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Radiation Induced Double Grafting of Polybutadiene Olygomers and Styrene onto Silica: Characterization of the Materials and Mechanistic Studies

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Summary: Ionizing radiations from a 60-Co source have been employed for inducing radical reactions finally leading to the grafting of unsaturated olygomers and vinyl monomers onto the surface and micropores of precipitated silica Zeosil 1165 (150–170 m^2/g). The target was to obtain modified silica with enhanced polar compatibility with respect to polybutadiene and styrene-butadiene copolymers rubber matrices and suited to favour the formation of chemically bound rubber in a vulcanization process. The latter property was expected to follow from the characteristics of free radical reactivity arising from the unsaturations present in the organic coating. Three classes of modified silica have been prepared: A)silica coated with polybutadiene olygomers with M_n in the range 1000–5000 and having a different relative content of 1,4-cis, 1,4-trans and vinyl double bonds [1,2]; B)Silica coated with polybutadiene olygomers further modified by subsequent grafting of styrene monomer. The type A samples were obtained by γ irradiation under vacuum of silica samples pre-impregnated with the oligomers in the dose range up to 30–200 kGy. Type B samples were obtained via three different steps as outlined in the scheme below:

$$SiO_2(PB) \xrightarrow[298\ K]{\gamma\ vacuum} SiO_2—PB \xrightarrow[298\ K]{\gamma\ air} SiO_2—PB—OOH \xrightarrow[Sty]{Fe^{2+}} SiO_2—PB—O\text{-}PS$$

The characterization of the modified silica was carried on by elemental and thermogravimetric analysis, FTIR (diffuse reflectance), Raman spectroscopy, inverse gas chromatography (IGC), CP/MAS 29-Si NMR, granulometry and TEM microscopy.

Keywords: bound rubber; coated silica; filler modification; gamma irradiation

Introduction

The reinforcement mechanism in rubber composites is determined by several factors among which the:

- The dimension and surface area of the filler particles which control the effective contact area between rubber and the polymer matrix
- The structure and the degree of roughness of the particle surface which is important in leading to bound rubber structures and hindering the chain slippering under strain
- The surface energy of the filler particles which is a key factor controlling the nature and intensity of the filler-filler and filler-polymer interactions

A strongly polar filler, like silica, with an high energy surface, during mixing with an apolar rubber matrix in a brabender will

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initially be homogeneously dispersed because of the overwhelming prevalence of the mechanical stress; this homogeneity however is bound to progressively decay with the storage time because of tendency of the filler toward self-aggregation driven by the stronger filler-filler specific interactions with respect to filler-rubber ones. A surface curing of the filler leading to a lowering of its polarity will compete with self aggregation leading to more stably homogeneous mixtures. However this positive effect is at least partially counterbalanced by the loss of the stronger filler-rubber specific interactions. A way for bypassing this unfavourable competition is a curing strategy aimed at contemporaneously improve the filler-rubber compatibility and the formation tendency of chemically-bound rubber during the mixing and/or a vulcanization procedure. The use of TESPT relies on this strategy. The use of coupling agents as silanes normally takes care exclusively of the rubber- filler compatibility problem. following a research line started in our laboratories within a FIRB project and a collaboration with Pirelli-Tyres, we have launched a strategy based on the coating of silica with polybutadiene olygomers induced by using 60-Co γ radiations. [1,2,3,4] The irradiation of silica preimpregnated with PB olygomers leads to grafting of PB by crosslinking and direct linkage with SiO_2. The curing agent causes a drastic decrease of the silica surface energy (both dispersive and specific components), thus improving the compatibility with the rubber matrix but contemporaneously, because of the double bond and allylic C-H bonds content, is capable of promoting the formation of chemically bound rubber in free radical crosslinking processes. [5] If the irradiation for obtaining grafted PB is performed in air, both grafting and oxidation of PB take place with consequent formation of high concentrations of hydoperoxides. The latter functions can be used as initiating agents for inducing subsequent functional modification of the silica surface through reaction with vinyl monomers. In this work we give a concise overview of the physicochemical characteristics of the polybutadiene-silica fillers so far prepared and report on their applications in the radiation induced crosslinking of SBR composites. Furthermore we refer on the first results of the double functional modification of silica obtained by using PB-hydroperoxides according to the scheme reaction sequence shown below:

$$SiO_2(PB) \xrightarrow[298\,K]{\gamma\ vacuum} SiO_2{-}PB \xrightarrow[298\,K]{\gamma\ air}$$

$$SiO_2{-}PB{-}OOH \xrightarrow[Sty]{Fe^{2+}} SiO_2{-}PB{-}O\text{-}PS$$

Results

Preparation and Characterizations of the Silica Based Fillers Modified by Polybutadiene Grafting

