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γ-Radiation Induced Functional Modification of Silica and Radiation Vulcanization of SBR-Silica Composites

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Summary: The γ-ray induced "grafting" of polybutadiene olygomers onto precipitated silica and the radiation induced crosslinking of the blends prepared with the modified silica in SBR matrices have been investigated in the dose range up to 290 kGy. Enhanced mechanical properties have been detected for the SBR blends containing the modified silica after γ-ray induced crosslinking. The comparison with the analogue mixtures containing pristine silica, supported by EPR measurements, suggests that the PB coating is effective in enhancing the mechanism of formation of filler-rubber chemical links.

Keywords: γ-radiation; SBR-silica composites

Introduction

The reinforcement mechanism by inorganic fillers is strongly influenced by the homogeneity of the filler distribution and the intensity of the filler-rubber interactions. Since inorganic fillers, like silica, have a strongly polar character, filler self aggregation is important and poor homogeneity of their dispersion in non polar rubber matrices are attained. A way out from this problem is to reduce the filler surface energy through a non polar coating. Furthermore, if the coating has an adequate degree of unsaturation, radical addition reactions can take place during the vulcanization process leading to chemically bound rubber. This is the strategy adopted in the present work, where silica modified by radiation grafting of polybutadiene olygomers containing 1-2 vinyl and 1-4 cis and trans double bonds was used as filler in SBR mixtures prior to the radiation induced vulcanization. The properties of the irradiated mixtures containing cured silica were tested for the mechanical properties and cross links densities in comparison with the mixtures based on pristine silica.

Results

Materials and Methods

Following the previously described procedure,[1–5] Silica Zeosil 1165 (165 m^2/g surface are) was pre-impregnated with 20% of polybutadiene olygomer PB-5000 from Sigma-Aldrich (Mn = 5000 dalton, 20% vinyl double bonds) and then submitted to radiation grafting under vacuum with a total dose of 40–60 kGy. After the irradiation and soxhlet extraction with THF, the content of the grafted PB was determined by TGA to be in the range 14–18%. Direct evidence of PB grafted onto silica was obtained by FTIR and micro Raman spectroscopy. The latter method was also used to monitor the decay of the total double bond content as a function of the radiation dose in the range 0–50 kGy (double bond bands at 1644 cm^{-1},vinyl; 1656 cm^{-1}, 1–4 cis; 1671 cm^{-1}, 1–4 trans). The results did show that more than 70% of the double bonds were preserved at the highest dose. By IGC measurements it was shown that the PB grafting led to a ca 50% decrease of both the dispersive

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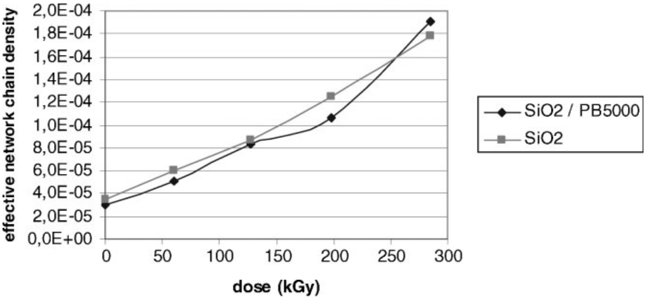


Figure 1.
Cross link densities determined by swelling method (see text) for irradiated mixtures containing pristine and modified silica.

component and the specific interaction of the silica surface energy thus enhancing the compatibility of the filler with the rubber matrix.[4]

Three different blends were prepared using the SBR copolymer (39.5% styrene; 38.5% vinyl; 37.5 phr extended oil), namely: blend A: SBR 70.9%, SiO_2 28.3%, stearic acid 0.8%; blend B: SBR 66.2%, SiO_2/PB5000, 33.1%, stearic acid 0.7%

Disk shaped samples of the compounds (0.5 cm height, 10 cm diameter) were irradiated under air in a 60-Co source at the dose rate of 0.34 kGy/h. Four different doses were delivered corresponding to 60.7, 127.0, 198.2 and 284.5 kGy. After the irradiation the samples were tested for the crosslink densities using the Flory-Rehner swelling method as reported in reference.[6] The distribution of the filler within the SBR matrix was investigated by TEM analysis prior and after the irradiations The following mechanical tests were performed on the unirradiated and irradiated blends: hardness test (IRHD) at 23° and 100 °C; static load at 22° (stress at 10, 50, 100, 300% elongation); breaking strength; lengthening at breaking; the dynamic modulus: E' and tan delta measured at 10 and 100 Hz at 10°, 23° and 100°C. The EPR analysis of the radiation vulcanization mechanism was carried out using a Bruker EMX/12 spectrometer by recording the spectra as a function of the temperature after irradiation under vacuum at 77 K.

