

Radiation curing of silica for silica-rubber composites*

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Abstract. The functional modification of silica samples based on the reaction of “grafting” of polybutadiene oligomers carried out by γ -irradiation in the presence of air at room temperature has been investigated. The yield of grafted PB reaches a maximum at doses of about 30 kGy, then decreases as a consequence of the oxidative degradation. The reaction is accompanied by the build up of carbonyls and peroxides up to 0.1 moles/kg and it leads to a rapid consumption of the double bonds concentration as determined by both FTIR and Raman spectroscopy. The results of the EPR analysis are diagnostic of a mechanism of immobilization of the oligomer based on cross-linking of polybutadiene which is initiated by the SiO_2 radiolytic species. Depending on the nature of the SiO_2 species, the mechanism of initiation leads to immobilized PB either really grafted to the silica surface or simply physically absorbed.

Key words: radiation • silica-rubber composites • modified silica

Introduction

The modification of inorganic fillers through the “grafting” of organic substrates is a general method especially used for obtaining novel reverse-phase HPLC stationary phases with the initiation carried out by peroxide decomposition, microwaves, thermoxidation and ionizing radiations ([7, 8] and references therein). This work is part of a research aimed at the synthesis and characterization of modified silica having enhanced compatibility with respect to elastomer matrices [2], but also having radical reactivity properties suited for obtaining “bound rubber” in vulcanization processes. To fit the target, γ -radiation has been used to bind oligomers, having different vinyl 1–4 *cis* and 1–4 *trans* double content to silica polybutadiene. The rationale of the method is that PB unsaturations are partially used in the “grafting” reactions and partly are expected to remain available for subsequent radical addition processes. In this paper, the results concerning the reaction carried out in the presence of air are described together with information concerning the reaction mechanism stemming from TGA, FTIR, Raman and EPR spectroscopy studies.

Experimental

The materials employed were: amorphous precipitated silica zeosil 1165 MP (Rhone Poulenc) with 160–200 m²/g surface structure; polybutadiene oligomers from Sigma

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Received: 24 October 2008

Accepted: 9 March 2009

* Presented on the International Conference on Recent Developments and Applications of Nuclear Technologies, 15–17 September 2008, Białowieża, Poland.

Table 1. Radiation-induced “grafting” of the polybutadiene oligomers PB-1800 and PB-5000 onto SiO₂ carried out in presence of oxygen. The yields of bound PB as a function of the dose were determined by TGA after soxhlet extraction. The initial content of the physically absorbed PB before irradiation was 20%

Sample	Dose (KGy)	% bound PB after irradiation	% H ₂ O
SiO ₂ /PB-1800	2.25	5.5	6.9
SiO ₂ /PB-1800	9.9	12.9	6.0
SiO ₂ /PB-1800	32.6	15.6	5.6
SiO ₂ /PB-1800	147.9	11.7	6.4
SiO ₂ /PB-5000	2.25	2.8	6.6
SiO ₂ /PB-5000	9.9	7.4	7.1
SiO ₂ /PB-5000	32.6	15.5	5.0
SiO ₂ /PB-5000	147.9	11.9	6.1

Aldrich with the following characteristics: PB-1500, Mn 1530–2070, double bonds 72% 1,4 *cis*, 72%, 1–4 *trans* 27%, vinyl 1%. PB-5000:Mn = 5000, double bonds 1–4 *cis* + 1–4 *trans* = 80%, vinyl double bonds = 20%. The silica samples containing about 20% of physically absorbed PB oligomers were prepared by rotavapor evaporation of silica dispersed in CHCl₃ solutions of the oligomers. The irradiations were performed at room temperature in air in a ⁶⁰Co source at a dose rate of 0.43 kGy/h. Total doses up to 200 kGy have been used. After irradiation, the samples were submitted to soxhlet extraction with THF solvent in order to remove unbound PB. The determination of bound PB was carried out by TGA analysis under air in the temperature range 25–700°C at the temperature rate increase of 5–10°/min. In the temperature range 60–140°C a 5–7% weight decrease was observed due to the release of absorbed H₂O; the yield of bound PB was determined from the overall weight loss corrected by the loss of absorbed water. Attempts to use FTIR and ponderal methods have afforded only semiquantitative results. FTIR spectra were recorded on a Perkin Elmer 1600 spectrometer equipped with diffuse reflectance and ATR devices. EPR measurements were carried out in the temperature range from 77 K up to 400 K using an X band EMX/12 Bruker spectrometer. The analytical determination of peroxides was made by spectrophotometric titration at 360 nm of the I₃⁻ ion generated in the peroxide-induced oxidation of I⁻ in KI/isopropanol/acetic acid solutions [4].

