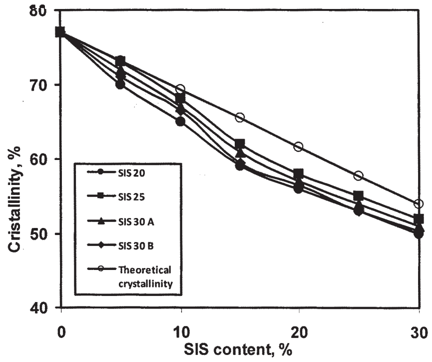

Fig. 1. Variation of the crystallinity degree of polypropylene composites depending on SIS content

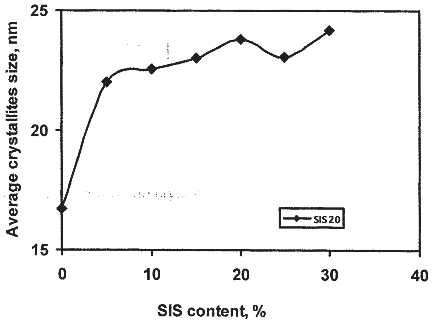

Fig. 2. Variation of the average crystallites size of polypropylene composites depending on SIS content

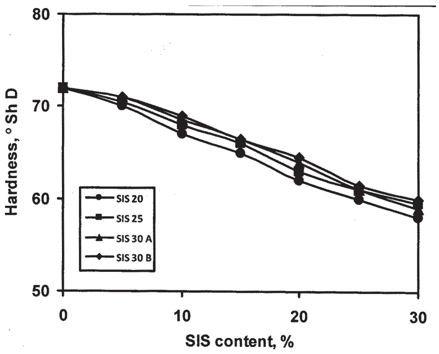

Fig. 3. Variation of the hardness of polypropylene composites depending on SIS content

crystallinity), being more pronounced in the case of all styrene-isoprene block copolymers. This finding indicates a major network disruption microcrystalline polypropylene.

Optical microscopy determinations by X-ray diffraction composites styrene-isoprene block copolymers with a polystyrene content of 20%, confirm the change microcrystalline network. As can be seen from figure 2, the average crystallite size increases more accentuated with raising weight styrene-isoprene block copolymer composite.

Correlating the data presented in figure 1 and figure 2, we conclude that the presence of styrene-isoprene block copolymer in the polyolefin matrix primarily disrupts the formation of microcrystalline network by reducing the active centers of crystallization, which is reflected by increased crystallite size. Secondly, the introduction of styrene-isoprene block copolymers in polypropylene matrix diluted system, thereby reducing the degree of alignment of polyolefin macromolecules, which leads to a decrease in overall crystalline phase composites.

From figure 1 it can be seen that the degree of disruption of crystallinity is less dependent on the composition of styrene-isoprene block copolymer. However, it will be appreciated that the maximum effect of reducing the degree of crystallinity is produced by styrene-isoprene block copolymer SIS 20 which shows the closest melt viscosity of the recovered polypropylene, observing the best criterion for the maximum change in the melt alloying incompatible polymers.

The introducing styrene-isoprene block copolymers in polypropylene matrix composites leads to decreasing hardness, as expected, its acting as extenders of polyolefin (fig. 3). The hardness of the composites decreases in an almost linear correlation with the dosage of elastomers, respecting the law simply mixing the two components with different values of this property.

The hardness styrene-isoprene block copolymers decreases with reduced content of polystyrene and this effect is transmitted also to polypropylene composites so that the lower hardness is shown by the SIS 20 block copolymer composites.

Styrene-isoprene block copolymers introduced in polypropylene matrix by melt alloying do not change only the crystalline phase but also the amorphous phase of polyolefin. In the amorphous phase, block copolymers are dispersed in the form of well-defined areas, playing the extender elasticizing effect of its specific effect manifested by increasing elongation at break (fig. 4) while reducing the tensile strength (fig. 5).

Particularly favourable effect of this block styrene-isoprene occurs at first elastomer dosages (5 and 10%), leading to increase both tensile and elongation at break. The phenomenon can be explained by the cumulative effects caused by styrene-isoprene block copolymers on the crystalline phase and the amorphous phase of polypropylene.

