Development of new recycled polypropylene/ styrene-isoprene-styrene block copolymers composites

M. RÂPĂ[a], P. N. GHIOCA[b], E. GROSU[a], L. IANCU[b], B. SPURCACIU[b], R. GRIGORESCU[b], A. TRIFOI[a], C. CINCU[c]
[a]SC ICPAO SA Medias, 8 Carpati Street, Medias, 551022, Sibiu, Romania
[b]INCDCP-ICECHIM, 202 Spl. Independentei, Sector 6, 060021 Bucharest, Romania
[c]SC ICAA SA, 49A Theodor Pallady Blv., 032258, Bucharest, Romania

Polypropylene (PP) is a thermoplastic polymer used as packaging for alcoholic and nonalcoholic beverages bottles, detergent and cosmetics, bags, transparent packaging for food and non-food industrial products, pipes, fittings and other applications. In this paper, wastes of PP resulted from textile cones were modified with poly (styrene-isoprene-styrene) (SIS). Recycled PP/SIS composites containing 0, 5, 10, 15, 20, 25 and 30 weight % of SIS were performed by melt alloying technique. By varying of SIS content can be tailored composites able to meet the service requirements when PP is used as recycled materials for specific end use applications. It is found that new developed composites show a good elasticity and notched impact IZOD compared with unmodified PP wastes and are suitable for industry field, e.g. automotive parts.

(Received March 25, 2013; accepted July 11, 2013)

Keywords: Polypropylene, Recycle, SIS thermoplastic elastomer, Composite, Mechanical Properties

1. Introduction

Polypropylene (PP) is a thermoplastic polymer used as packaging for alcoholic and nonalcoholic beverages bottles, detergent and cosmetics, bags, transparent packaging for food and non-food industrial products, pipes, fittings and other applications [1, 2].

Polypropylene has various excellent properties as a general-purpose resin, such as mechanical rigidity, resistant to heat, chemicals and fatigue, etc. [3].

Because of extensive use of PP, the generated wastes have also increased greatly. There are known several papers reporting the scraps of PP resulted from injection and extrusion processes, e.g. automotive parts [1, 4], packaging [5], disposable syringes [6], textile industry [2], pipes [7], tapes [8] etc.

Processing of PP by injection and extrusion technologies represents more than 90-95% of the PP processing areas leading to the generation of large amounts of wastes.

Several methods such as landfills, incineration, and the reuse and recycling of the plastic wastes have been used commonly to disposal of wastes [9-15].

In Romania, the amount of plastic waste per year is 331,000 tons. From this amount, according to Government Decision no. 621/2005, by 2013 it should be achieved a recycling rate of 22.5% plastics.

The approaches that have been proposed for recycling of waste polymers include: primary recycling (referring to the “in-plant” recycle of the scrap material of controlled history), mechanical recycling (where the polymer is separated from its associated contaminants and it is reprocessed by melt extrusion), chemical or feedstock recycling and energy recovery (leading in total depolymerization to the monomers, or partial degradation to other secondary valuable materials).

Recycling of the industrial wastes is not only an attempt to decrease environmental pollution but also an effort to increase economical effectiveness [16].

Several papers were dedicated to investigations of PP wastes in the production of wood plastic composites, construction material and insulation material. For example, PP wastes are promising alternative raw materials for making low cost WPCs (wood plastic composites) [17-19].

Polypropylene offers, potentially, a route to improved insulation systems by virtue of its higher melting point and excellent dielectric properties [20]. Yildirim et al. [21] studied the use of PP wastes generated mostly from packaging to produce insulation and other building materials by reinforced with fly ash. Hugo et al. [22] reported the use of $CaCO_3$ for the same purpose. Giannadakis et al. [23] investigated a composite made of recycled carbon fibers in recycled polypropylene matrix. Such composites could be used as house-heating sources in template and cold climates [6].

Wang et al. [2] studied the use of carpet waste fibers in fiber reinforced concrete and demonstrated that such reinforcement can effectively improve the shatter resistance, toughness and ductility of concrete.

According to Konin [24] plastic waste of PP was melt and mixed with a varying proportion of sand (between 50 and 80% in weight) in the manufacturing of roofing tiles. Murphy et al. [25] reported the use of recycled PP to improve the performance of bitumen.

