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Modification of Silica by Liquid Polybutadienes Containing Alkoxysilane Groups

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Summary: The present work describes a method to modify the surface of silica, reducing its polar character and making it compatible and dispersible into hydrocarbon based elastomers. A liquid low molar mass polybutadiene (PB) was grafted with mercaptopropyltrimethoxysilane (MPTS) via radical addition of the thiol group to the double bonds. The silanized PB was reacted with silica via thermal condensation with its silanol groups. ^{29}Si NMR spectra showed that the condensation reaction of the trifunctional silane involved one or two alkoxy groups, while the third alkoxy group remained unreacted, probably for steric reasons. The characterization of the functionalized silica particles was performed by contact angle measurements and TGA analysis.

Keywords: alkoxysilane; grafting; polybutadiene; silica surface; solid state NMR spectroscopy

Introduction

The interface structure plays an important role in determining the final properties of a polymeric composite, therefore polymers are usually reinforced by adding nano- or micro- inorganic particles after a suitable surface modification. The surface modification is an important step as it is recognized that it enhances the interaction between the inorganic particles and the polymer matrix and promotes the final performance.

Among the many fillers, silica is one of the most commonly widely used in a wide range of industrial fields, including the tyre industry. After having used carbon black, at the beginning of the nineties, SBR-silica filled products showed remarkable improvements in terms of wet grip and rolling resistance, leading in turn to enhanced safety of the car and lower fuel consumption.[1–3] However silica particles show a strong tendency to form aggregates and agglomerates due to their high polar and hydrophilic character, which makes the processing of rubber compounds very difficult. The modification with appropriate coupling agents was investigated and typically multifuctional organic alkoxysilane were used,[4–6] which can eventually react both with the silica surface and the polymer.[7–9] In the years, many improvements were obtained preparing silica organophilic particles that are more easily dispersible into elastomer matrices, by reducing the filler-filler interactions and improving the filler-matrix ones.[7–9]

In this context, the aim of the study described in the present paper is the modification of the silica surface by reacting the –SiOH groups with alkoxysilanes prepared on purpose by reaction of mercaptopropyltrimethoxysilane with a low molar mass polybutadiene (PB), adding the thiol group on the double bonds of the oligomer.[10] Solid state NMR spectroscopy is used to characterize the silica surface modified with the silanised polybutadiene.[11,12]

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Materials and Methods

Materials

The SiO_2 employed was a commercial micro-sized powder silica Zeosil 1165 MP® by Rhone Poulenc, specific surface area by BET: 165 m^2/g

The liquid polybutadiene used was Lithene 900, kindly supplied by Synthomer UK: the M_n is 900, its microstructure is reported in the Results and discussion section.

Azobisisobutyronitrile (AIBN, purchased by Aldrich), was used as radical initiator. Mercaptopropyltrimethoxysilane (MPTS purchased by Aldrich) was the coupling agent, its chemical structure is reported in Figure 1:

Preparation of Silanised Polybutadiene

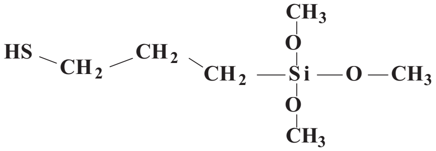
The grafting of polybutadiene with MPTS was obtained according to a procedure similar to that reported in.[10]

9.0 g of polybutadiene Lithene 900 was added of 1.96 g of MPTS (stoichiometric amount, corresponding to a 1: 1 molar ratio between MPTS and polybutadiene chain). Then 100 mg of AIBN as radical initiator were dissolved in the mixture. The system was heated at 75 °C and kept under stirring for 3 h in nitrogen atmosphere. The residual -SH content was 4% with respect to the initial concentration, as determined by iodine titration method.[10]

Modification of Silica Particles

The procedure is similar to that reported by other authors.[13]

10 g of Zeosil 1165 were dispersed in methylene chloride. Then 5 g of polubutadiene dissolved in CH_2Cl_2 was added under stirring. The solvent was evaporated continuing the stirring. The powdered mixture was heated at 135 °C and kept under stirring for 2 h.



$HS-CH_2-CH_2-CH_2-Si(OCH_3)_3$

Figure 1.
Chemical structure of the coupling agent (MPTS).

After cooling, the sample was extracted with CH_2Cl_2 in a Soxhlet for 10 h to remove the unreacted coupling agent. The resulted sample was finally dried under vacuum at room temperature.

Characterization

Thermal gravimetric analysis (TGA) was performed with a Mettler TGA/SDTA 851 instrument at a heating rate of 10 °C/min in air, in the temperature range 25–800 °C.

