

Evaluation of Mechanical and Thermal Properties of Polypropylene Random Copolymer and Triblock Copolymer Blends

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*This investigation concerns the preparation of binary PPR/SEBS and PPR/SBS blends by melt mixing procedure with the goal of studying the effect of thermoplastic elastomers on performance of polypropylene random copolymer (PPR) in the extrusion and injection molding processes. Effect of poly[styrene-*b*-(ethylene-co-butylene)-*b*-styrene] (SEBS) and poly(styrene-*b*-butadiene-*b*-styrene) (SBS) respectively on the mechanical and thermal properties of PPR have been investigated. The melt processability, melt flow index (MFI), tensile properties, VICAT softening temperature (VST), heat deflection temperature (HDT), Shore hardness and IZOD measurements highlighted that SEBS is more efficient than SBS.*

Keywords: binary blend, melt processability, toughness, stiffness

Polypropylene random copolymer (PPR) is a thermoplastic polymer widely used in many applications including high clarity/transparency packaging, injection molding, blow molding and industrial products, such as pipes, fittings and auto parts [1, 2]. Despite its versatile properties and low cost it has been still necessary to improve the mechanical performance in order to meet the industrial requirements for certain applications. The improvements made thus far include greater rigidity and impact strength. Data from literature have been revealed the use of various types of fillers for incorporation into thermoplastic matrix to enhance the mechanical performance of polypropylene (PP), such as wood fiber [3-8], hemp fibers [9], talc [10], kaolin [11] and recycled polyamide 66 fibers [12]. Recently, cellulose nanocrystals [13, 14], multiwall carbon nanotube [15, 16], organoclay [17], almond shell flour [18], graphene [19] and ZnO [20, 21] have been found as attractive fillers for green polymer nanocomposites based on polypropylene. Irradiation is another way to increase the mechanical properties of the polypropylene composites [22-24]. Beside these, compounding of PP with thermoplastic elastomers (TPEs) is another method to improve the mechanical properties of PP blends. TPEs belong to a class of materials that have the combined physical properties of thermoplastics and elastomers [25]. Ethylene-propylene-diene elastomer [3, 26], acrylonitrile butadiene rubber (NBR) [25, 27], styrene-ethylene/butylene-styrene (SEBS) [6, 28], styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS) [29], natural rubber [25, 30], etc., have been used as TPE impact modifiers for PP properties.

This paper is focused on investigation of the effect of SEBS and SBS on mechanical and thermal properties of PPR. Melt viscosity, tensile properties, melt flow index (MFI), VICAT softening temperature (VST), heat deflection temperature (HDT), hardness Shore and IZOD impact strength properties are critical to the performance of PP blends in the extrusion and injection molding processes.

Experimental part

Materials

Polypropylene Random Copolymer β PPR RA 7050 (PPR) was supplied by Borealis Polyolefine GmbH (Linz, Austria), it has MFI of 0.3 g/10 min (at 230°C/2.16 kg), tensile stress at yield of 25 MPa; tensile modulus of 800 MPa and Charpy notched impact of 20 kJ/m² (at +23°C) and is designed for plumbing and heating applications.

Two block-copolymers were used as impact modifiers:

a) CALPRENE H6144 (SEBS) from Spain, a linear poly[styrene-*b*-(ethylene-co-butylene)-*b*-styrene] was obtained by polymerization in solution and is characterized by 5.23 % toluene solution viscosity of 30 cSt; volatile matter, max. 0.5 %; total styrene (on polymer) 31 %, hardness of 75° Shore A; saturation degree > 99 %.

b) SOL T161 C (SBS) from Versalis, Italy is a poly(styrene-*b*-butadiene-*b*-styrene) star copolymer characterized by total styrene (on polymer) 30 %, hardness of 69° Shore A, 170,000 g/mol molecular mass, 10,500 g/mol polystyrene block mass, 98,000 g/mol polybutadiene block mass, T_g of polybutadiene block of -80°C, T_g of polystyrene block of +88°C.

