Influence of Talc and SEBS-g-MA on PP/SEBS-g-MA/Talc Composites under Gamma Irradiation Sterilization Conditions

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Summary: Among thermoplastics, polypropylene is outstanding with respect to its attractive combination of low cost, low weight, heat distortion temperature above 100°C, and extraordinary versatility in terms of properties and applications. With the appropriate modification, it is possible to improve the existing properties of the polypropylene, or even obtain the new ones. As a result of its originally superior properties, polypropylene is commonly used in medical purposes, where it has to undergo the process of sterilization beforehand. The sterilization of the polypropylene in medicine is most often being carried out with low dose of gamma irradiation, which can influence the changes of properties of both the polymeric matrix and modifiers. Therefore, the purpose of our research work was to determine the mechanical properties of unirradiated and gamma irradiated isotactic polypropylene (iPP) composites with talc filler and poly-(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) block copolymer, grafted with maleic anhydride (SEBS-g-MA) as elastomeric modifier, as well as of corresponding binary blends. Unirradiated and gamma irradiated composites and blends were characterized by tensile measurements, measurements of notched impact strength and FTIR spectroscopy. The effects of composition and gamma irradiation on the properties of the iPP composites and blends are discussed, with emphasis on the study of the stabilizing effect of talc in irradiated iPP composites.

Keywords: gamma irradiation; isotactic poly(propylene); mechanical properties; SEBS-g-MA; talc

Introduction

In the last few years the production and use of polypropylene (PP) has shown the highest growth rate among all commodity polymers. The volume of production is expected to exceed that of the total amount of polyethylene[1]. The success of this polymer is due to its attractive

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price/performance ratio, combined with heat distortion temperature above 100°C and high stiffness[2]. With the appropriate modification, the properties of polypropylene can cover a very wide range of mechanical properties, from soft elastomeric materials to engineering thermoplastics[3].

Due to its excellent properties, polypropylene is used in medicine, where it normally undergoes the procedure of sterilization. Among several sterilization procedures, available for polymeric materials, the sterilization procedure with heat is usually not appropriate due to low heat deflection temperature of some commonly used materials. Cold sterilization procedures, especially with low dose irradiation, are cost effective and widely used. Radiation processing of polymers can also be regarded as a way of modifying the molecular structure of polymers, as an alternative method to more traditional chemical methods[4]. Polymer processing by ionizing radiation is environmentally and energetically safe, as it does not need solvents or initiators at high temperature, and allows one to avoid degradation phenomena and other side reactions, typical for polymer processing in the melt. The possibility to process the polymer material in solid state in its final shape, gives new opportunities to obtain materials with well-tailored properties[5]. The influence of irradiation on pure iPP is well researched, however, there is not much research dealing with properties of the PP blends and composites in the lower dose range of gamma ionizing radiation (about 25 kGy)[6].

Modification of iPP with styrenic blockcopolymers and talc is not only interesting for the improvement of mechanical properties, but they may also improve the radiation stability of blends and composites due to their ability to act as an energy scavenger or radical scavenger, respectively[7].

The aim of present work was to study the changes of properties, in particular mechanical properties of the iPP/SEBS-g-MA blends, modified with talc and subjected to gamma irradiation, usually used for medical purposes. The influences of irradiation as well as the content of talc and SEBS-g-MA on mechanical properties were investigated.

Experimental

Materials

An isotactic PP (BASF), a lamellar talc (Luzenac) and a poly-(styrene-*b*-ethylene-*co*-butylene-*b*-

styrene) block copolymer grafted with maleic anhydride (SEBS-g-MA) as polymer matrix and modifiers were used in this study, respectively. The characteristics of the iPP and modifiers are listed in Table 1 as received, while the molecular weights were determined additionally by size-exclusion chromatography.

Table 1. Properties of materials used.