The kinetics of double bond decay under irradiation were determined from the Raman bands in the 1610–1680 cm⁻¹ region using a Micro-Raman Labram Dilor H10 spectrometer.

Results

TGA measurements

The results of the TGA measurements performed on irradiated SiO₂ samples, impregnated with PB-1800 and PB-5000 oligomers, are summarized in Table 1.

In each TGA diagram, a 5–7% weight loss was observed in the temperature range between 60° and 140° which was attributed to the release of physically absorbed water. The principal weight loss due to the thermal degradation of “grafted” polybutadiene was observed in the temperature range between 400 and 700°C.

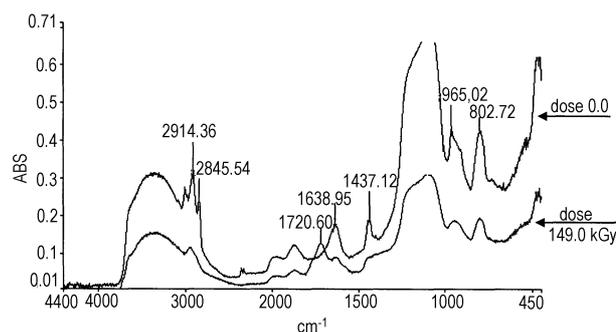


Fig. 1. Diffuse reflectance FTIR spectra of SiO₂ impregnated with the polybutadiene oligomer PB-5000, recorded after irradiation in air in the radiation dose range 0.0–149 kGy.

Starting with samples containing initially 20% of physically absorbed PB. The yield of grafted PB reaches a maximum at about 30 kGy, then decreases. No significant differences in the maximum yields of bound PB are observed between the two oligomers, but the kinetics of the reaction seems to be somewhat faster in the case of PB-1800. The decay of bound PB above 30 kGy is imputed to the oxidative degradation with chain scission leading to the formation of low molecular weight fragments which are easily lost in the soxhlet extraction treatment.

IR and analytical measurements

The modified silica thus obtained appear to contain significant concentration of oxidation products, carbonyls and hydroperoxides as shown by the build up of the FTIR absorption band centred at 1720 cm⁻¹ (Fig. 1) and by iodometric analysis. The build up of the carbonyl products level-off at about 70 kGy and 100 kGy for PB-1800 and PB-5000, respectively (Fig. 2); the concentration of peroxides peaks at about 40 kGy for PB-5000 and at 10 kGy for PB-1800 (Fig. 2). These observations confirm the faster oxidation rate of the lower molecular weight oligomer and at the same time are diagnostic of the occurrence of extensive secondary reactions with induced decomposition of the peroxides.