Preparation of PPR/SEBS and PPR/SBS blends

Binary PPR/SEBS and PPR/SBS blends with content ratios of 100/0, 95/5, 90/10, 85/15, 80/20, 75/25 and 70/30 wt.% were prepared by melting in a Brabender Plastograph. A processing temperature of 190°C, rotor speed of 40 rpm, and mixing time of 10 min. were used for preparation of the blends. Square sheets with (150 x 150 x 4) mm and (150 x 150 x 1) mm dimensions were prepared from melted blends by rolling and pressing, at temperature of 175 °C and 125 atm.

Test specimens for tensile strength, hardness Shore, VICAT softening temperature (VST), heat deflection temperature (HDT) and IZOD impact strength measurements were prepared with a puncher.

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Melt processability

Melt processability (torque and melt viscosity) of the prepared blends was evaluated to constant values of 10 min and 40 rpm. Melt viscosity (η) is given as the ratio of shear stress to shear rate, and herein can be obtained from the ratio of torque to rotor speed:

$$\eta = K(M/S) \quad (1)$$

where:

K is a constant depending on temperature; M is torque value (Nm) and S is the rotor speed (rpm).

Melt flow index (MFI) measurement

Measurement of melt flow index (MFI) was performed following the ISO 1133 standard at a temperature of 190°C by applying a loading of 2.16 kg to the piston in the heated barrel. The test was performed in triplicate on about 10 g material and the average value was reported.

Tensile properties

Standard tensile tests were conducted on dumbbell shaped specimens using a FP 10/1 machine. Test speed was kept at 200 mm/min, according to ISO 527-2 standard. At least five samples were tested for each composition, and the average value was reported.

Hardness Shore

Hardness measurements were determined 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 blend, and the average value was reported.

VICAT softening temperature (VST) analysis

Determination of VICAT softening temperature was performed according to ISO 306, A50 Method. The test was conducted at a heating rate 50°C/h using a HDT/VICAT SOFTENING POINT Apparatus (CEAST Test Equipment). Three test specimens with thickness of 4 mm were measured and the average value was reported. The softening point is the temperature where the needle penetration reaches the specified distance (deep of 1 mm).

Heat deflection temperature (HDT) analysis

Heat deflection temperature (HDT) measurements were carried out by using specimens with (80 x 10 x 4) mm dimensions according to EN ISO 75, A Method. The test was conducted at a heating rate of 120°C/h and a load of 1.8 MPa using a HDT/VICAT SOFTENING POINT Apparatus (CEAST Test Equipment). HDT was the temperature at which the specimen distortion increased to 0.32 mm during the heating process. Three test specimens were performed and the average value was reported.

Notched IZOD impact strength

The notched IZOD impact strength was used to evaluate the brittleness or toughness of the blends. The specimens with (80 x 10 x 4) mm dimensions were measured by means of an IZOD hammer (CEAST, Italy) according to ISO 180. 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 and the values reported were an average calculated from at least ten specimens. IZOD impact strength (α_{IN}), expressed as kJ/m² is calculated by dividing impact energy by the area under the notch, according to formula (2):

$$a_{IN} = \frac{E_c}{hxb} \times 10^3, \text{kJ/m}^2 \quad (2)$$

where:

E_c is energy used for breaking of specimen, J; h is thickness of specimen, mm and b is 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 %.

Results and discussions

Torque-time curves

The torque - time curves of PPR/SEBS and PPR/SBS blends are illustrated in figure 1a and b.

First the PPR was melt mixed for 4 min, then the SEBS and SBS respectively were added in corresponding ratio. The torque of the physical blends decreases slowly until the end of mixing compared with neat PPR due to decrease in the viscosity and elasticity of the rubber phase. At 6 minutes, the torque indicated a complete melting of PPR and full homogenization of SEBS and respectively SBS into the PPR matrix. The torque registered a higher value at the end of melting (10 min.) with the increasing of elastomer content, as can be seen from figure 1. Blends based on PPR and SBS showed higher values of torque than those with SEBS.

Melt viscosity of polymers is a significant factor with respect to processing operations involving the melt flow such as compression moulding, extrusion and injection molding. The melt viscosity index of PPR/SEBS and PPR/SBS blends is presented in figure 2.