For some applications, particularly at low temperatures, PP shows a lack of toughness [3, 26].

Impact property of this polymer can be improved by blending with an amorphous elastomeric material without compromising its thermal and other structural properties.

There are presented in literature composites including PP reinforced with wood flour and impact modified with elastomers (ethylene propylene-diene (EPR) elastomer) [3, 27-31], acrylonitrile-butadiene rubber (NBR) [32], styrene-ethylene-butylene-styrene block copolymer (SEBS) [9, 33, 34] to increase stiffness and impact resistance simultaneously.

In this study post-consumer polypropylene and styrene-isoprene-styrene block copolymer (SIS) composites have been prepared by melt alloying technique and they were characterized by mechanical properties, such as elongation at break, tensile strength, hardness and IZOD impact strength.

Also, the mechanical properties of RPP/SIS composites were evaluated in comparison to a recycled unmodified PP.

By varying of SIS content can be tailored composites able to meet the service requirements when PP is used as recycled materials for specific end use applications. The obtained composites can represent a potential raw material for industry field, e.g. automotive parts.

2. Experimental

2.1 Materials and Methods

A *recycled polypropylene (RPP)* with 14 g/10 min melt index measured at 230 ºC and 2.16 kg and density of 0.8920 g/cm^3 was selected as a matrix of all the composites prepared. This material was kindly supplied by a local recycler; it was obtained from post-consumer textile cones.

Styrene-isoprene-styrene (SIS) block copolymers have synthesized by ICECHIM according to the method described by Hsieh [35] and Ghioca et.al. [36]. SIS block-copolymers contain 20 wt. % and respectively 30 wt. % styrene.

Table 1. The characteristics of the studied SIS block copolymers

SIS block copolymer	Characteristics
SIS with 20 wt.% styrene	Tensile strength = 7.20 MPa Elongation at break = 1520 % T_g of polystyrenic phase = 90 ºC T_g of polyisoprenic phase = -61 ºC Hardness Shore A = 34 ^{0}ShA
SIS with 30 wt.% styrene	Tensile strength = 8.70 MPa Elongation at break = 1080 % T_g of polystyrenic phase = 92 ºC T_g of polyisoprenic phase = -60 ºC Hardness Shore A = 47 ^{0}ShA

SIS block copolymers have some fascinating properties due to its elastomeric - (polyisoprene) and thermoplastic (polystyrene) properties. Due to the covalent linkage between chemically dissimilar segments, the rigid polystyrene domains may form a three-dimensional network of crosslink sites. Consequently, SIS block copolymers exhibit mechanical properties that are, in many ways, comparable to those of a vulcanized (covalently cross linked) rubber [37].

The characteristics of SISs used in this paper are presented in Table 1.

SISs have synthesized by anionic polymerization of monomers in cyclohexane solution using n-butyl lithium, as initiator. Materials for synthesis of SIS were: styrene, isoprene, n-buthyllithium in 1 M cyclohexane solution (max. 5 ppm content of humidity), 2,6-ditert-buthyl-4-methyl fenol TOPANOL OC) as antioxidant, methylcellulose, azot. Polymerisation was carried out sequentially: to start the first polystyrenic block was synthesized by polymerization of styrene using n-butyl lithium; after polymerizing the first polystyrene block, isoprene is added, followed by polymerisation of the polystyrene end block.

This technique allows obtaining of block copolymers having a right composition, the molecular mass of polystyrene and polyisoprene blocks being well defined and showed a low distribution. Both SISs possess a molecular weight of 100,000 g/mol.

2.2 Preparation of the Composites

Seven composites formulations are given in Table 2 as original formulations for each type of SIS. The content of SIS was varied from 0 to 30 wt. %.

There are known papers concerning the maximum elastomer in PP composites up to 40 % [28, 38, 39].

Melt alloying of RPP with SIS block copolymers was performed using a lab two roll mixing mill with diameter of rolls of 140 mm. First, RPP was processed on two roll mixing mill for sheeting it out. The sheets were further cut into small pieces for easy incorporation into the machine for blending with SIS.