The materials employed were: precipitated silica Zeosil 1165MP, 165 m^2/g, from Rhodia, polybutadiene olygomers PB-1800 and PB-5000 from Aldrich with the following characteristics: PB-1800: Mn = 1800, vinyl content 1–2%, 1,4-cis 72%, 1,4- trans 27%; PB-5000: Mn = 5000, vinyl content 20%, cis- and trans-1,4 80%. Silica samples impregnated with PB at 20% by weight were prepared by evaporation of suspensions of silica in $CHCl_3$ solutions. After evaporation the samples were irradiated under vacuum or under air in a 60-Co source at a dose rate of 0.4 kGy/h with total doses up to 200 kGy. After the irradiation the samples were soxhlet-extracted overnight with THF in order to remove ungrafted PB. The grafted PB yields were determined by TGA under air with a temperature scan up to 700 °C. Doses of 30–50 kGy were found to be sufficient to achieve 70–90% of the grafting yield; higher doses led to a decrease of the grafting yield because of radiolytic and radiooxidative degradation. [3]

Because of the absence of interfering bands from SiO_2, Raman spectroscopy was found to be the best suited for the analysis of grafted PB (Fig. 1). Of special relevance the bands at 1644, 1656, 1671 cm^{-1} which were used for the quantification of vinyl,

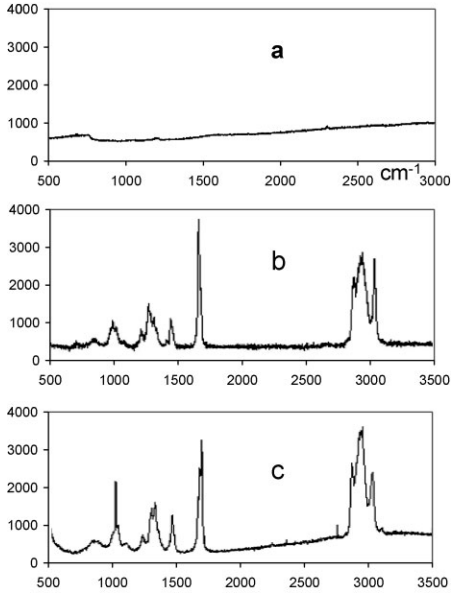
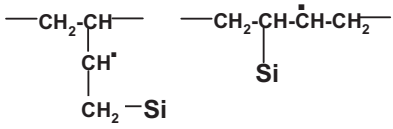


Figure 1.
Raman spectra of a) pristine silica, b) pure PB-5000, c) SiO_2-PB5000 irradiated and soxhlet-extracted.

1,4-cis and 1,4-trans double bonds respectively. The decrease of the overall double bond content as a consequence of the radiolytic grafting treatment was found to be lower than 15–20% when the irradiation was performed under vacuum; contra wise the irradiation in air caused 80–90% decay of the overall unsaturations.

^{1}H-^{29}Si CP/MAS NMR measurements on Q_4 units in pristine SiO_2 and SiO_2-Polybutadiene samples have shown through the decrease from 3.3 ms to 2.2 ms of the CP contact time that the olygomer chains are at a molecular contact distance (few Å) with the silica surface. This strongly support the view that a real grafting of the PB onto silica has occurred. [4]

EPR measurements have led to the identification of PB radicals linked to the silica surface with the hf couplings: $3a_{(H)} = 22.7$ G; $1a(H) = 15.3$ G (see below)



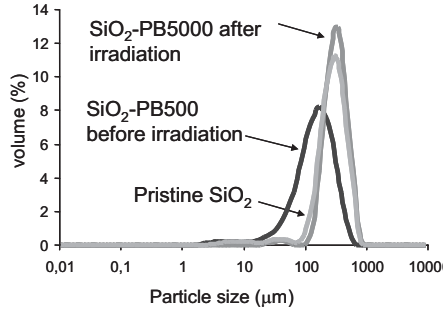


Figure 2.
Granulometric analysis for neat silica and samples before and after irradiation.

The overall picture emerging from the EPR measurements performed as a function of the temperature after irradiation at 77 K is that the radiolytic species are produced prevalently within the SiO_2 mass and then migrates at the surface where act as initiators of the PB crosslinking and grafting. Depending on the nature of the radiolytic species (Si and O centred radicals, H atoms, electrons, holes,) the crosslinked PB chains may be really anchored or simply immobilized at the silica surface.

IGC (Inverse Gas chromatography) measurements were consistent with a drastic decrease of the silica surface energy as a consequence of the PB grafting. At 20 °C, the dispersive component γ_s^d and the specific interaction were found to decrease from 86.0 and 142.6 (mJ/m^2) to 40.8 and 68.4 (mJ/m^2) respectively. [2]

The granulometry measurements performed by applying a laser technique on n-hexane dispersion of the silica samples have shown that the radiolytic grafting causes only a limited increase of the average silica particle size (Fig. 2).