Material	Mark	Trade name (source)	Properties
Isotactic Polypropylene	iPP	Novolen 1100 L (BASF)	MFI=6g/10min, ρ=0.908g/cm^3, Mn=47000, Mw/Mn=9.3
Talc with aminosilane surface treated (2%)	T-V592	Talk Naintsch A-20 V592 (Luzenac)	particle size (top cut)= 20μm, ρ=2.8g/cm^3, specific surface= 6.5 m^2/g
Blockcopolymer poly-(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) grafted with maleic anhydrid	SEBS-g-MA	Kraton KG-1901 (Shell)	Mn=47300, Mw/Mn=1.55, w(PS) =29 %, w(MA)=2 %

Sample preparation

Binary blends iPP/SEBS-g-MA with content ratios 97.5/2.5, 95/5, 90/10 and 80/20 vol.%, as well as ternary composites iPP/SEBS-g-MA/talc with volume ratios 93.5/2.5/4, 91/5/4, 86/10/4, 76/20/4 and 85.5/2.5/12, 83/5/12, 78/10/12, 68/20/12 vol.% were prepared in a Brabender kneading chamber. The components were kneaded for 6 minutes in a chamber, preheated to 200°C, with a rotor speed 50 min^{-1}. The melt was transferred to a laboratory press and compression molded into 1- and 4- mm plates. The pressing temperature was 220°C, pressure 100 bar, pressing time 14 min for 1-mm and 9.5 min for 4-mm thick plates. Afterwards, the plates were cooled to ambient temperature.

Gamma irradiation

The specimens prepared for mechanical measurements were subjected to γ irradiation at ambient temperature in air using Co-60 panoramic radiation source. The dose rate was 50 kGy/h and the total dose was 25 kGy.

Test methods

Tensile properties (Young's modulus, yield stress, elongation at yield, and elongation at break)

were measured by Zwick 147670 Z100/SN5A apparatus at 23°C and strain rate of 2 mm/min (ISO 527). Notched impact strength was measured according to Charpy test (DIN 53453) by Zwick apparatus at 25°C. Infrared spectra of the sample films were recorded on a Perkin Elmer Fourier Transform Infrared (FTIR) spectrophotometer at a resolution of 2 cm^{-1} and integrating 16 scans.

Results and discussion

Young's modulus

The incorporation of talc into the iPP matrix affects Young's modulus (E) more significantly than the addition of the SEBS-g-MA elastomer. The values of Young's modulus of modified iPP intensively increase with talc content and slightly decrease with elastomer content (Figure 1). The addition of low contents of the SEBS-g-MA decreases Young's modulus in the iPP/SEBS-g-MA/talc composites more significantly than higher elastomer contents, where the E values tend to those of the corresponding binary blends.

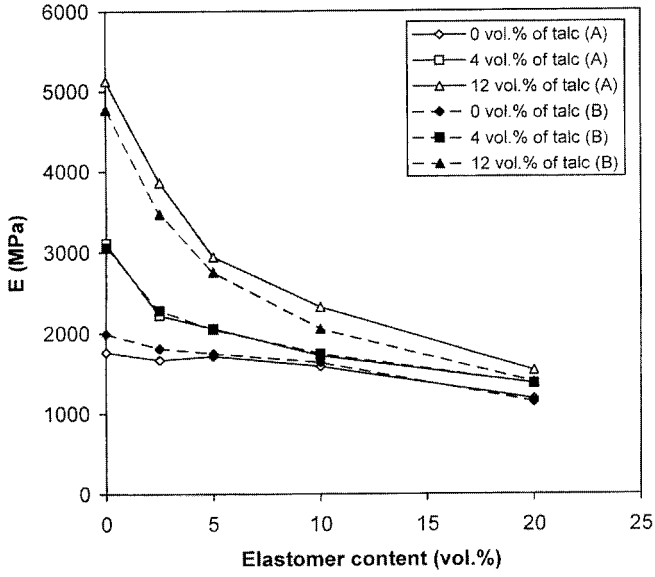

Figure 1. Young's modulus (E) of unirradiated (A) and irradiated (B) iPP blends and composites in dependence on elastomer content. The γ irradiation dose was 25 kGy.

The irradiation of the iPP binary composites decreases the values of Young's modulus at talc content 12 vol.% and slightly increases in the iPP/SEBS-g-MA blends. Young's modulus of composites with 4 vol.% of talc seems to remain independent of irradiation.