Table 2. Composition of the investigated composites

Code recipe	RPP (wt. %)	SIS (wt. %)
RPP:SIS 100:0	100	0
RPP:SIS 95:5	95	5
RPP:SIS 90:10	90	10
RPP:SIS 85:15	85	15
RPP:SIS 80:20	80	20
RPP:SIS 75:25	75	25
RPP:SIS 70:30	70	30

Then, a hot press lab was used for obtaining of plates with dimensions of (150x150x1) mm and (150x150x4) mm. Specimens for measurements of the mechanical properties were cut from these plates.

Technical parameters are specified in Table 3.

Table 3. Technical parameters for sheets and plates

Parameters	U.M.	Value
Rolling		
Rolling Temperature	^0C	185 – 190
Rolling Time	minute	10
Friction ratio	-	1 :1.2
Pressing		
Preheating Time	minute	4
Pressing Time	minute	2
Pressing Temperature	^0C	185
Pressure	atm.	150
Cooling time	minute	30

2.3 Characterization

Tensile Properties

Tensile properties were tested using a FP 10/1 machine according to ISO 527 standard procedures. It was used test specimens of 1 mm thickness and a crosshead speed of 50 mm min^{-1}. At least five samples were tested for each composition, and the average value was reported.

Hardness Shore

Hardness Shore was tested using a Durometer with Shore D scale, according to ISO 868. Test specimens of 4 mm thickness and a loading force of 4536 g were used. At least five points were tested for each composition, and the average value was reported.

IZOD Test

The impact test was carried out using a IZOD Pendulum (CEAST, Italy) according to ISO 180 on specimens with dimensions of (80 x 10 x 4) mm. Notching of 8 mm depth on the sample was done by using notching apparatus by CEAST, Italy. The test was performed with a hammer of 2 J energy. At least, 10 specimens of each sample were tested to obtain the impact strength.

IZOD Impact strength (a_{IN}), expressed as kJ/m^2 is calculated by dividing impact energy in J by the area under the notch, according to formula (1):

$$a_{IN} = \frac{E_c}{hxb} x\ 10^3,\ kJ/m^3 \qquad (1)$$

where:

E_C energy used for breaking of specimen, J;
h thickness of specimen, mm;
b width of specimen under notch, mm.

All measurements were performed at ambient conditions, i.e., a temperature of 23°C and a relative humidity of approximately 50%.

3. Results and discussions

Fig. 1 plotted the tensile strength of the RPP/SIS composites made with various formulations.

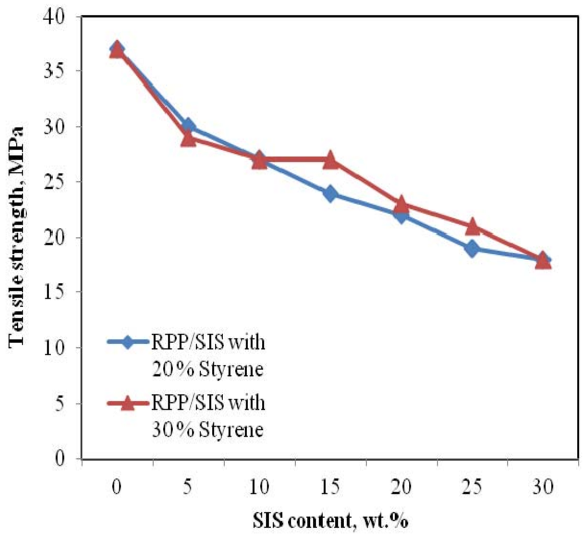

Fig. 1. Tensile strength of RPP/SIS composites plotted against SIS content

It can be seen from Fig. 1 that the stiffness is not significantly affected by the styrene content of two SIS block copolymers; the composites show the same behavior.

The stiffness of the composites significantly decreases with the increase of SIS content. Investigated samples show a decrease of tensile strength even the addition of 5% thermoplastic elastomer to thermoplastic matrix, it continued to decline to about 50% of the recycled unmodified PP. Initial value of tensile strenght was 36 MPa and by increase of SIS content up to 30%, the tensile strength reached 17 MPa. The decrease of tensile strength is due to the poor miscibility between polypropylene matrix and elastomeric phase. As tensile strength significances the force reported to section, the diluting the polypropylene matrix with thermoplastic elastomer leads to decrease of tensile strength.