Results

The cross link densities increase almost linearly in the dose range 0–100 kGy then a moderate acceleration trend is observed which can be reckoned with the radical inhibition effects by trace stabilizer residues. The comparison with pristine SiO_2 does not show major differences in the dose range exploited (Figure 1).

The rate of the crosslinking reaction is likely to have been lowered by the presence of the oil used as ‘‘extension’’ agent for the rubber. This oil has an aromatic structure and aromatic compounds are known to act as radiation stabilizers through a mechanism of degradation of the radiation energy to thermal energy.

The comparative EPR measurements carried out with the blends containing pristine and treated silica afford clear evidence that, in both type of samples, the formation of carbon centred radicals linked to the SiO_2 surface takes place (Figure 2A,B). Such species give EPR spectra which are interpreted in terms of the unequivalent interaction of 4 protons with coupling constants $3a(H) = 22.7$ G; $1a(H) = 15.3$ G.

The number of interacting protons and the magnitude of their couplings strongly suggest that such radicals can formally be accounted for by the addition of precursors species to vinyl double bonds of the SBR and PB chains. A distinctive property of the grafted radicals, which enables to distinguish them from normal unbound rubber

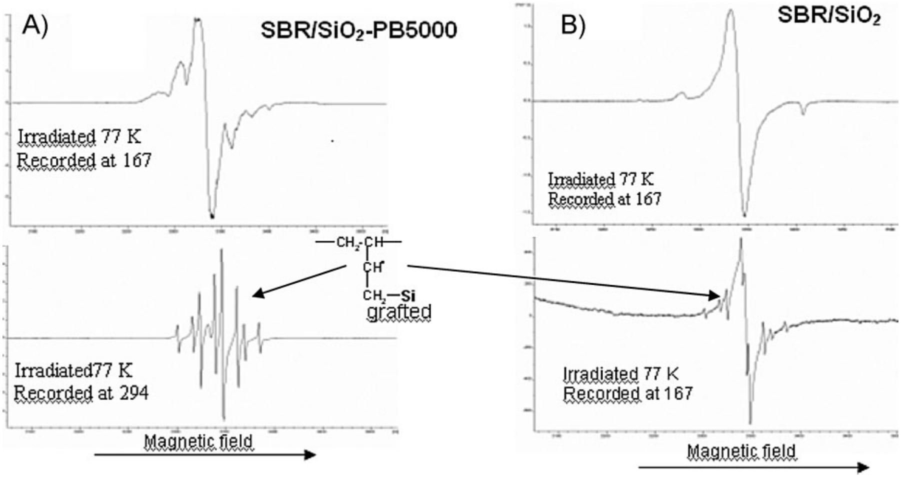
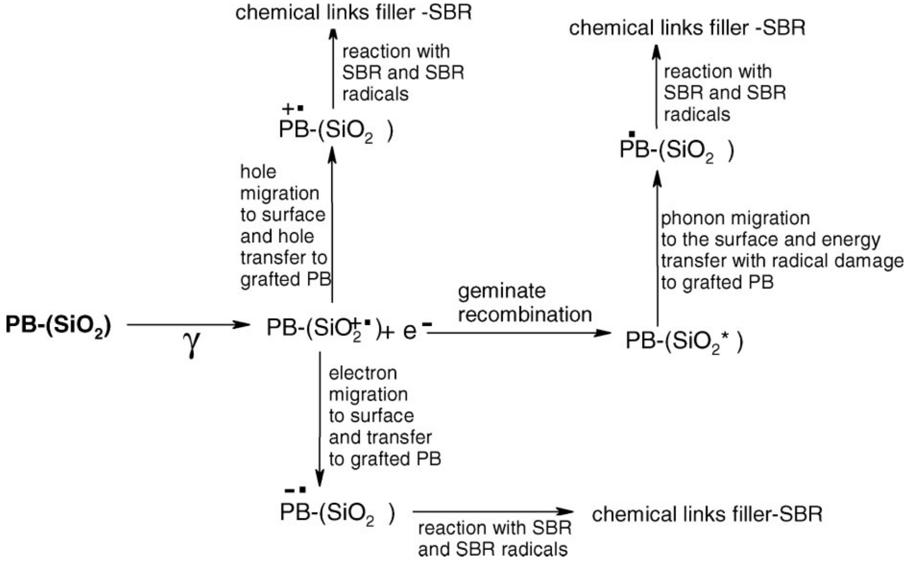


Figure 2.
EPR spectra form the irradiated SBR compounds containing treated SiO_2 (A) and pristine SiO_2 (B). The inset shows the formula of the radical formed by double bond addition at the PB vinyl double bond.