Yield stress

The yield stress (σ_y) of the iPP/SEBS-g-MA blends decreases linearly with the increase of block copolymer content (from 2.5 vol.%) (Table 2). Scanning electron micrographs in the previous paper[8] have shown that different types of styrenic rubber blockcopolymer particles are dispersed in the iPP matrix as up to 1 μm sized spheres. Supposing the same shape and size of all dispersed elastomer particles, it is easy to calculate that the specific elastomer surface in the iPP matrix resembles a specific talc surface. Specific surface of modifiers, reflecting the size of the interphase, is the key factor in determining interactions (adhesion) between the individual components in the composites. The values of interaction parameter B, determined by semi-empirical equation from σ_y [9,10] are in a good agreement with theoretical calculations[8]. The adhesion of the iPP - talc (B=3,20)[11] is significantly higher than the adhesion of the iPP - SEBS-g-MA (B=0,86)[8]. Previous researches have also shown the impact of multiple factors on decrease of the adhesion (interaction intensity) in the iPP/SEBS blends, like higher molecular weight of elastomers and consequently smaller interface area, higher content of polystyrene blocks and grafting with maleic anhydride[8].

Table 2. Yield stress of unirradiated and gamma irradiated blends and composites.

	σ_y (MPa)				
Elastomer content (vol.%)	0	2.5	5	10	20
Talc content (vol.%)					
0 [a)]	33.4	33.4	31.8	27.7	21.1
4 [a)]	32.4	28.7	28.9	25.5	21.7
12 [a)]	32.7	30.3	26.6	24.3	20.6
0 [b)]	35.5	32.5	31.7	28.7	22.7
4 [b)]	32.8	29.5	28.4	25.6	21.0
12 [b)]	33.6	30.2	27.2	23.3	20.7

[a)] Unirradiated.
[b)] γ Irradiated (25 kGy).

The σ_y values for the iPP/SEBS-g-MA/talc composites are lower than σ_y values of corresponding

iPP/SEBS-g-MA blends. These results indicate that talc influences structural changes in the system, resulting in decrease of adhesion between the phases. The values of σ_y for PP/SEBS-g-MA/talc composites are also lower than those of the PP/SEBS/talc composites[3] by about 10%. Decrease of σ_y is mostly the result of encapsulation of the filler with elastomer caused by interactivity between aminosilane, bonded to talc surface, and maleic anhydride grafted on SEBS[3,12]. Due to so formed morphology, the interphase surface, enabling stress transfer between the matrix and a dispersed phase, decreases markedly. As a consequence, the σ_y values proportionally decreases.[13] The σ_y values of unirradiated and irradiated ternary composites are almost the same, which indicates that in spite of the formation of free-radicals, there are no significant changes in adhesion.

Elongation at yield

The elongation at yield (ε_y) and elongation at break (ε_b) of the iPP/talc composites considerably decrease with talc content[14], therefore the composites become stiffer (higher E) and consequently less ductile (lower ε_y). It is very interesting that the addition of SEBS-g-MA to iPP matrix practically does not affect ε_y values (Figure 2), whereas the addition of SEBS to iPP increases both, ε_y and ε_b.[8] Since it is known that σ_y and ε_y reflect interactions (adhesion) in blends, it can be assumed that the adhesion between SEBS-g-MA and iPP is very weak. It seems that sinergistic effect appears at higher contents of both components. As a consequence, ε_y values of composites remarkably prevail those of the iPP/SEBS-g-MA blends at 20 vol.% of SEBS-g-MA (Figure 2). The irradiation somewhat decreases ε_y values of the iPP/SEBS-g-MA blends as well as the ternary composites.

Elongation at break

The best fitted line for ε_b values with great dissipation (scattered) of iPP/SEBS-g-MA blends, ilustrated in Figure 3, shows the increase of this value with added SEBS-g-MA. Inspite of this increase the iPP/SEBS-g-MA blends show less ductility than the iPP/SEBS blends.[8] Increased polarity of SEBS-g-MA, as a result of grafted maleic anhydride, reduces adhesion between SEBS-g-MA and iPP matrix (B(SEBS)=1.10, B(SEBS-g-MA=0.86), thus reducing the ductility of binary blends[8]. The incorporation of talc into pure iPP and the iPP/SEBS-g-MA blend

significantly decreases elongation at break, which could be due to a reduced mobility of the SEBS-g-MA chains (Figure 3).