Static contact angle measurements were performed with a Krüss DSA10 instrument equipped with a video camera using the sessile drop technique. The analyses were carried out on particles compressed in the form of disks, at room temperature. Five measurements were performed on each sample and the values were averaged. Double distilled water was used as measuring liquid ($\gamma = 72.1\ mN \cdot m^{-1}$).

The solid-state NMR spectra were run at 75.5 MHz for C and 59.6 MHz for Si on a Bruker Avance 300 instrument operating at a static field of 7.04 T equipped with 4 mm double resonance MAS probe. The samples were spun at the magic angle at a spinning speed of 15 kHz, and ramped-amplitude cross-polarization (RAMP-CP) transfer of magnetization was applied. The 90 ° pulse for proton was 2.9 μs.

^1H MAS NMR experiments were performed with a recycle delay of 20 s. Cross polarization (CP) ^{29}Si CP MAS NMR experiments were performed using a recycle delay of 10 s and a contact time of 8 ms. ^{13}C MAS NMR single pulse experiments were performed with a recycle delay of 10 s; ^{13}C CP MAS NMR were performed with a contact time of 2.5 s.

When the samples were liquid (like the unmodified polybutadiene and the silanised one) they were dispersed in celite.

Results and Discussion

Synthesis of the Modified Silica

Firstly liquid polybutadiene was reacted with MPTS, a trifunctional molecule which is able to give radical addition to the double bonds according to Scheme 1 and then to establish molecular bridges with the silica surface, as schematically depicted in Scheme 2.

In fact, in the presence of the radical initiator, MPTS forms thiyl radicals, which react with 1,2-double bonds: it was reported that 1,2 unsaturations of polybutadiene are more reactive than 1,4.[10]

The silanised polybutadiene described in this paper contains one MPTS group per chain: the reaction was almost complete as proved by titration of the free thiol content, which was less than 4%.

The modified polymer was grafted onto the Zeosil 1165, a silica usually used as matting agent for polymers and as filler for elastomeric matrices. The reaction conditions are reported elsewhere [13]: Scheme 2 describes the reaction, assuming that just one alkoxy group reacts.

Properties of the Modified Silica and Characterization

The modified silica, after Soxlet extraction, was first evaluated by thermal gravimetry under air. The thermogram is plotted in Figure 2 and compared to that of the pure silica. We can observe that for both samples there is a first weight loss at 100 °C, due to the evaporation of the water adsorbed on the particles: for the pure inorganic silica the water content is around 6%, while the modified silica has a smaller amount of water, about 3.5%. At 800 °C, the TGA thermograms indicate that the total weight loss of the functionalized silica is 22%, corresponding to 3.5% of water plus 18.5% of silanized polybutadiene condensed on the silica surface.

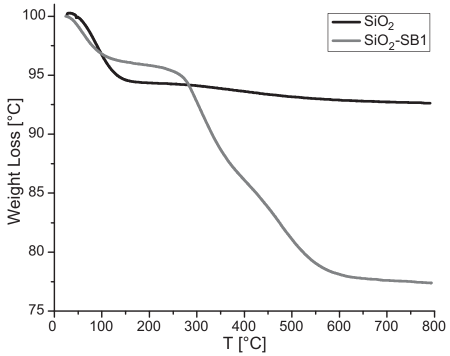
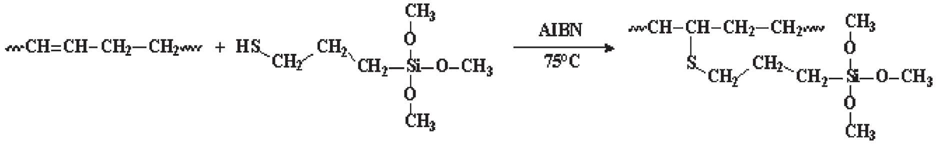
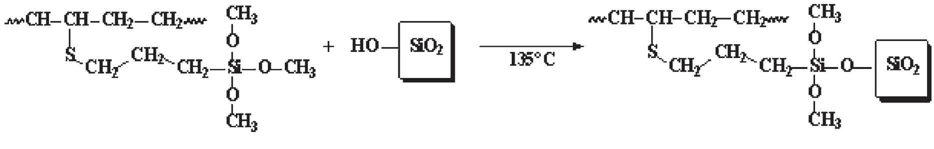


Figure 2.
TGA thermograms in air of pure silica and silanized silica particles.