These data are in accordance with data obtained by Balkan et. al. [34] that studied the mechanical properties of PP/SEBS blends. By increasing of SEBS content in polyolefin matrix up to 20%, they found decreasing of tensile strength from 19.42 MPa to 17.82 MPa.

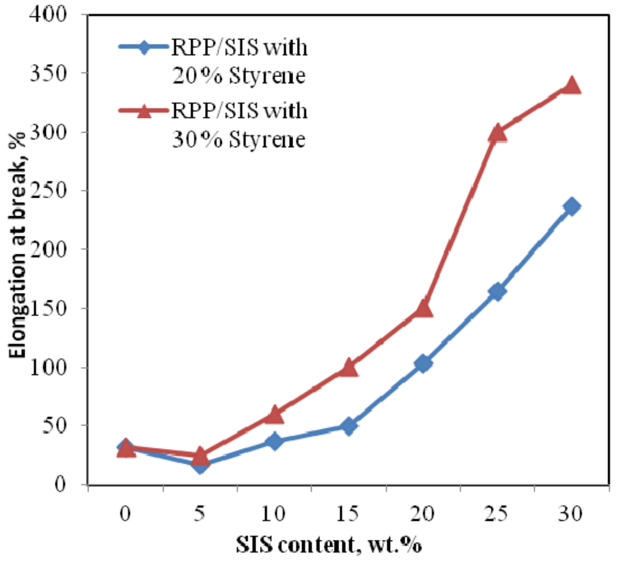

Fig. 2. Elongation at break of RPP/SIS composites plotted against SIS content

Elongation at break is illustrated in Fig. 2. Elongation at break exhibited a significantly increase with the increase of SIS content. The increase in elongation at break is due to the substitution of PP matrix with SIS elastomer. As can be seen from Figure 2, the composites made with 30 % styrene show the higher elongation at break than those with 20 % styrene. This is due to low viscosity of block copolymer containing 30 % of styrene.

It is generally known that the thermoplastic elastomer shows high elongation. At 5 % SIS in composites is observed a decrease of elasticity. At 10% SIS in composites already recorded an increase in elongation at break of 17 % for RPP/SIS composite with 20 % styrene, respectively of 87 % for RPP/SIS composite with 30 % styrene, in comparison with one recycled unmodified PP. This increase of elongation is strongly dependent on the content of SIS, reaches up to 7 times, respectively 10 times from unmodified RPP.

Hardness Shore D of RPP/SIS composites with 20% and 30% styrene in content is shown in Fig. 3. As rubber content is added into PP matrix the hardness decreases, as is expected. Hardness Shore depends on the viscoelastic properties of the material. These data are in accordance with elongation at break. That means the rubber elastomer can act as plasticizer for PP matrix.

Fig. 4 shows the IZOD impact strength of the composites made with the different SIS content. Impact test provides information about the performance of polymeric blends.

The graphical representation of the notched impact strength shows a similar trend to that observed for elongation at break, giving higher impact values as SIS content increases. By adding of 30 % SIS in composites, impact strength reaches up to 15 times from unmodified RPP. Also, the content of styrene from SIS block copolymers does not affect the impact strength. RPP/SIS composites in the low elastomer content region (< 10 %) show low values of the Izod impact strength and both, elastomer content and impact strength, are directly proportional to the addition of elastomer.