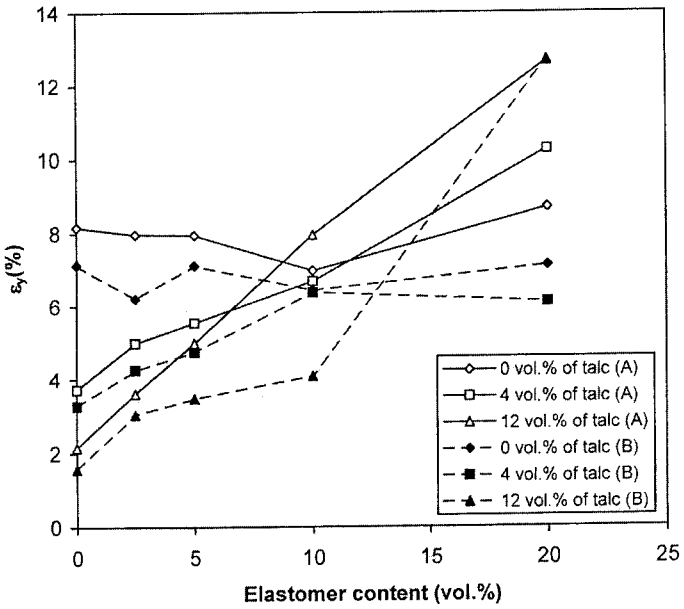

Figure 2. Elongation at yield of unirradiated (A) and irradiated (B) iPP blends and composites in dependence on elastomer content. The γ irradiation dose was 25 kGy.

It is well known[15] that ε_b is a measure of degradation in polymer blends and composites. Significant decrease of ε_b in the iPP/SEBS-g-MA blends indicates strong influence of irradiation, which reduces the influence of elastomer as impact modifier and coupling agent. The decrease of ductility of irradiated composites could be explained with degradation of polymeric components and subsequently partial cross-linking or grafting on the SEBS-g-MA interlayer, or even with chemical reaction leading to imide formation. In this way, the SEBS-g-MA chains become less mobile. Strong interaction between SEBS-g-MA and talc leads to the smaller differences between ε_b of unirradiated and irradiated composites than in blends. Higher talc content increases similarities in ε_b values and their curves of unirradiated and irradiated composites as can be seen from Figure 3.

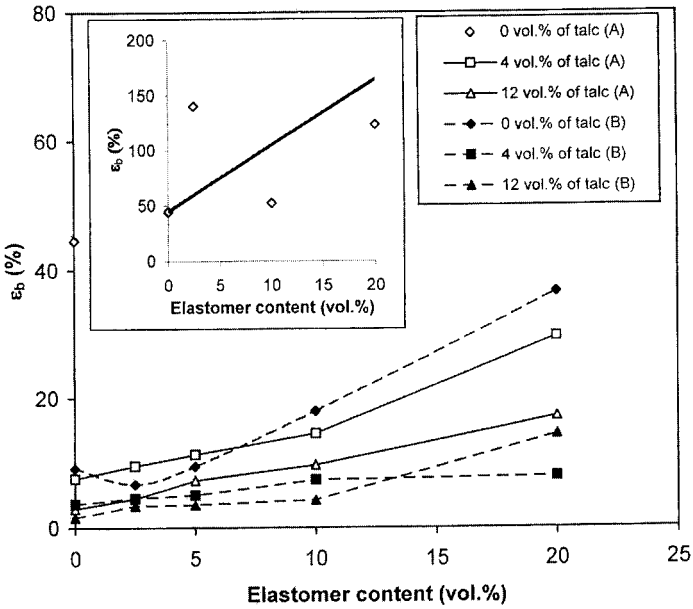

Figure 3. Elongation at break of unirradiated (A) and irradiated (B) iPP blends and composites in dependence on elastomer content. The γ irradiation dose was 25 kGy.