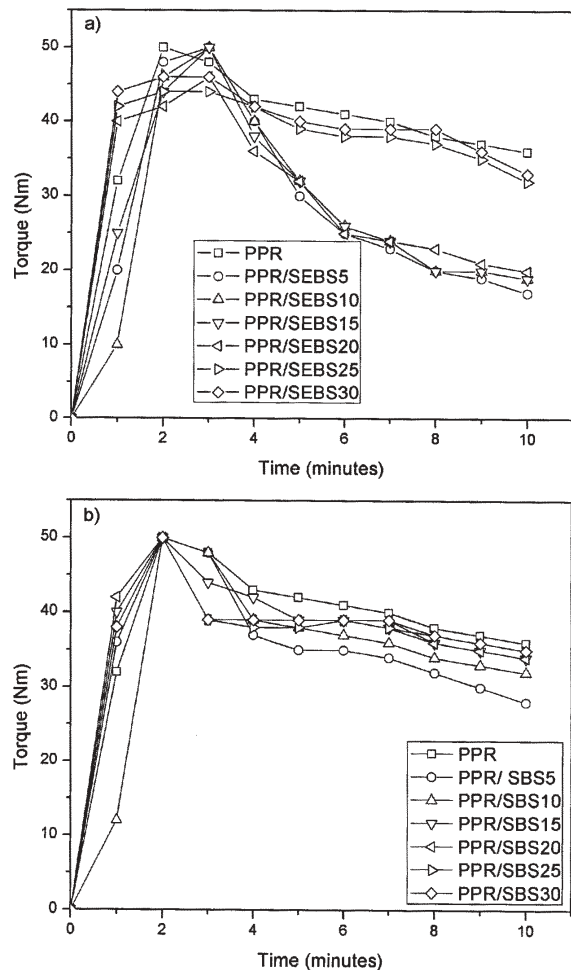


Fig. 1. Torque time curves of the PPR/TPE blends at 190 °C and 40 rpm a) PPR/SEBS blends; b) PPR/SBS blends

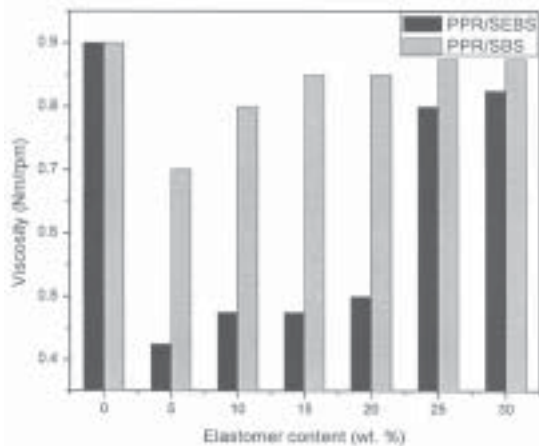


Fig. 2. Melt viscosity index of PPR/SEBS and PPR/SBS composites vs. elastomer content

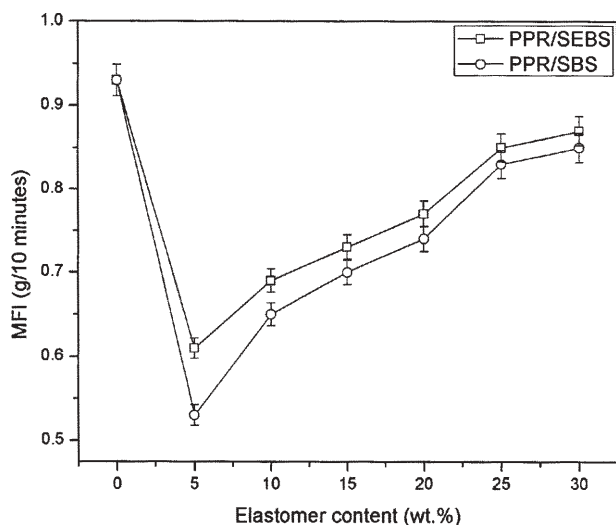


Fig. 3. Dependence of MFI on elastomer content. Error bars represent standard deviation, $n = 3$

From figure 2 it is obvious that the lowest melt viscosity is registered at 5 % elastomer. A slow increase in melt viscosity of PPR/SEBS blends is observed up to 20 % SEBS. PPR/SEBS blends present lower viscosity than PPR/SBS; all blends showed lower viscosity relative to neat PPR. This is due to the improvement of the mobility of ethylene-butylene chains of SEBS leading to the reduction in melt viscosity. PPR/SEBS blends with SEBS content between 5 and 20 wt.% indicated the best processability during mixing at temperature of 190°C and 40 rpm.