Beside the expected build up of the carbonyl band in the 1720 cm⁻¹ region, the IR spectra show a decrease of the overall area of the absorption bands in the region 2850–3070 cm⁻¹ which, in agreement with TGA measurements, can be reckoned with the decrease of the yield of grafted PB due to oxidative degradation. Furthermore, in this IR region, a selective decay is observed

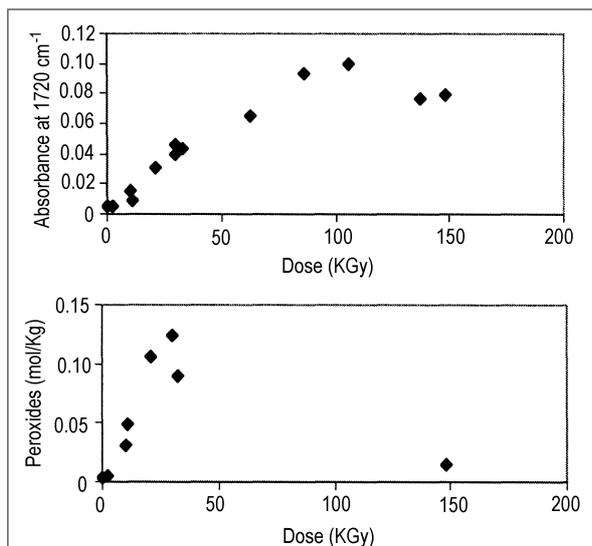


Fig. 2. Kinetics of formation of carbonyl groups and peroxides during the irradiation in air of SiO₂ impregnated with the polybutadiene oligomer PB-5000.

for the bands at 3005 cm⁻¹ [5] (asymmetric stretching of 1-4 *cis* CH=CH), 3074 cm⁻¹ (asymmetric stretching of vinyl CH₂=, Ref. [5]), 965 cm⁻¹ (1-4 *trans* CH=CH out of plane vibrations, Ref. [5]) which are reckoned with the consumption of unsaturations (Fig. 1).

A more clearcut evidence of the double bonds decay during the radiooxidative process was obtained by following the band at 3074 cm⁻¹ which, despite the low intensity, has the advantage of not being overlapped with other SiO₂ bands (Fig. 3).

Raman spectroscopy

The fate of double bond in the oxidation process was more safely assessed by micro-Raman spectroscopy due to the lack of overlapping bands from silica. The unfolding of the bands at 1644 cm⁻¹ (symmetric stretching of the vinyl C=C), 1656 cm⁻¹ (symmetric stretching of the 1-4 *cis* C=C), 1671 cm⁻¹ (symmetric stretching of *trans* 1-4 C=C) up to a radiation dose of 32.4 kGy, has confirmed the decay down to < 20% of the overall double bond concentration; furthermore, it was demonstrated that the relative abundance of the vinyl and 1-4 double bonds remains substantially unchanged during the course of the reaction.

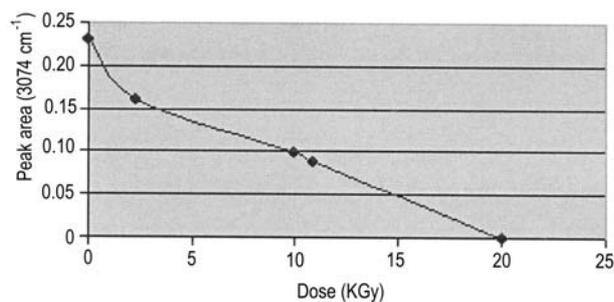


Fig. 3. Irradiation under air of SiO₂ impregnated with PB-5000 oligomer: decay of the vinyl double bond band at 3074 cm⁻¹ recorded as a function of the radiation dose.

This result, which may appear surprising because of the expected greater reactivity of vinyl double bonds, has a reasonable explanation when it is considered that the initial concentration of vinyl double bonds is only 20% of the overall unsaturations. As a consequence, the experimental observation implies that the vinyl double bonds are about 5 times more reactive with respect to 1-4 double bonds.