However additional experiments performed as a function of the different type and intensity of stirring have demonstrated that the PB grafting enhances the structural stability of the silica particles thus hindering further fragmentation under mechanical stress.

Surface Functional Modification of SiO_2 by Consecutive Double Grafting

Radiation processing is also useful to achieve a secondary chemical modification

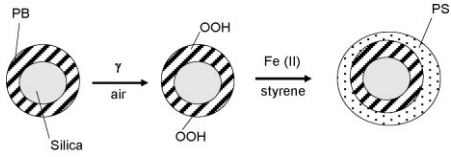


Figure 3.
Pictorial representation of the radiooxidation and subsequent polystyrene (PS) grafting process.

on the PB-coated silica since gamma irradiation in the presence of oxygen results in the oxidation of the PB coating with formation of relatively large yields of alcohols, carbonyl compounds and hydroperoxides. [3] The latter compounds, which can attain concentrations up to 0.12 mole/kg at radiation doses of 25–30 kGy, have been used for inducing the graft polymerization of styrene onto SiO_2/PB-5000 fillers by electron transfer from Fe^{2+} ions, according to Figure 3.

The FTIR spectra from samples reacted after irradiation in air with a γ dose of 12 kGy, afford evidence of the styrene grafting through the build-up of the absorbance bands of the aromatic moieties at the frequencies 3022–2996, 1965, 1492 and 1450 cm^{-1} (Fig. 4)

The kinetics of the styrene grafting reaction as a function of the radiation doses and for each dose as a function of the reaction time were estimated on a semi-quantitative basis from the ratios at 1492 and 2947 cm^{-1} of the absorbance bands due to polybutadiene and polystyrene in the FTIR spectra (Fig. 4). The grafting rates

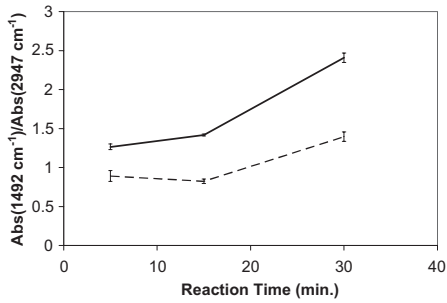


Figure 5.
PS/PB ratio estimation by IR spectroscopy vs. the grafting reaction time. Continuous line: SiO_2-PB5000 radiooxidised with 4.8 kGy, dotted line: SiO_2-PB5000 radioxidised with 2.1 kGy.

increase with increasing the irradiation dose in air from 2.1 to 4.8 kGy and show an induction period presumably due to residual oxygen in the reacting system (Fig. 5).

The quantitative determination of the grafted organic material was performed by using TGA analysis under oxygen in the temperature range up to 700 °C at a rate of 10 °C /min. The results are shown in Fig. 6 and Table 1.

The TGA curves show clearly three inflection points at the temperatures 120–150 °C, 280 -320 °C and 370 to 470 °C which, by comparison with the TGA curves from binary SiO_2/PB samples, were assigned respectively to the loss of physically bound H_2O, the decomposition of grafted polystyrene and the decomposition of grafted polybutadiene. The enhanced thermal instability of polystyrene with respect to

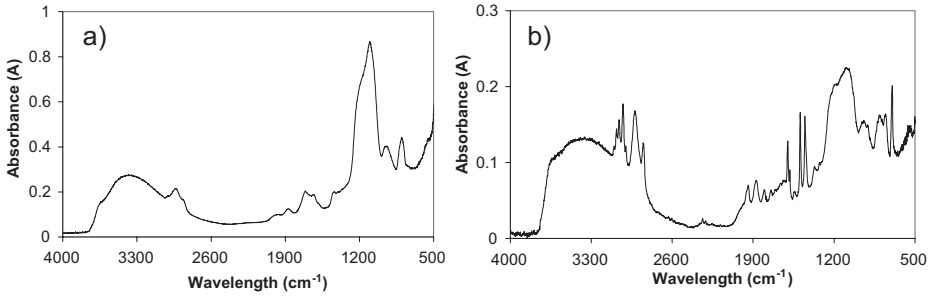


Figure 4.
Diffuse reflectance FTIR spectra of SiO_2-PB5000 a) radio oxidised in air with a total dose of 12 kGy b) the same sample after styrene grafting for 15 minutes.