Melt flow index (MFI) measurement

Figure 3 shows the effect of elastomer content on the melt flow index of PPR/SEBS and PPR/SBS blends.

From figure 3 it is noticed that all investigated blends follow approximately the same curve profiles for MFI values. However, PPR/SEBS blends exhibit higher MFI values than PPR/SBS blends, meaning the easier flow under a given temperature and pressure. In other words, SEBS led to a lower viscosity of PPR blends than those containing SBS. The easier flow requires less pressure and energy for extrusion of products. Flow properties of PPR blends are in good agreement with the melt viscosity index evaluated from Brabender plastograms (fig. 2).

Tensile properties

The influence of elastomer type and concentration on the mechanical properties (tensile strength and elongation at break) of PPR blends is depicted in figures 4 and 5.

As can be seen from figure 4, the tensile strength values decreased linearly as the percentage of elastomer increased. Minor differences between two types of elastomers can be attributed to standard uncertainty. At 30 % elastomer, the tensile strength decreased with about 40% than that of neat PPR due to the molecular entanglements in the rubber chains which are unable to prevent rapid flow and fracture in response to the applied stress [25, 31]. It was also observed from figure 4 that the tensile strength of PPR with 5% elastomer reached the higher values compared to polypropylene matrix. This can be attributed to the presence of additives including processing fillers or reinforcements, plasticizers, stabilizers, antioxidants, colorants/pigments, flame retardants, internal or external lubricants into polymeric matrix.

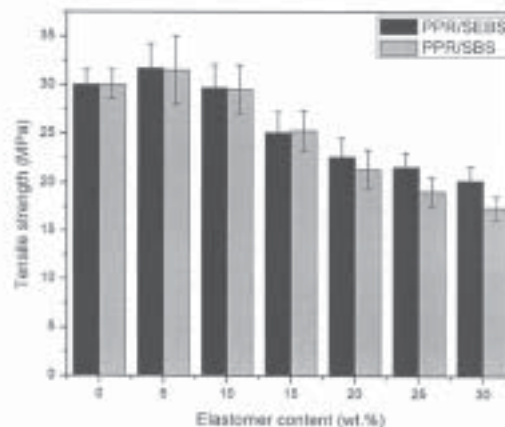


Fig. 4. Dependence of the tensile strength on the elastomer content for the PPR blends. Error bars represent standard deviation, $n = 5$

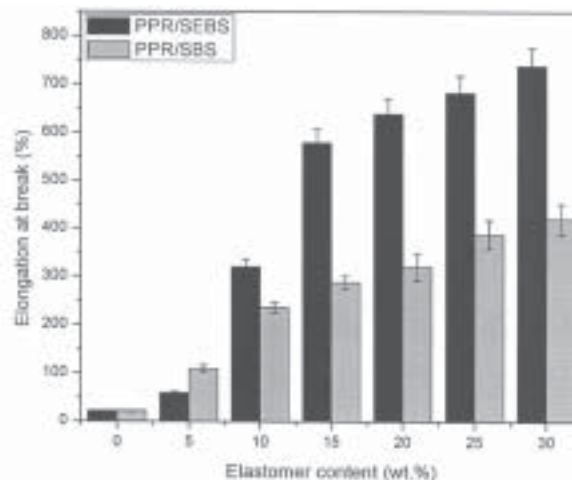


Fig. 5. Dependence of the elongation at break on the elastomer content for the PPR blends. Error bars represent standard deviation, $n = 5$

From figure 5 is observed that the elongation at break increased with elastomer content due to the presence of elastomer which favors the flow and mobility of PPR/TPE blends. Even at 10 % elastomer an increase of elongation at break of almost 14 times than pure PPR is recorded. The elongation at break increased to about 33 times and respectively to about 19 times for PPR/SEBS and PPR/SBS blends containing 30 wt.% elastomer. These results are in good agreement with other researchers which reported that addition of elastomer reduced the stiffness and increased the elongation at break of blends [3, 25, 28, 31].

Hardness Shore measurement

In figure 6 the hardness Shore D of investigated PPR/TPE blends is depicted.