EPR measurements

The EPR measurements were carried out with SiO₂ impregnated with PB oligomers and with neat SiO₂ samples which were irradiated under vacuum at 77 K temperature and then submitted to programmed stepwise annealing at higher temperature. The EPR spectra obtained from the neat SiO₂ show the presence of several paramagnetic centres among which H atoms with the typical splitting of ca. 500 G (Fig. 4a). Preliminary results from computer simulations and DFT calculations suggest at least 4 other different species arising during the SiO₂ radiolysis are present whose *g* can be reckoned with a major fraction of the spin density on Si and oxygen atoms. These SiO₂ species are highly unstable with respect to the temperature, their decay being complete above 130 K, exception being made for a narrow singlet centred at *g* = 2007, which is stable indefinitely at room temperature (Fig. 4c). The irradiation at 77 K of SiO₂ impregnated with the

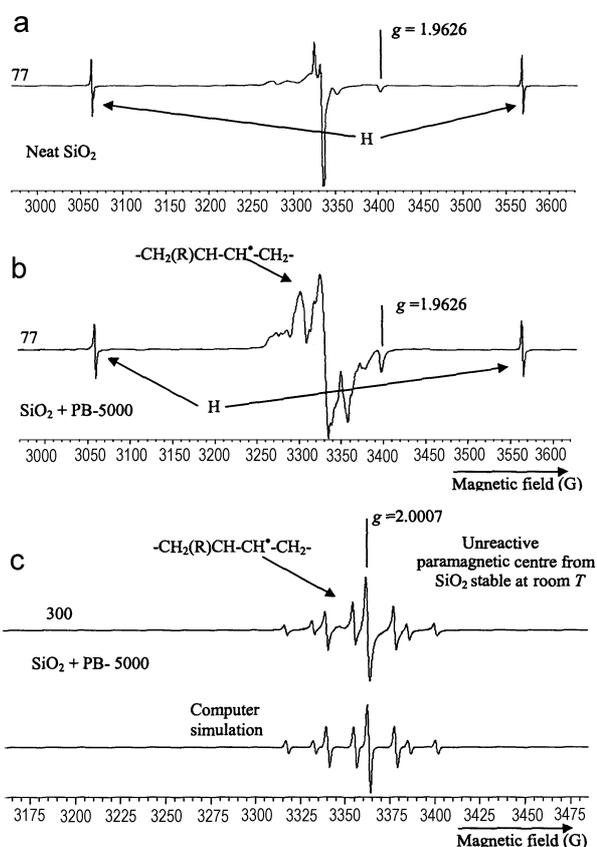
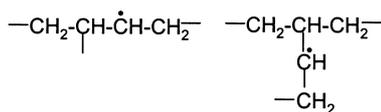


Fig. 4. EPR spectra of neat SiO₂ (a) and SiO₂ impregnated with polybutadiene oligomer PB-5000 (b, c) recorded after irradiation at 77 K before and after annealing at room temperature.

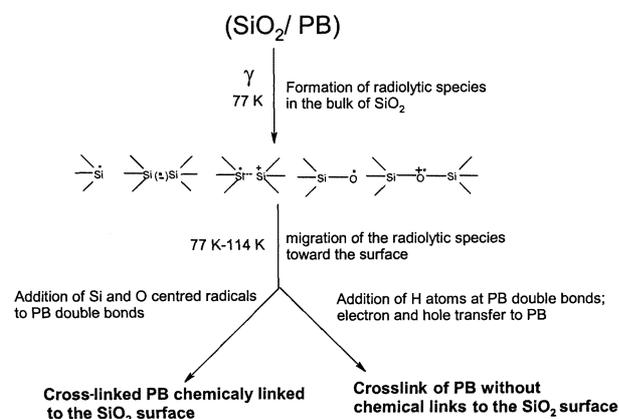


Scheme 1. Formula of the propagating radicals in the radiation induced cross-linking of polybutadiene absorbed onto silica. The radical addition at the 1–2 and 1–4 double bonds give similar radicals bearing the same number of α and β interacting protons.

polybutadiene oligomers PB-5000 affords a spectrum where most of the SiO_2 radicals are replaced by a broad composite quintet with an average 21 G peak to peak splitting (Fig. 4b). This latter signal is stable at room temperature where, thanks to the improved resolution, it could be analyzed in terms of the following proton coupling constants: $2A(\text{H})_{\text{CH}_2\beta} = 22.7$ G; $1A(\text{H})_{\text{CH}\beta} = 15.3$ G; $1A(\text{H})_{\text{CH}\alpha} = 22.7$ G (Fig. 4c). These hf couplings are diagnostic of the presence of the polybutadiene cross-linked radicals, having the same number of α and β interacting protons, as those arising from the addition of the initiating species at the vinyl and (to a lesser extent) 1–4 double bonds (Scheme 1).