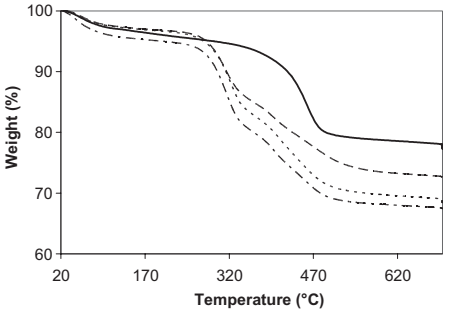


Figure 6.
TGA analysis of pristine SiO2-PB5000 (continuous line), SiO2-PB5000 radioxidised with 4.8 kGy and grafted for 5 (dashed line), 15 (dotted line) and 30 minutes (dash-dot line).

polybutadiene is consistent with literature data. [6] The grafting yield of polystyrene, is seen from the data in Table 1, to reach a limit yield at reaction times of about 15–30 min.

The silica modified by double consecutive grafting of polybutadiene olygomers and styrene will be now submitted to characterization with respect to the surface energy, Raman spectroscopy and TEM analysis on the polymer composites. It is hoped that the addition of the polystyrene component will enhance the compatibility with SBR rubbers which will be the first to be exploited.

Comparative Radiation Induced Vulcanization of SBR Mixtures Containing Pristine SiO_2 and Modified SiO_2/PB-5000

Mixtures of the copolymer SBR (39.5% styrene and 37.5 phr extended oil) with pristine and PB-5000 modified zeosil SiO_2 (28–33 phr) were submitted to radiation crosslinking at room temperature in the dose range 50–280 kGy. After the irradiations, the samples were submitted to TEM analysis, crosslink density determination by the swelling method () and to the following mechanical tests: hardness test (IRHD) at 23 ° and 100 °C; static load at 22 °C (stress measured at 10, 50, 100, 300% elongation and breaking strength; % lengthening at breaking); dinamic modulus (E' and tang Delta measured at 10 and 100 Hz at 10 °, 23 °, 100 °C).

Table 1.
Calculated loading of water, PS and total organics for the grafting of PB5000/SiO_2 oxidised with 4.8 kGy.

reaction time (min)	weight % H_2O	weight % PS	weight % total organic[a]
0	3.3	0	18.7
5	2.9	11.7	25.1
15	3.0	14.1	28.0
30	4.6	15.5	28.4

[a]corrected for water content.

The cross links build-up curves were found to be almost linear in the dose range exploited and essentially identical for both the mixtures containing pristine SiO_2 and SiO_2 cured with grafted PB.

TEM analysis has shown that the curing with the PB olygomer does not lead to significant improvement of the filler homogeneity dispersion.

Mechanical tests have afforded different results. The comparison between the mixtures prepared with the pristine and the PB-5000 modified silica have shown that the latter are more responsive to the radiation dose, reaching at 280 kGy an higher 300% modulus, higher breaking strength and higher 100 °C hardness. These results are diagnostic of an higher overall networking efficiency and stronger filler-rubber interactions which are imputed to effects stemming from the PB-5000 curing of silica.

Since, according to the TEM analysis, the advantage of a more homogeneous distribution of the filler cannot be invoked, the higher overall crosslink networking efficiency in the mixtures containing modified silica is explained with the radical scavenging ability of the curing agent leading to the enhancement of the yield of chemically bound rubber during the irradiation. The EPR measurements supports this interpretation by showing a far greater yield of Si bound radicals in the mixtures containing the SiO_2/PB-5000 filler.

Conclusion

The preparation and characteristics of novel functionally modified silica with

enhanced compatibility for rubber matrices in rubber-silica composites is described. The two methods employed involve the radiation induced grafting of poybutadiene olygomers and a three step double grafting procedure with styrene monomer as shown in the scheme below:

$$SiO_2(PB) \xrightarrow[298\,K]{\gamma\,\text{vacuum}} SiO_2-PB \xrightarrow[298\,K]{\gamma\,\text{air}}$$

$$SiO_2-PB-OOH \xrightarrow[Sty]{Fe^{2+}} SiO_2-PB-O\text{-}PS$$

Among the favourable characteristics of the silica modified by PB grafting are the reduced surface energy (both the dispersive and specific components), which approaches that of SBR and polybutadiene rubbers, and the free radical scavenging activity stemming from the double bond content of the grafted PB. Among the unfavourable characteristics is the enhanced stability with respect to particle fragmentation under mechanical stress which might lead to a reduction of the rubber-filler contact surface. Comparative experiments of radiation crosslinking with SBR mixtures containing pristine SiO_2 and SiO_2 modified with grafted PB have afforded for the latter mixture mechanical properties which are diagnostic of an improved overall networking efficiency and stronger filler-rubber interactions. A major source of this result is thought to be the yield enhancement of the chemically bound rubber taking place through free radical reactions with grafted PB. Support for this interpretation have been obtained from the EPR identification of Si-grafted PB radicals.

The performance and properties of the ternary modified silica SiO_2/PB/PS are now being exploited as filler in the radiation induced vulcanization of SBR based composites.

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