radicals, is their stability under vacuum at room temperature, which stems from their anchorage at the filler surface. When using treated silica, SiO_2 linked radicals can be formed by addition of precursor SBR radicals at the vinyl double bonds of grafted PB units. A concomitant mechanism can involve radiation induced silica reactive centres migrating at the surface and subsequently reacting with grafted PB or with adsorbed external SBR chains. Evidence for the latter mechanisms is afforded by the detection of the SiO_2 grafted radicals in the blends containing only untreated pristine silica (Figure 2B) and by previous EPR experiments carried out with irradiated treated silica not dispersed in the SBR matrix.[3] SiO_2 grafted radicals can lead to formation of silica-rubber chemical links by coupling with SBR rubber radicals or by addition at SBR vinyl unsaturation. As the EPR signal from SiO_2-grafted radical is far less intense in the blends containing pristine silica with respect to the blends with treated silica (Figure 2 A, B), it can be inferred that the PB grafting significantly enhances the yield of silica-rubber chemical links.

According to the Compton mechanism of interaction of the electromagnetic radiations with matter in the energy range of the 60-Co γ photons, 60–70% of the radiation energy delivered to the blend is expected to be absorbed to the rubber fraction; however also the energy absorption by the SiO_2 structure is significant. The scheme below shows the expected reaction mechanism when the active radicals are generated within the SiO_2 matrix. PB-SiO_2 represents the silica particles bearing 15–18% of grafted polybutadiene olygomer. The primary ionizations are expected to be concentrated on the SiO_2 moiety giving the species formally represented as PB-($SiO_2^{+\bullet}$). The competition between geminate recombination and electron escape gives rise to three possible reaction paths based on cationic, anionic and excited intermediates. The relative importance of such mechanisms depends on the polarity of the medium, the ionic paths being enhanced with increasing the polarity. In hydrocarbons the dominant mechanism is excitation whilst in water is ionization;[7] in the silica system, due to the presence of significant concentrations of OH silanol groups, both ionization and excitation are expected to play significant roles. Previous EPR measurements performed on Zeosil silica after gamma irradiation at 77 K have demonstrated that an efficient mechanism



Scheme 1.

Reaction mechanism for the radiolytic formation of filler-SBR chemical links in SBR blends containing SiO_2 modified by PB grafting.

exists enabling the SiO_2 radiolytic centres to migrate at the surface at very low temperature.[3]

Presumably hole and electron transfer are involved for the migration of charged species whilst the phonon mechanism, which is greatly favoured in covalent structures, may account for the excitation energy migration. At the surface, the SiO_2 species react with grafted polybutadiene chains giving grafted carbon centred radicals which are the precursors of filler –SBR chemical links. In absence of grafted PB, the great majority of the SiO_2 species decay at very low temperature leaving exclusively the unreactive stable well known E' centres.[3] The PB coating therefore works as an efficient spin trapping agent for the SiO_2 species.

TEM Measurements

TEM microphotographs were obtained for the compounds with pristine and modified silica prior and after irradiation.

According to previous IGC measurements,[4] the PB coating is very effective in lowering the filler surface energy γ_s from 96.0 to 40.8 mJ/m^2 and the specific components I^{sp}_s from 142.6 to 68.4 mJ/m^2 for pristine silica and treated silica respectively. However this improved silica-filler compatibility does not lead to a concomitant homogeneity enhancement of the filler particles distribution in the SBR matrix (Figure 3 A,B).

Measurements of the particle size distribution performed on samples submitted to different stirring times in n-hexane suspensions have indeed shown that PB-coated SiO_2 particles are more resistant to fragmentation. It is thought that this enhanced structural stability, by reducing the silica fragmentation by mechanical stress during the blending process, may overcompensate the positive effects stemming from the improved filler-rubber compatibility. A modification of the silica impregnation method is actually being exploited in order to circumvent this problem.

Mechanical Measurements

The breaking strength shows for all samples a marked increase as a function of gamma-

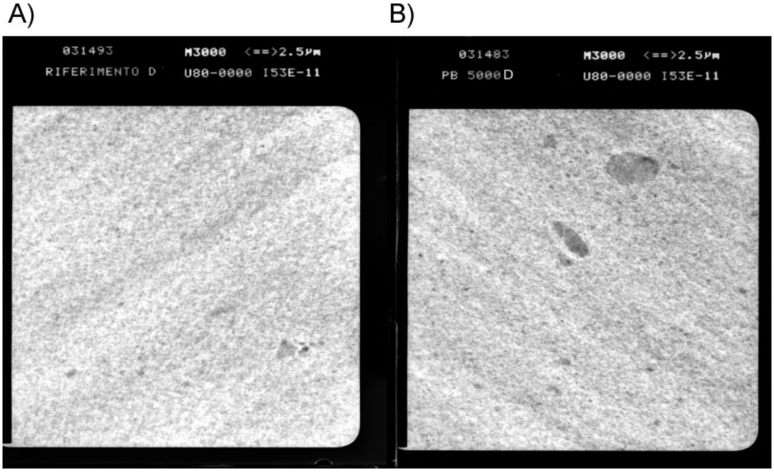


Figure 3.
TEM microphotographs of gamma crosslinked SBR mixtures containing pristine (A) and PB-cured SiO_2 (B).