Notched impact strength

Notched impact strength (a_k) is a measure of energy, absorbed by the material under load. Factors, which contribute to the improvement of the impact strength of the composites are filler aspect ratio, particle size, filler rigidity and its concentration, interaction with the matrix, nucleation, orientation and consequent structural changes in the matrix.[16] The most influential factor among the enumerated is the interactivity between phases, which probably leads to encapsulation phenomenon (core-shell), to the thickenning of elastomeric interlayer and energy dissipation. The toughness of the PP/SEBS-g-MA blends increases with higher elastomer content (Figure 4). Due to relatively low molecular weight of elastomer (Table 1), what is related to high elastomer's melt flow index, the SEBS-g-MA elastomer disperses into numerous fine particles.[8] Fine SEBS-g-MA dispersion in iPP matrix enables better energy dissipation, which strongly depends on the number of dispersed elastomer particles, as well as their size. The incorporation of talc into iPP and into the PP/SEBS-g-MA blends decreases the values of a_k. The decrease of a_k is more pronounced at higher SEBS-g-MA content (Figure 4). This could be a consequence of

interactivity between talc and SEBS-g-MA and the changes in morphology (core-shell formation), which could decrease the interface of talc with iPP. The SEBS-g-MA elastomer affects toughness stronger than talc, resulting in higher a_k values of ternary composites (Figure 4).

The toughness of blends and composites decreases with gamma irradiation. The shape of the curves a_k as the function of elastomer content remains almost unchanged. The difference between the a_k values of irradiated and unirradiated blends and composites decreases with a higher talc content. This could be a result of the stabilizing effect of talc. Significantly lower a_k values for the iPP/SEBS-g-MA/talc composites than for the iPP/SEBS/talc composites[17] at higher elastomer content are caused by lower elasticity of SEBS-g-MA than SEBS dispersed particles, as well as by stronger interactivity at SEBS-g-MA – iPP than SEBS – iPP interface. Probably, the SEBS-g-MA elastomer, relocated from the iPP matrix to the shell of plane-parallel talc crystals, acts as a strong coupling agent because of high interactivity at talc/silaneNH_2 – MA-g-SEBS as well as at iPP – MA-g-SEBS interface. The irradiation decreases a_k values of the iPP/SEBS-g-MA/talc composites in similar way as in the iPP/SEBS/talc composites.[17]

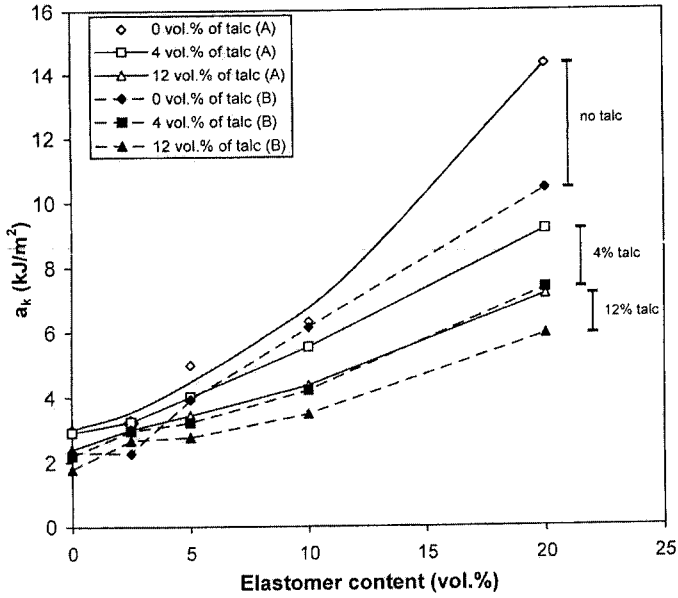

Figure 4. Notched impact strength (a_k) of unirradiated (A) and irradiated (B) iPP blends and composites in dependence on elastomer content. The γ irradiation dose was 25 kGy.