Since in the SiO_2 /PB-5000 system more than 80% of the electron fraction belongs to the SiO_2 component, the EPR results are diagnostic of the radiation damage originating in the bulk of the SiO_2 structure and then migrating at the surface where the reaction with the physically absorbed oligomer takes place. This free valence (and perhaps also energy) migration phenomena is characterized by a low activation energy since it takes place at very low temperature, in the range 77–115 K. Within this framework, reactions like H atoms addition as well as a hole and electron transfer to absorbed PB would lead to unbound cross-linked PB, whilst the double bond addition of Si and $\equiv\text{Si}^{\cdot}$ and $\equiv\text{Si}-\text{O}^{\cdot}$ species are expected to lead to really grafted cross-linked PB (Scheme 2).

A specific comment has to be deserved to the role of H_2O in the SiO_2 /PB radiolysis mechanism. The 5–7 weight % of physically absorbed H_2O detected by TGA may be expected to contribute to the overall mechanism through the radiolytic production of H atoms, OH radicals and electrons; these species are suited for initiating the cross-linking of PB, but without chemical links to the SiO_2 surface. OH radicals have a well-known EPR spectrum with g tensor 2.0038, 2.0071, 2.0457 and a



Scheme 2. Proposed mechanism of “grafting” of polybutadiene oligomers onto silica according to EPR spectroscopy measurements.

single proton hf tensor -22.3 G, -45.8 G, 7.2 G [9]. As these features have not been detected in the 77 K EPR spectra, we are inclined to assume that the role of the physically absorbed water within the overall radiolysis mechanism is of minor importance.

The radicals related to the cross-linking mechanism are stable under vacuum at room temperature; contrarily, the radicals trapped in pure polybutadiene matrices are reported to decay rapidly well below room temperature [10]. This difference of stability may be imputed to chemical and physical links occurring between polybutadiene radicals and the SiO_2 surface, which hinder the translational diffusion needed for bimolecular couplings. Upon the admission of oxygen, the cross-linked radicals are rapidly converted into the corresponding peroxy radicals which are expected to be the major intermediates in the propagation of the hydroperoxidative process taking place when the irradiation is carried out under air. The latter process is responsible for the formation of carbonyls and peroxides products and concomitantly leads to degradation of the chains to smaller fragments. A major role in this mechanism is expected to be played by the β -scission of alkoxy radicals and the cyclic formation of allylic hydroperoxides which are known to be the precursors of epoxides [1, 3, 4, 6].

Conclusions

The functional modification of silica samples based on the reaction of “grafting” of polybutadiene oligomers carried out by γ -irradiation in the presence of air at room temperature has been investigated. The yield of grafted PB reaches a maximum at doses of about 30 kGy then decreases as a consequence of the oxidative degradation. The reaction is accompanied by the build up of carbonyls and peroxides up to 0.1 moles/kg and it leads to a rapid consumption of the double bonds concentration as determined by both FTIR and Raman spectroscopy. The results of the EPR analysis are diagnostic of a mechanism of immobilization of the oligomer based on cross-linking of polybutadiene which is initiated by the SiO_2 radiolytic species. Depending on the nature of the SiO_2 species, the mechanism of initiation leads to immobilized PB either really grafted to the silica surface or simply physically absorbed. The decay of the double bond content caused by the oxidative process is a severe drawback with respect to the aim of obtaining modified silicas with enhanced free radical reactivity in vulcanization processes. The possibility is being now exploited of using the functional groups developed following the radiooxidation as initiators of monomer grafting reactions.

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