Changing the crystal lattice polypropylene (fig. 2) produces a decrease of its friability and allows more uniform takeover efforts during the stretching mechanical deformation of the material, thereby increasing the tensile strength of composites. The elastomeric domains dispersed in the amorphous polypropylene acts as a plasticizer in these first dosages of styrene-isoprene block copolymers, which allows a greater stretching of the material, leading to increased elongation of the composites. Increasing dosage of styrene-isoprene block copolymers does not significantly alter polypropylene microcrystalline network (fig.2) and therefore occurs predominantly amorphous phase enlargement effect certified by elongation growth while reducing the tensile strength. The effect of modification is not significantly influenced by the composition of styrene-isoprene block copolymers, it

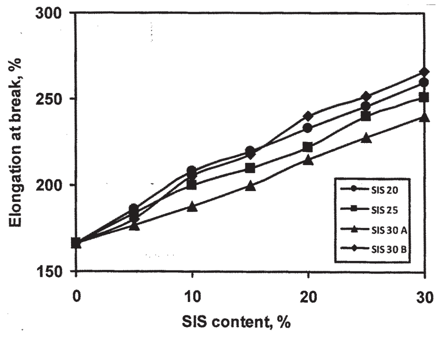

Fig. 4. Variation of the elongation at break of polypropylene composites depending on SIS content

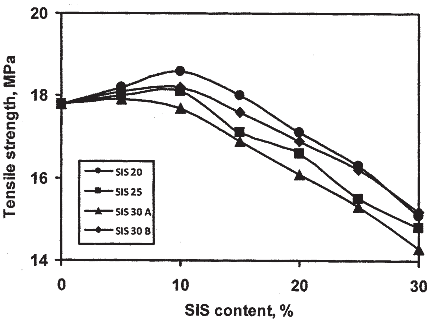

Fig.. 5. Variation of the tensile strength of polypropylene composites depending on SIS content

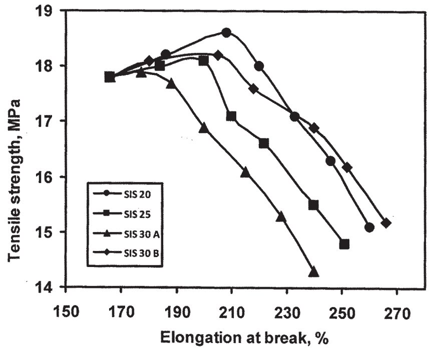

Fig. 6. Variation of the tensile strength of polypropylene composites depending on the elongation at break

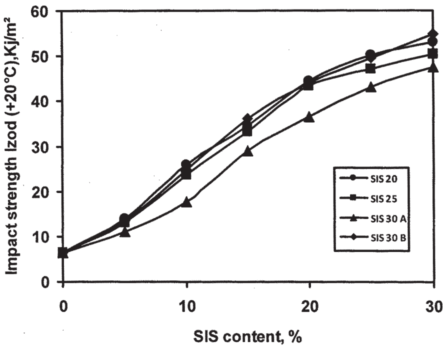

Fig. 7. Variation of the impact strength of polypropylene composites at temperature 20 ^{0}C depending on SIS content

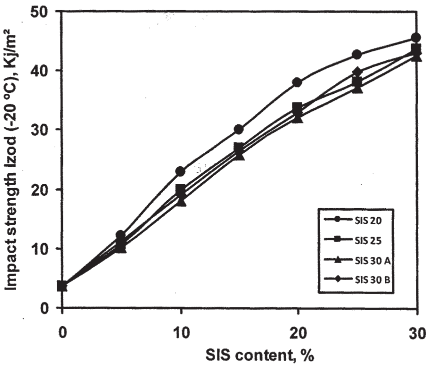

Fig. 8. Variation of the impact strength of polypropylene compositesat temperature -20 ^{0}C depending on SIS content

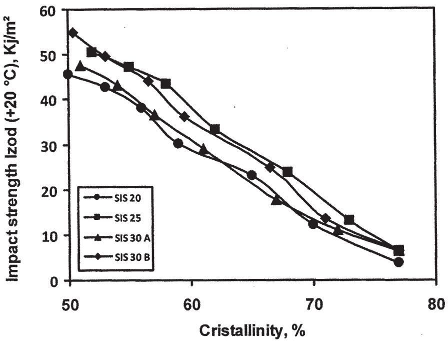

Fig. 9. Variation of the impact strength of polypropylene composites at temperature 20 ^{0}C depending on the crystallinity degree

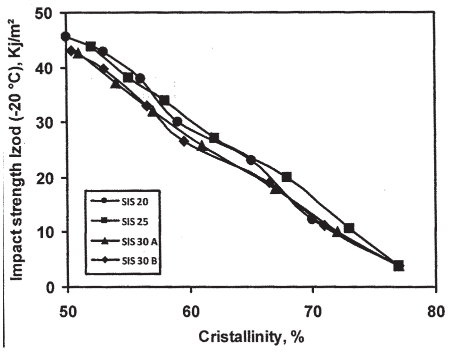

Fig. 10. Variation of the impact strength of polypropylene composites at temperature -20 ^{0}C depending on the crystallinity degree