An important aspect of the modification of silica is the transformation of its hydrophilic character into a hydrophobic one. For this purpose, the surface characteristics of the functionalized silica particles were evaluated by means of contact angle measurements. The contact angle values with water of silica increased from nearly 0 ° for the pure silica to around 90 ° for the



Scheme 1.
Addition of MPTS to the polymer matrix in the presence of initiator.



Scheme 2.
Condensation of silanized polybutadiene on the silica surface.

organo-modified silica. This results confirms that a strong enhancement of the organophilicity of the silica surface was obtained after the silanization reaction.

In order to understand the structure and composition of the silica surface after reaction with the silanised polybutadiene and asses the presence of chemical anchoring of the organic compound onto silica surface, 1H-NMR and 29Si-NMR solid state experiments were conducted. They are powerful tools to characterize the surface modification of silica particles [12,14,15]; moreover they are powerful and convenient techniques to study the structure and dynamics of polymers due to their high sensitivity to local chemical environments.

Figure 3 shows the 1H-NMR spectra recorded, under 12.5 kHz spinning frequency, from three samples: polybutadiene, polybutadiene functionalized with MPTS and silica modified with silanized polybutadiene. The spectrum (1) shows all the species related to the raw polybutadiene, as in the spectrum at the liquid state. In the range 5.62–4.90 ppm one finds the unsaturated hydrogens (signals f,b,h,e), at a higher field (2.38–1.21 ppm) the saturated hydrogens (signals c,g,a,d). At 1.66 and 1.53 ppm the signals are due to the end groups. By simulation of the peaks due to unsaturated hydrogens, the microstructure of polybutadiene could be confirmed: the pendant vinyl groups are 38.5%, the cis 1,4 are 17.5% and the trans isomer are 44%.

After the reaction with MPTS (spectrum 2) three different signals are clearly evident at 3.4, 2.4 and 0.7 ppm attributed to the –OCH_3, -CH_2S- and –CH_2Si- groups respectively. The signal of the middle CH_2 group of the mercaptosilane resonates at about 1.7 ppm and overlaps the PB peaks. When the grafting reaction with silanised poly-

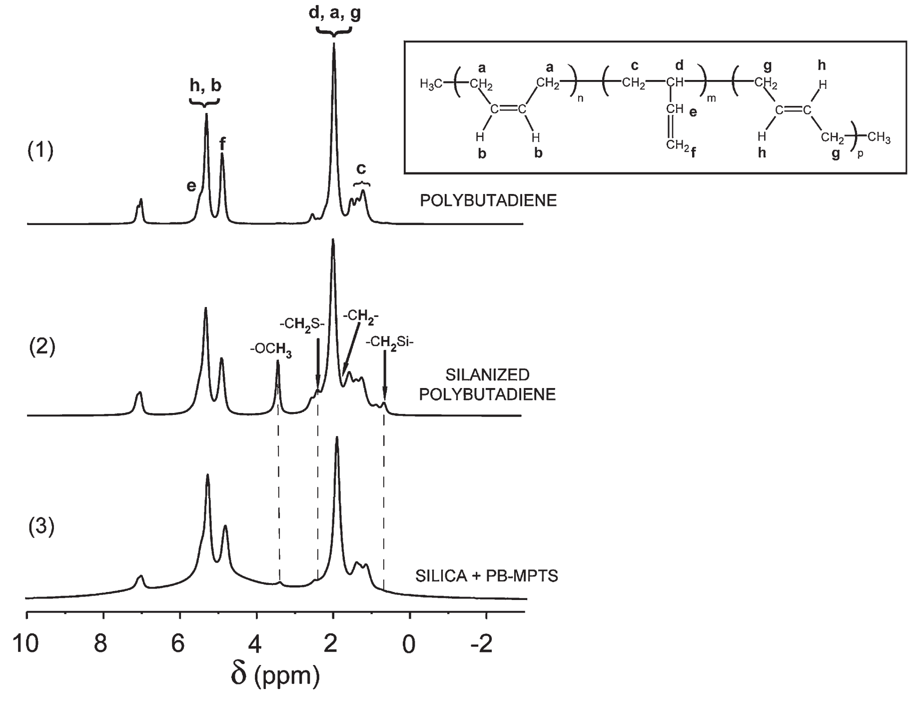


Figure 3.
^{1}H-MAS solid state NMR spectra of polybutadiene (1), silanized polybutadiene (2) and silica functionalized with silanized polybutadiene (3).

butadiene takes place onto the silica surface, in spectrum (3) the signals appear broader, indicating that the polymer is interacting with the silica surface and its chain is stiffer. There is a clear shift of the signals related to the -CH_2S- and –CH_2Si- groups toward lower values. At the same time, the peak related to the methoxy group of the mercaptosilane disappeared: the groups -OCH_3 of the modified polybutadiene are firstly hydrolysed and then condensed on the silica surface. The residue peak indicates that in the final sample there is still a small amount of unreacted methoxy groups.