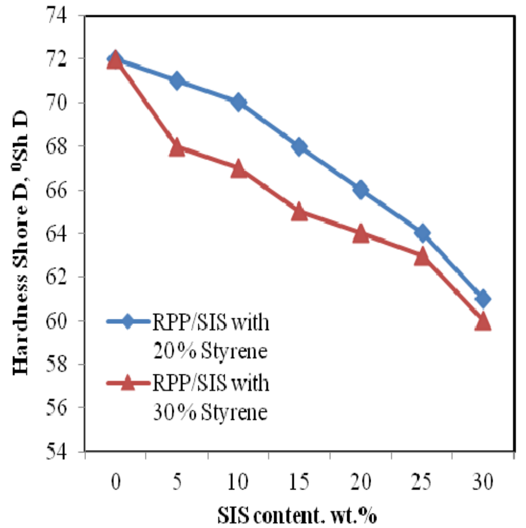

Fig. 3. Hardness Shore D of RPP/SIS composites plotted against SIS content

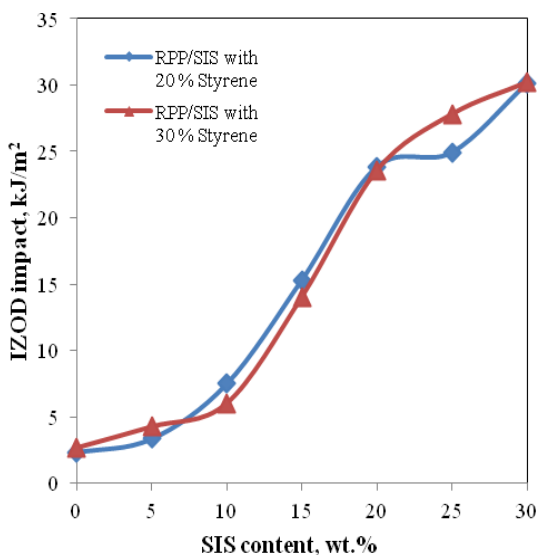

Fig. 4. IZOD notched impact strength of RPP/SIS composites plotted against SIS content

It is well known that addition of a low T_g rubber like material to a high T_g, hard polymer may result in dramatic improvement in the toughness of the hard polymer [40]. The improvement in impact strength when an elastomer is added to a polymeric matrix normally implies in a reduction of its stiffness, which is usually related to a decrease in tensile strength and an increase in the elongation in good agreement with data from [26, 29, 33]. SIS block copolymer works as an effective impact modifier for the RPP.

The typical applications of these composites with high impact property are found in automobile field. The most important physical properties for selecting and engineering such materials include stiffness, toughness, melt index, density, etc.

Therefore, a proper combination of those components should be selected in order to achieve the balance of the mechanical behavior of such engineering composites.

There are known impact copolymers of polypropylene with applications in injection moulding, as caps&closures, batteries, pails, automotive, etc. For example, Moplen EP1006 can be used in injection moulding for applications requiring a high resistance to temperature degradation, in particular for battery cases and automotive components. It has Charpy notched impact strength of 21 kJ/m^2, while other copolymers for a variety of industrial and consumer applications have Izod notched impact strength of 24 kJ/m^2. Non painted automotive bumpers are characterised by tensile stress at break of 13 MPa, elongation at break 100 % and notched Izod impact strength without break at 23 ^{0}C [41].

From setting the optimal RPP/SIS composites we plotted tensile strength of RPP/SIS composites against elongation at break (Fig. 5) and notched IZOD impact against tensile strength (Fig. 6).

From Figure 5 is observed that an elongation at break of minimum 100 % corresponds to a tensile strength of minimum 22 MPa. By analyzing the results of tensile properties from Figures 1 and 2 is shown that these requirements can be fulfilled by composites containing 15 % SIS in formulation.

Also, analyzing Fig. 6, it was noted that high impact strength values correspond to composites with tensile strength up to maximum 25 MPa. Even at small values of tensile strength of 15-20 MPa are recorded high values for Izod strength of 30 kJ/m^2. This corresponds to high percent of SIS in compositions.

Between two types of studied block copolymers for fulfilled the requirements about tensile properties and Izod strength the most appropriate is that with 30 % styrene in content.

Therefore, depending on the desired properties, the composites of the present paper can be tailored to meet performance specifications for diverse industrial applications.