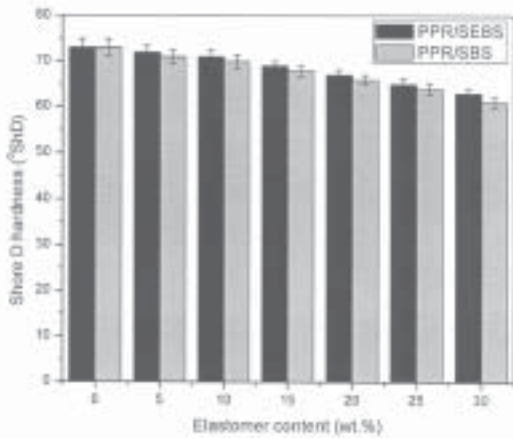


Fig. 6. Effect of type and concentration of elastomer on Shore D hardness for PPR blends. Error bars represent standard deviation, n = 5

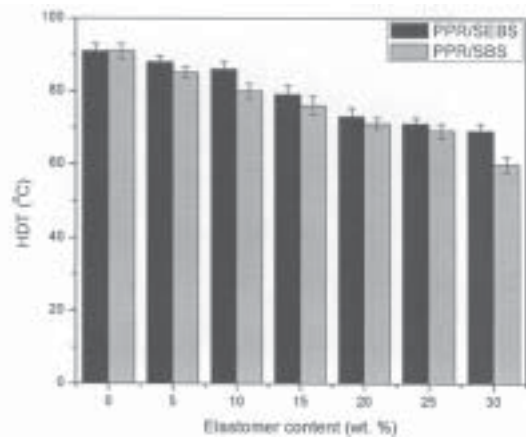


Fig. 8. HDT for PPR/TPE blends vs. elastomer content. Error bars represent standard deviation, n = 3

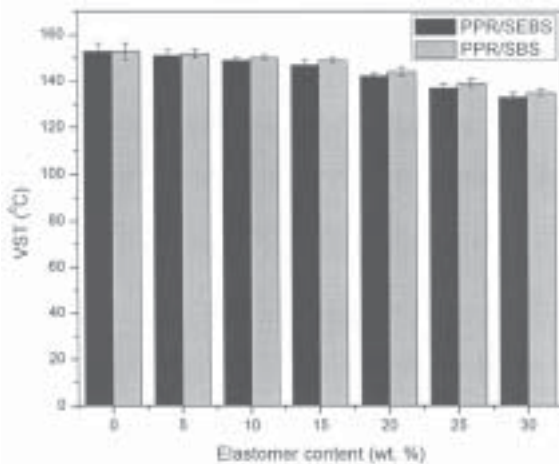


Fig. 7. VST for PPR/TPE blends vs. elastomer content. Error bars represent standard deviation, n = 3

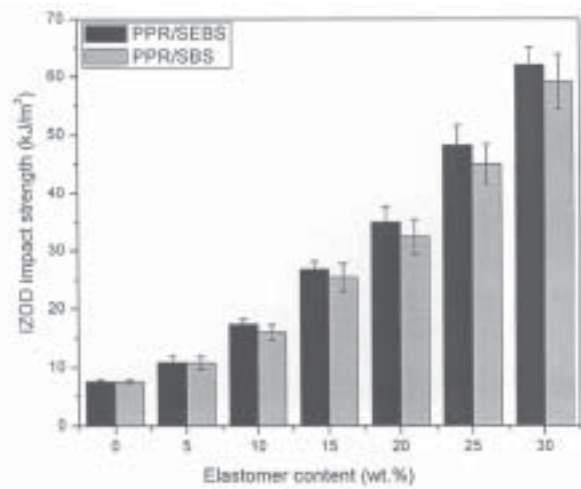


Fig. 9. IZOD impact strength of PPR blends vs. elastomer contents. Error bars represent standard deviation, n = 10

The addition of elastomer into PPR matrix led to decrease of Shore hardness values, and consequently of the resistance of material toward indentation (fig. 6). PPR/SBS blends recorded lower Shore D values than PPR/SEBS.

VST and HDT measurements

VST and HDT measurements were carried out to determine the influence of used elastomers on the thermal properties of PPR (figs. 7 and 8).

The obtained data plotted in Figure 7 show a decrease of softening temperature as the elastomer content increases. SEBS and SBS exhibited almost the same VST up to 10% incorporation in PPR, but higher VST was recorded for SBS at contents between 15 – 30 %.