ray dose, confirming the expected relationship between crosslinking and irradiation dose in SBR matrix (Table 1). The static Load at 100% elongation does not show an appreciable increment with the dose whilst, for the 300% load, a clear increment is observed at the highest dose. These observation are explained by considering that the effect of the crosslinks network is more evident the greater is the displacement from the equilibrium conditions; as a consequence the most significant data for the sake of the comparison are the ones pertaining the highest doses and the largest strains (load at 300% elongation and breaking strength).

Within this framework, the comparison between the samples prepared with the grafted PB-5000 and those prepared with pristine silica, reveals that the former are more responsive to dose, since they reach, at the highest dose of 284.5 KGy, an higher load at 300% elongation (L-300) and higher breaking strength. The fact that lower modulus are measured for samples with treated SiO_2 in the low dose range, where the crosslink networks are less responsive, is likely to reflect a lower filler volume % content.

The ratio between the load at 300% elongation and at 100% is often taken as an indicator of rubber-filler interaction: also this index grows with irradiation dose, and grows more in the case of PB-5000 treated silica than in the case of pristine silica, suggesting that PB-5000 silica manages to link to polymer matrix better than pristine silica.

Hysteresis is a measure of energy dissipation under dynamic conditions, and

Table 1.
Measurements of the static load at 100% and 300% elongation as a function of the radiation dose

	SBR compound with pristine SiO_2				SBR compound with SiO_2 modified by PB-5000 grafting			
γ Dose (KGy)	60.7 (A)	127.0 (B)	198.2 (C)	284.5 (D)	60.7 (A)	127.0 (B)	198.2 (C)	284.5 (D)
L-100% elongation (MPa)	0.46	0.32	0.46	0.47	0.35	0.35	0.37	0.40
L-300% elongation	1.04	0.8	1.06	1.85	0.55	1.03	1.09	2.76
Breaking strength (MPa)	2.32	5.28	7.29	10.82	1.83	6.35	7.66	12.08
L300/L100	1.39	1.23	1.45	2.18	1.00	1.56	1.60	2.82
Δ(L-300 D - L-300-A) (%)	0	−23.1	1.9	77.9	0	87.3	98.2	401.4

Table 2.
Measurements of tan delta as a function of the radiation dose

	SBR compound with pristine SiO_2				SBR compound with SiO_2 modified by PB-5000 grafting			
γ dose (kGy)	60.7 (A)	127.0 (B)	198.2 (C)	284.5 (D)	60.7 (A)	127.0 (B)	198.2 (C)	284.5 (D)
Tang delta at 23° and 100 Hz	0.324	0.318	0.301	0.315	–	0.324	0.296	0.284
Δ(tang delta) at 23° and 100 Hz	–	0	-5.3	-0.9	–	0	-8.6	-12.3

thus it is expected to decrease as a function of crosslink: this is evident in the case of the compounds featuring SiO_2 coated with PB (Table 2). Overall tan-delta measured under these conditions appears to be little sensitive with respect of the other parameters, but confirms the higher overall networking efficiency of radiation in the crosslinking of treated silica: as we might assume that efficiency of radiation in the crosslinking of the polymer matrix is the same for all samples, the difference between the two series (with/without treated silica) can be explained with the ability of the grafted silica to be bound to the polymer matrix through the PB grafted oligomer.

Conclusion

The radiation induced grafting of polybutadiene olygomers onto the precipitated silica Zeosil 1165 significantly reduces the silica surface energy but does not lead to a significant homogeneity improvement of the filler dispersion within a rubber SBR matrix. However the grafted polybutadiene coating is active as radical scavenger thus enhancing the mechanism of formation of rubber-filler chemical links. SiO_2 grafted radicals have been detected by EPR in irradiated blends containing only untreated pristine silica, thus demonstrating that silica radiolytic centres do participate to the formation of rubber-SiO_2 chemical links. However, judging from the intensities of the EPR signals, the concentration of the grafted radicals is far more abundant when silica cured with PB is used. It is inferred that the PB coating is acting as radical scavenger with respect to the silica species thus giving more stable silica-bound carbon centred radicals. The latter species, by coupling with SBR rubber radicals and/or by reaction with adsorbed SBR vinyl double bonds lead to filler-rubber chemical links.

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