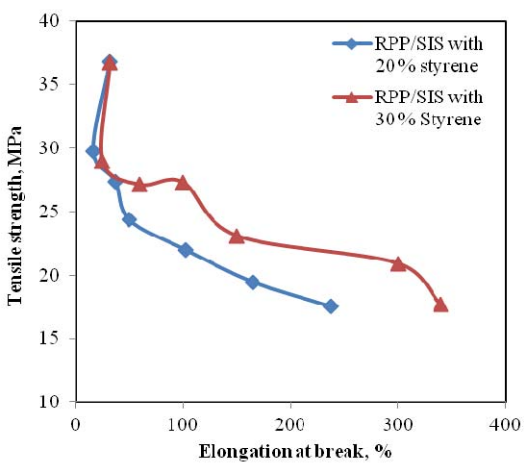

Fig. 5. Tensile strength of RPP/SIS composites plotted against elongation at break

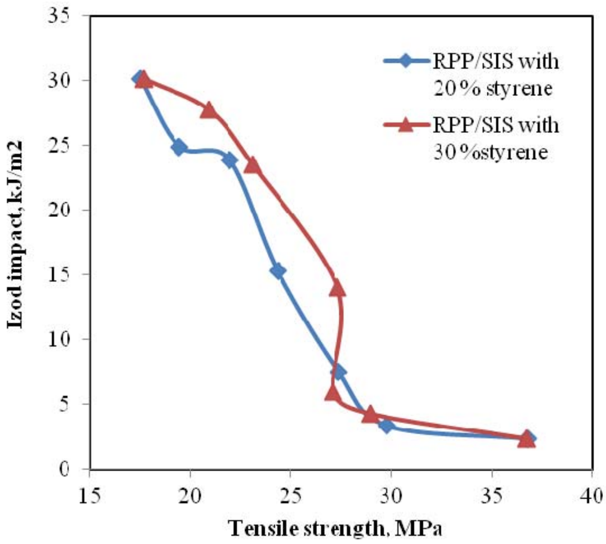

Fig. 6. Izod impact of RPP/SIS composites plotted against tensile strength

4. Conclusions

Based on the results of this study the following conclusions can be drawn.

The toughness (elongation at break and Izod impact strength) of the composites made with RPP and SIS increases with SIS content, while the stiffness (tensile strength) decreases with incorporation of SIS.

By comparison of composites with different styrene content in block copolymers, it can be stated that there are no significantly difference between mechanical properties of composites regarding tensile and impact strength, only difference being to elongation at break and hardness. In order to improve impact property of RPP/SIS composites, it is thought that 30 % styrene content in SIS block copolymers is preferable.

The results showed that recycled polypropylene from textile cones compounded with (styrene-isoprene-styrene) block copolymer is a promising alternative of raw materials for making materials with higher properties of elongation at break and impact strength.

The composites can be adapted to meet the performance specifications in some or all of the properties simultaneously. The optimal stiffness and impact balance provides utility in industrial applications.

Acknowledgements

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

References

[1] S. Moritomi, T. Watanabe, S. Kanzaki, R&D Report, "Sumitomo Kagaku", 1-16 (2010).