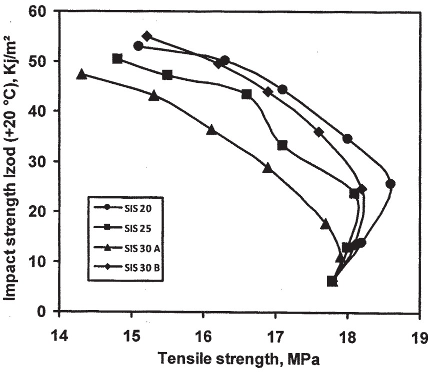

Fig. 11. Variation of the impact strength of polypropylene composites at temperature 20 ^{0}C depending on the tensile strength

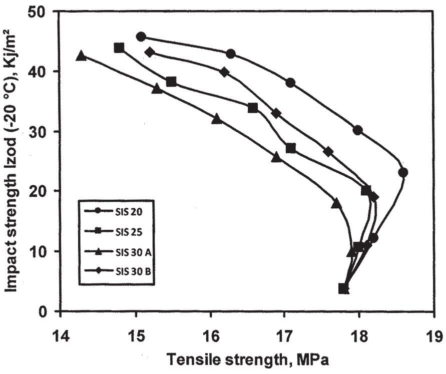

Fig. 12. Variation of the impact strength of polypropylene composites at temperature -20 ^{0}C depending on the tensile strength

amplification of being controlled its by melt rheological behaviour of elastomers. Thus SIS 20 block copolymer which shows a melt viscosity nearest of recovered polypropylene gives the most balanced composites properties, with maximum values of tensile strength and elongation at break, as can be seen from the diagrams shown in figure 6, which correlates this physico-mechanical.

The elasticizing of polypropylene composites produced by styrene-isoprene block copolymers dispersed in the form of domains in the polyolefin matrix is manifested most strongly in the growth of particular importance of compounds impact strength at ambient temperature (fig.7) and especially at a negative temperature (fig.8), the phenomenon is in direct correlation with decreasing degree of crystallinity, as can be seen from figure 9 and 10.

From figures 7 and 8 it can be seen that the effect of improving the impact strength of the composites can not be correlated with the composition of styrene-isoprene block copolymers, this indicator for each dosage elastomer featuring virtually the same values within the limits of experimental error, two exceptions: SIS 30 A and SIS 20 block copolymers.

The SIS 30 A block copolymer composites shows lower values of impact strength at positive temperatures (fig.7), and tensile strength (fig. 5) and elongation at break (fig. 4) have the lowest values, which indicate lower effect compared to other elastomers.

The optimal change criterion of incompatible polymers imposes a rheological behaviour in the melt as close to the components, the criterion being the least respected by SIS 30 A block copolymer which has melt flow index farthest from the polypropylene (table 1) and thus the degree of modification is lowest. It should be mentioned however that this styrene-isoprene block copolymer produces a considerable improvement of physico-mechanical composites of polypropylene, compared to the recovered polypropylene properties without additives.

The SIS 20 block copolymer has a melt flow index close to the recovered polypropylene, respecting the criterion of the optimum modification by melt alloying, so producing maximal change which is also confirmed by the high values of impact strength, especially at the negative temperatures (fig. 7 and 8).

As mentioned before, there are not observed significant differences between the values of impact strength polypropylene composites that contain different block copolymer containing polystyrene. The explanation is that polystyrene blocks do not come in direct contact with the polyolefin matrix, these have been dispersed in continuous polyisoprene phase. In this case, the effect of the change is produced especially from the polyisoprene phase of the block copolymers. Since blocks polyisoprene shows very similar molecular weights (table 1) and the degree of alloying is similar, polypropylene composites have almost the same impact strength at identical elastomer dosages.

The significant undifferentiated impact strength values at the same dosage of elastomer composites can be explained by the fact that styrene-isoprene block copolymers have tensile strength and elongation at break very close (table 1) and thus the weight of destructive effort taken over by phase elastomeric component composites is practically the same.

The maximal change of SIS 20 block copolymer can be seen more clearly from Patrick diagrams presented in figures 11 and 12.

The SIS 20 block copolymer composites show the highest values of impact strength, while the highest tensile strength. These charts correlate the most important indicators of physico-mechanical polypropylene composites: impact strength and tensile strength, the block copolymers dosage increasing in steps of 5% from right to left. Diagrams allow easy selection of the styrene-isoprene block copolymers dosage, which provides an optimal balance between the two properties, corresponding to the requirements of the application range of composites.