Also, HDT measurement shows the same decreasing trend as VST test (fig. 8). The decrease in HDT is more pronounced for PPR/SBS blends than for PPR/SEBS, fact which is in good agreement with elongation at break.

Impact Izod strength

Variations of IZOD impact strength of PPR/TPE blends with loading of elastomer are shown in figure 9.

Notched IZOD impact strength (α_{IV}) of blends is a measure of energy absorbed by the material under load. As shown in figure 9, the impact strength increases dramatically from 7.59 kJ/m² for pure PPR to a maximum value of 62 kJ/m² for blend containing SEBS 30 wt.% and of 59.2 kJ/m² for blend with SBS content of 30wt.% respectively. The increase of impact resistance of PPR/TPE blends is

consistent with results of other researchers [23, 28, 29, 32].

From the two types of TPEs, SEBS is considered more efficient than SBS. This is due to absence of carbon-carbon double bonds and to the poor interface adhesion and compatibility between PPR and SBS and core-shell structure of dispersed particles [33].

The improvement in toughness (impact strength) when an elastomer is added to a polymeric matrix normally implies a reduction of its stiffness, which is usually related to a decrease in tensile strength. A balance between toughness and stiffness is always required for optimum performance of the rubber-toughened polymer. A combination of figures 5 and 9 indicates that a compromise between toughness and tensile strength is needed in order to obtain an improving of mechanical properties of PPR/TPE blends. Therefore, this comparison is shown in figure 10 (dotted lines represent tensile strength and continuous lines represent Izod impact).

As shown in figure 10, the presence of just 10% elastomer led to a very significant increase of the impact strength. 17.4 kJ/m² for PPR/SEBS was recorded and 7.59 kJ/m² for neat PPR, while the tensile strength decreased up to 1.16 times than that of pure PPR. A loading level of elastomer not higher than 10 wt. % may be considered optimal for processes involving extrusion or injection molding. Also, the good processability, flow and thermal properties were obtained for blends with a content of elastomer up to 10 wt%.

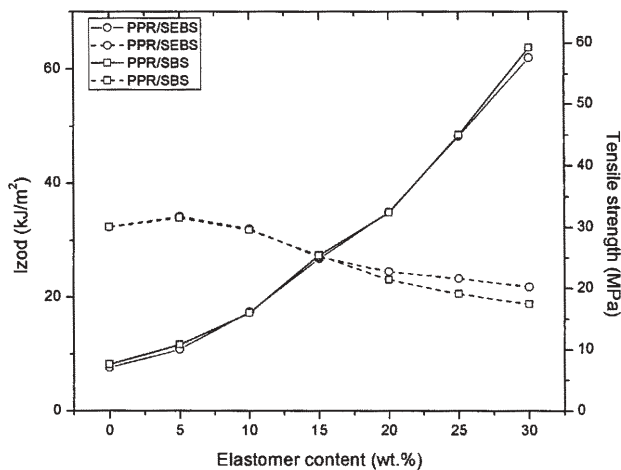


Fig. 10. Izod impact strength vs. tensile strength for PPR/elastomer blends (dotted lines represent tensile strength and continuous lines represent Izod impact)

Conclusions

In this paper the evaluation of mechanical and thermal properties of PPR/SEBS and PPR/SBS blends prepared by melt mixing procedure was performed.

The melt processability, melt flow index, tensile properties, VICAT softening temperature, heat deflection temperature, Shore hardness and IZOD measurements highlighted that SEBS is more efficient than SBS.

Based on mechanical and thermal properties data it was revealed that the loading level of elastomer up to 10 wt.% into PPR matrix may be considered optimal for processes involving extrusion or injection molding.

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References

1. YU L., WU T., CHEN T., YANG F., XIANG M., *Thermochimica Acta* **578** (2014) p. 43.
2. WANG X.C., PENG Y.Y., YUAN H.Y., LIU C.T., TURNG L.S., SHEN C.Y., *Polymer Testing* **41** (2015) p. 73.
3. CLEMONS C., *Composites: Part A* **41** (2010) p. 1559.
4. CONZATTI L., GIUNCO F., STAGNARO P., PATRUCCO A., TONIN C., MARANO C., RINK M., MARSANO E., *Composites: Part A* **61** (2014) p. 51.
5. SALLIH N., LESCHER P., BHATTACHARYYA D., *Composites: Part A* **61** (2014) 91.
6. NAGHMOUCHI L., ESPINACH F.X., MUTJÉ P., BOUFI S., *Materials and Design* **65** (2015) p. 454.