[2] Y. Wang, A.H. Zureick, B.S. Cho, D.E. Scott, Journal of Materials Science **29,** 4191 (1994).
[3] G.S. Jang, W.J. Cho, C.S. Ha, W. Kim, H.K. Kim, Colloid Polym Sci **280,** 424 (2002).
[4] R.T. Quazi, S.N. Bhattacharya, E. Kosior, Journal of Materials Science **34**, 607 (1999).
[5] A. Nishijima, J. Nakatani, K. Yamamoto, F. Nakajima, J Mater Cycles Waste Manag **14**, 52 (2012).
[6] F.H.-Sánchez, P.J. Herrera-Franco, Polymer Bulletin **45**, 509 (2001).
[7] N. O. Cabrera, B. Alcock, E. T. J. Klompen, T. Peijs, Appl Compos Mater **15**, 27 (2008).
[8] B. Alcock, N. O. Cabrera, N. M. Barkoula, T. Peijs, Appl Compos Mater **16**, 117 (2009).
[9] Y.M. Song, Q.Wen Wang, G.P. Han, H.G. Wang, H. Gao, Journal of Forestry Research **21**(3), 373 (2010).
[10] D.S. Achilias, E. Antonakou, C. Roupakias, P. Megalokonomos, A. Lappas, Global Nest Journal **10** (1), 114 (2008).
[11] D.S. Achilias, A. Giannoulis, G.Z. Papageorgiou, Polym. Bull. **63,** 449 (2009).
[12] G. Grause, A. Buekens, Y. Sakata, A. Okuwaki, T. Yoshioka, J Mater Cycles Waste Manag **13,** 265 (2011).
[13] R. Irinislimane, N. B. Bensemra, A. Benlefki, J. Polym Environ **15,** 119 (2007).
[14] A. Aboulkas, K.E. Harfi, A.E. Bouadili, M. Ben Chanâa, A. Mokhlisse, J of Therm Anal and Calorim **89**(1), 203 (2007).
[15] D.S. Rosa, M.A.G. Bardi, L.D.B. Machado, D.B. Dias, L.G.A. Silva, Y. Kodama, J Therm Anal Calorim. **102**, 181 (2010).
[16] J. A. Kajaks, S.A. Reihmane, M.G. Tsiprin, Mechanics of Composite Materials **35**(2), 139 (1999).
[17] A. Nourbakhsh, A. Ashori, H.Z. Tabari, F. Rezaei, Polym. Bull., **65**, 691 (2010).
[18] A. Ares, R. Bouza, S.G. Pardo, M.J. Abad, L. Barral, J Polym Environ **18**, 318 (2010).
[19] M. Tajvidi, A. Takemura, J Polym Environ **18,** 500 (2010).
[20] I.L. Hosier, A.S. Vaughan, S.G. Swingler, J. Mater Sci. **46**, 4058 (2011).
[21] M. Sükrü Yildirim, Y. Bícer, C.Yildiz, Journal of Porous Materials **3,** 189 (1996).
[22] A.M. Hugo, L. Scelsi, A. Hodzic, F. R. Jones R. Dwyer-Joyce, Plastics, Rubber and Composites **40**(6/7), 317 (2011).
[23] K. Giannadakis, M. Szpieg, J. Varna, Experimental Mechanics **51**, 767 (2011).
[24] A. Konin, Materials and Structures **44**, 1381 (2011).
[25] M. Murphy, M. O'Mahony, C. Lycett and I. Jamieson, Materials and Structures/Matériaux et Constructions **33**, 438 (2000).
[26] C. Lotti, C.A. Correa, S.V. Canevarolo, Materials Research, **3**(2), 37 (2000).
[27] S.G. Echeverrigaray, R.C.D. Cruz, R.V.B. Oliveira, Polym. Bull., 1-14 (2012).
[28] G. Keledi, A. Sudár, Ch. Burgstaller, K. Renner, J. Móczó, B. Pukánszky, eXPRESS Polymer Letters, **6**(3) 224 (2012).
[29] C. Clemons, Composites: Part A. **41,** 1559 (2010).
[30] Y. G. Shang-Guan, F. Chen, Q. Zheng, Science China Chemistry, **55**(5) 698 (2012).
[31] G. Ragosta, P. Musto, E. Martuscelli, P. Russo, Journal of Materials Science **35,** 3741 (2000).
[32] J. Jose, A. Nag, G. B. Nando, J Polym Environ **18**, 155 (2010).
[33] S. M. Hong, S. S. Hwang, B. H. Jeon, J. S. Choi, H.B. Kim, S.T. Lim, H.J. Choi, Journal of Materials Science **40,** 3857 (2005).
[34] O. Balkan, H. Demirer, E. Sabri Kayali, Journal of Achievements in Materials and Manufacturing Engineering **47**(1), 26 (2011).
[35] H.L. Hsieh, R.P. Quirk, Anionic Polymerization, Marcel Dekker, New York, (2008).
[36] P. Ghioca, E. Buzdugan, Brevet RO 109850, (1995).
[37] M. Xue, Q. Chen, E. W. Hansen, J. Shu, IJRRAS **5**(2), 129 (2010).
[38] S.K. Ong, Azanam S. Hashim, International Journal of Engineering & Technology IJET-IJENS, **11**(4), 39 (2011).
[39] K. Oksman, C. Clemons, J. of Appl Polym Science, **67**, 1503 (1998).
[40] T. Whelan, Polymer technology dictionary. Chapman & Hall: London, 439 (1994).
[41] http://www.lyondellbasell.com/.

*Corresponding author: rapa_m2002@yahoo.com