Conclusions

In a study it was determined that the same total molecular weight polystyrene content increases leading to decrease the effect of the change. Increasing the share of polystyrene blocks of block copolymers having the same molecular weight, has the effect of increasing the melt flow index, being different is more pronounced at the polypropylene recovered. This deviation from the optimal criterion melt alloying of incompatible polymer (melt rheological behavior of the components as close as) explain the decrease in the degree of modification of styrene-isoprene block copolymers with increasing of polystyrene content.

The increasing the total molecular weight in the case of styrene-isoprene block copolymer with 30% polystyrene (SIS 30 A) led to a reduction in the melt flow index of the new polymer (SIS 30 B), close to that of the recovered polypropylene, and that increased due to the effect of modification result is evidenced by improving physical and mechanical properties of composites.

In conclusion, the study of melt alloying recovered polypropylene by styrene-isoprene block copolymers containing polystyrene differently determined that all thermoplastic elastomers shows a good effect amending recovered polyolefin, producing composites with enhanced properties. The maximal modification presents SIS block copolymer molecular weight of 100,000 g/mol and containing 20% polystyrene.

References

1.JANG G.S., CHO W.J., HA C.S., KIM W., KIM H.K., Colloid Polym Sci, 280, 2002, p. 424

2.BIRON M., Thermoplastics and Thermoplastic Composites, Elsevier, 2007

3.KARGER-KOCSIS, J., Polypropylene: An A-Z Reference, Kluwer Publishers, Dordrecht, 1999

7. *** Plastic – the Facts 2013, Plastics Europe - Association of Plastics Manufactures, Brussel, p. 3

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

6.LAZAREVIC, D., AOUSTIN, E., BUCLET, N., BRANDT, N., Resources, Conservation and Recycling, 55, 2010, p. 246

7.ULTRACKI, L.A., Polypropylene Blends with Elastomers, Kluwer Publishers, Dordrecht, 1999

8.ULTRACKI, L.A., Polymer Blends Handbook, Kluwer Publishers, 2002 Dordrecht, p.1139

9.GU F., PHILIP H, MILES N.J., DING Q., WU T., Materials and Design 62, 2014 p.189

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

11.ULTRACKI, L. A., Polymer Blends Handbook, Hanser Publishers, Munich, 2003, p.37

12.DA SILVA P.A., JACOBI M.M., SCHNEIDER L.K., BARBOSA R.V., COUTINHO P.A., OLIVEIRA R.V.B., MAULLER R.S., Polymer Bull. 64, 3, 2010, p.245

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

14.LOTTI, C., CORREA, A. C., CANEVAROLO, S.V., Materials Research 3 (2), 2000, p. 37

15.CLEMONS, C., Composites: Part A., 41, 2010, p. 1559

16.HONG S.M., HWANG S.S., JEON B.H., CHOI J.S., KIM H.B., LIM S.T., Journal of Materials Science 40, 2005, p. 3857

17.KARGER-KOCSIS J., Polypropylene: Structure, Blends and Composites, Chapman & Hall, 1995

18.SMIT, I., DENAC, M., SVAB, I., RADONJIC, G., MUSIL, V., JURKIN, T. , PUSTAK, A., Polimeri, 30, 2009, p. 183

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

20.GHIOCA P., IANCU L., GRIGORESCU R. M., SPURCACIU B., BUJANCA I.C., Mat. Plast., **50** , no. 4, 2013 p. 231

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

22.GHIOCA, P., BUZDUGAN, E., et al., Brevet RO. 109.850, 1995

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

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

25.XUE M., CHEN E.W., HANSEN J., SHU I., JARRAS 5 (2), 2010, p.129

26.CRAVER, C.D., CARRAHER, C.E., Applied Polymer Science, New York, 2010

27.KELEDI G., SUDAR A., BURGSTALLER C., RENNER K., MOCZO J., PUKANSZKY B., EXPRESS Polymer Letters, 6 (3) 2012, p.224

28.ONG S.K., HASHIM A.S., International Journal of Engineering & Technology, 11 (4) 2011, p.39

29.OKSMAN K, CLEMONS C. J., Applied Polym. Sci., 67,1998, p.1503

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

31.PUKANSZKY, B., in Popypropylene A-Z, Ed. J. KARGER-KOCSIS, Kluwer Publishers, Dordrecht, 1999

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

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

34.PIERONI, P., ERCOLI, D., GOIZUETA, G., CAPIATI, N., J. Of Elastomer and Plastics, 34, 2002, p. 131

Manuscript received: 29.10.2014