FTIR spectrometry

FTIR spectra confirm the presence of functional groups (hydroxide from talc (hydrogen bond) 3676 cm^{-1}, amide 1672 cm^{-1}, weak anhydride doublet 1820 and 1760 cm^{-1}), which may interact and/or even react with each other, resulting in formation of imide group between the filler and the elastomer. The changes in mechanical properties, as a result of changed structure, indicate the strong effect of interactions. It is possible that chemical reaction proceeded between maleic anhydride from SEBS-g-MA and aminosilane bonded to the talc surface, although it is not visible from the FTIR spectra. It is estimated that the changes in the spectra are negligible due to chemical similarity of amines and imides, which absorb electromagnetic radiation at almost the same wave numbers. The FTIR spectra of some examined blends and composites are presented in Figure 5.

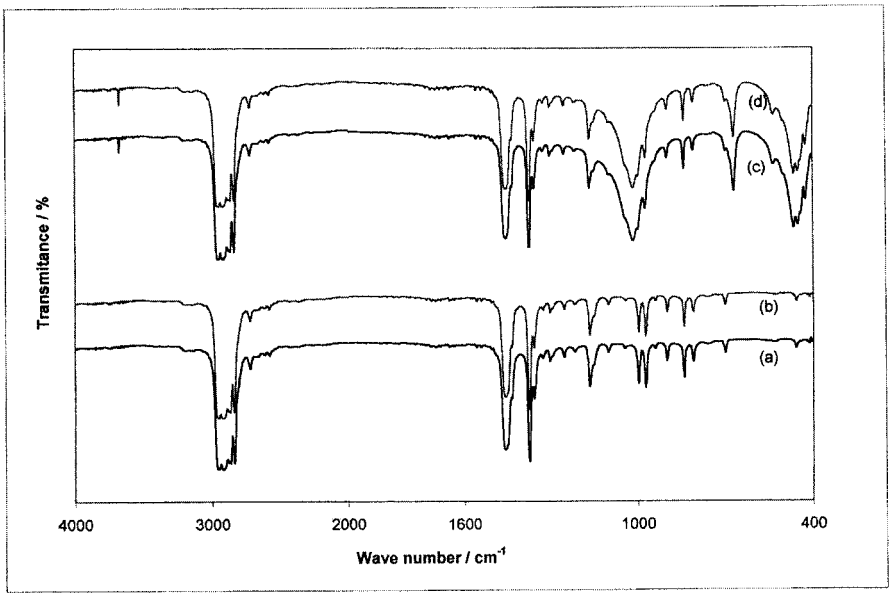

Figure 5. FTIR spectra of unirradiated (a) and 25 kGy irradiated (b) blend iPP/SEBS-g-MA (95/5) and unirradiated (c) and 25 kGy irradiated (d) composite iPP/SEBS-g-MA/talc (91/5/4).

During gamma radiation, the interaction of high energy radiation with polymers leads to a cascade of very fast physical and physicochemical processes, that culminate in the generation of free radicals and the formation of other detected products.[18] Within polyolefines, the PP is of particular interest, because its chemical constitution is intermediate between that of poly*iso*butylene, which exhibits molecular degradation, and that of polyethylene, in which cross-linking predominates, although some degradation occurs.[19] PP undergoes simultaneously and approximately equal cross-linking and degradation during irradiation.[20] Gupta[21,22], who irradiated iPP with different neutron dosages, concluded that cross-links are produced predominantly in the amorphous region, which is an O_2 accessible phase[18]. FTIR spectra of irradiated blends and composites are identical to FTIR spectra of corresponding unirradiated systems, which indicates low number of breaks produced in the main polymer chain, which is at least directly proportional to the radiation dose given to the sample.[19] The absence of carbonyl, hydroxyl and hydroperoxide peaks confirms that no oxidative degradation occurred in irradiated specimens. It could be a result of the irradiation conditions, especially high irradiation dose rate and possible stabilizing effect of SEBS-g-MA and talc in the blends and composites.

Conclusions

The mechanical properties of unirradiated and gamma irradiated iPP/SEBS-g-MA/talc composites and corresponding binary systems have been studied. The iPP/SEBS-g-MA blends are immiscible two-phase systems, where SEBS-g-MA particles are dispersed in the iPP matrix, which enables good energy dissipation. Addition of SEBS-g-MA into iPP significantly increases toughness (a_k) and decreases stiffness (E) simultaneously, while incorporation of talc into iPP/SEBS-g-MA blend significantly increases the toughness of the composite formed. Modification of iPP with both SEBS-g-MA and talc results in tougher and stiffer composites. Significantly lower a_k values for the iPP/SEBS-g-MA/talc than for the iPP/SEBS/talc composites are caused by lower elasticity of the SEBS-g-MA than the SEBS copolymer dispersed particles, as well as by stronger interactivity between SEBS-g-MA – iPP than the SEBS – iPP at the interface.