7. LEI B., ZHANG Y., HE Y., XIE Y., XU B., LIN Z., HUANG L., TAN S., WANG M., CAI X., *Materials and Design* **66** (2015) p. 103.
8. UNTERWEGER C., BRÜGGEMANN O., FÜRST C., *Composites Science and Technology* **103** (2014) p. 49.
9. PANAITESCU D.M., VULUGA Z., GHIUREA M., IORGA M., NICOLAE C., GABOR R., *Composites: Part B* **69** (2015) p. 286.
10. QIU F., WANG M., HAO Y., GUO S., *Composites: Part A* **58** (2014) p. 7.
11. SAW L.T., LAN D.N.U., RAHIM N.A.A., KAHAR A.W.M., VIET C.X., *Polymer Degradation and Stability* **111** (2015) p. 32.
12. SACCHI A., DI LANDRO L., PEGORARO M., SEVERINI F., *European Polymer Journal* **40** (2004) p. 1705.
13. IWAMOTO S., YAMAMOTO S., LEE S.H., ENDO T., *Composites: Part A* **59** (2014) p. 26.
14. IYER K.A., SCHUENEMAN G.T., TORKELESON J.M., *Polymer* **56** (2015) p. 464.
15. DAS D., SATAPATHY B.K., *Materials Chemistry and Physics* **147** (2014) p. 127.
16. HUANG J., RODRIGUE D., *Materials and Design* **65** (2015) p. 974.
17. GABR M.H., OKUMURA W., UEDA H., KURIYAMA W., UZAWA K., KIMPARA I., *Composites: Part B* **69** (2015) p. 94.
18. ZAHEDI M., KHANJANZADEH H., PIRAYESH H., SAADATNIA M.A., *Composites: Part B* **71** (2015) p. 143.
19. QIU F., HAO Y., LI X., WANG B., WANG M., *Composites: Part B* **71** (2015) p. 175.
20. ESTHAPPAN S.K., NAIR A.B., JOSEPH R., *Composites: Part B* **69** (2015) p. 145.
21. LI M., LI G., JIANG J., TAO Y., MAI K., *Composites Science and Technology* **81** (2013) p. 30.
22. SHUBHRA Q.T.H., ALAM A.K.M.M., KHAN M.A., SAHA M., SAHA D., GAFUR M.A., *Composites: Part A* **41** (2010) p. 1587.
23. LUAN S., YANG H., SHI H., ZHAO J., WANG J., YIN J., *Nuclear Instruments and Methods in Physics Research B* **269** (2011) p. 94.
24. STELLER R., ZUCHOWSKA D., MEISSNER W., PAUKSZTA D., GARBARCZYK J., *Radiation Physics and Chemistry* **75** (2006) p. 259.
25. ISMAIL H., SURYADIANSYAH S., *Polymer Testing* **21** (2002) p. 389.
26. KELEDI G., SUDAR A., BURGSTALLER CH., RENNER K., MÓCZÓ J., PUKÁNSZKY B., *eXPRESS Polymer Letters* **6** (2012) p. 224.
27. XU C., CAO X., JIANG X., ZENG X., CHEN Y., *Polymer Testing* **32** (2013) p. 507.
28. BALKAN O., DEMIRER H., KAYALI E.S., *Journal of Achievements in Materials and Manufacturing Engineering* **47** (2011) p. 26.
29. ZHANG X., LI B., WANG K., ZHANG Q., FU Q., *Polymer* **50** (2009) p. 4737.
30. JOSE J., NAG A., NANDO G.B., *J. Polym. Environ.* **18** (2010) p. 155.
31. ISMAIL H., GALPAYA D., AHMAD Z., *Polymer Testing* **28** (2009) p. 363.
32. DENAC M., MUSIL V., ŠMIT I., *Composites: Part A* **36** (2005) p. 1282.
33. CHEN F., QIU B., SHANGGUAN Y., SONG Y., ZHENG Q., *Materials and Design* **69** (2015) p. 56

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