Sterilization dose of gamma irradiation increases stiffness of the blends, but reduces their

toughness. The incorporation of talc reduces the changes of mechanical properties after irradiation due to stabilizing ability of talc. The stabilizing activity of talc is a result of termination of free radicals on the talc surface. The absorption of (dissipated) energy by PS blocks in SEBS-g-MA could decrease degradation additionally.

There are no peaks in FTIR spectra of irradiated blends and composites, which are characteristic for the oxidative processes. This may be a result of high dose rate and low total irradiation dose. The talc could act as a stabilizer in composites additionally.

Acknowledgements

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[1] G.Krotkine et al., *Kunststoffe* **1999**, 89, p.42-46.
[2] F.Stricker, R.Mülhaupt, *Polym. Eng. Sci.* **1998**, 38, p.1463-1470.
[3] M.Denac; *Binary and Ternary Composites Based on Isotactic Polypropylene* (Masterscience Thesis), University of Maribor, Faculty of Chemistry and Chemical Engineering, 1999.
[4] A.Bhattacharya, *Prog. Polym. Sci.* **2000**, 25(3), p.371-401.
[5] G.Spadaro, A.Valenza, *Polym. Degr. Stab.*, **2000**, 67, p.449-454.
[6] L.Deping, R.Guan, *Polym. Int.* **2000**, 49, 1389-1394.
[7] R.Clough, in: *"Encyclopedia of polymer science and engineering"*, vol.13, J.Willey & Sons, New York etc. 1988, p.686-687.
[8] M.Denac, V.Musil, M.Makarovič, *Materials and Technology* **2001**, 35(5), p.243-249.
[9] B.Turcsanyi, B.Pukanszky, F.Tüdos, *J. Mater. Sci. Lett.* **1988**, 7, p.160-162.
[10] B.Pukanszky, B.Turcsanyi, F.Tüdos, in: *"Interfaces in Polymer, Ceramic and Metal Matrix Composites"*, H.Ishida, Ed., Elsevier, New York 1988, p.467.
[11] M.Denac, V.Musil, M.Makarovič, *Metals Alloys Technologies* **1998**, 32(1-2), p.69-72.
[12] M.Denac, V.Musil, I.Šmit, I.Švab, M.Makarovič, in: *"Proceedings Slovenski kemijski dnevi 2003"*, 25-26. September **2003**, CD ROM.
[13] B.Pukanszky, F.Tüdos, J.Jančar, J.Kolarik, *J. Mat. Sci. Lett.* **1989**, 8, p.1040-1042.
[14] M.Denac, V.Musil, I.Šmit, F.Ranogajec, *Polym. Degr. Stab.* **2003**, 82, p.263-270.
[15] A.K.Kulshredhtha, in: *"Handbook of polymer degradation"*, S.H.Hamid, M.B.Amin, A.G.Maadhah, Eds., Marcel Dekker, New York 1992, p.55.
[16] G.Wypych, *"Handbook of fillers"*, 2nd ed., Chem-Tec Publishing, Toronto 1999, chapter 8.
[17] M.Denac, V.Musil, I.Šmit, *Composites Part A: Appl. Sci. Manufact.* (considered for publication).
[18] D.J.Carlsson, D.M.Wiles, in: *"Encyclopedia of polymer science and engineering"*, vol.4, J.Willey & Sons, New York etc. 1986, p.647.
[19] R.M.Black, B.J.Lyons, *Nature* **1957**, 180, p.1346-1347.
[20] W.Schnabel, M.Dole, *J. Phys. Chem.* **1963**, 67, p.295-299.
[21] R.P.Gupta, *Kolloid Z.* **1961**, 174, p.74.
[22] R.P.Gupta, *J. Phys. Chem.* **1962**, 66, p.849.