Figure 4 shows the ^{13}C-NMR spectra of modified SiO_2. Spectrum (1) was recorded by CP (Cross Polarization)/MAS NMR experiment and spectrum (2) by the MAS experiment.

Spectrum (1), obtained with a 2.5 ms contact time, describes the polybutadiene chains either grafted or at least strongly interacting with the silica: due to the increased rigidity of the chains, the signals are broad. Spectrum (2), obtained with a single pulse and a short recycle time (10 s), describes the polymeric chains which keep their mobility, as they are either far away from the solid surface or not grafted to it. In the region 150–110 ppm one can find the unsaturated carbons, while the signals between 50 and 20 ppm describe the saturated carbons. These signals are complex and difficult to identify, however the peak at 44 ppm could be attributed to the vinyl groups. It is important to observe that at 50 ppm there is a signal that could be attributed to the methoxysilane groups, meaning that not all the -OCH_3 functions condensed with silica, in agreement with the interpretations given for the ^{1}H-NMR spectrum of Figure 3.

In Figure 5, the ^{29}Si-CPMAS NMR spectrum of the functionalized silica particles is reported. It shows the three peaks at −91 ppm, −101 ppm and −110 ppm, characterizing silica and assigned to the Q^2 ((Si-O)$_2$-Si-(OH)$_2$), Q^3 ((Si-O)$_3$-Si-OH), and to the Q^4 ((Si-O)$_4$-Si), respectively. Moreover it is possible to observe the presence of signals, T^n, in the range between −40 and −80 ppm: they characterize the structure of the different alkoxysilane groups.

At −50 ppm we can see the signal T^0 related to the unreacted silane. The signals T^1 and T^2 at −60 and −71 ppm

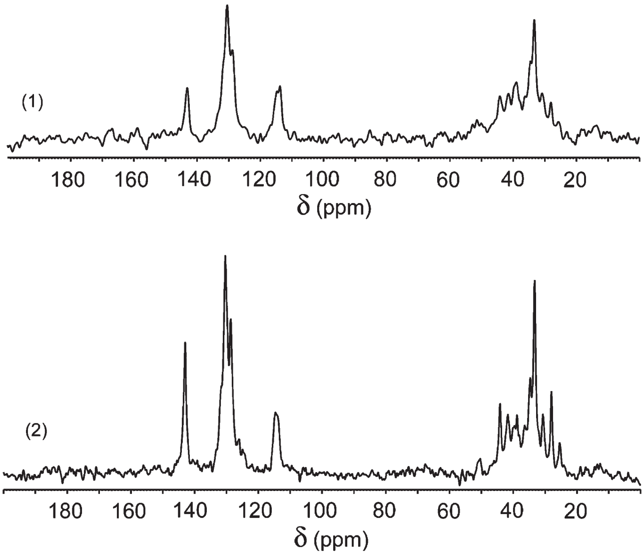


Figure 4.
^{13}C-NMR spectra of modified silica particles.

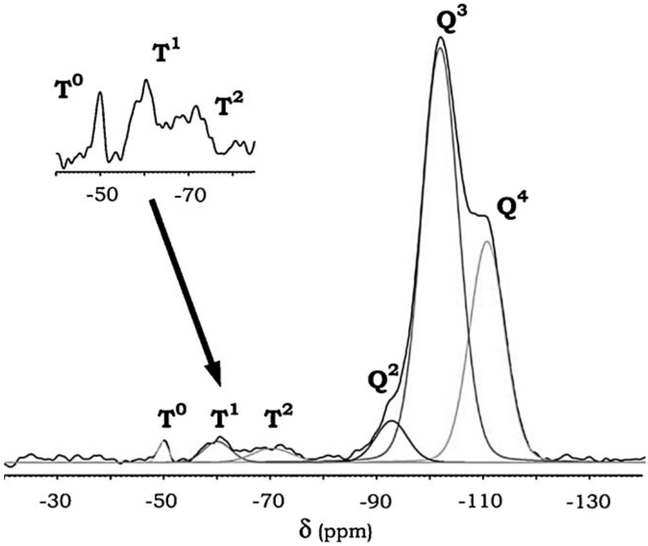


Figure 5.
^{29}Si-CPMAS spectrum of silica functionalized with silanized polybutadiene.

are attributed to the condensation on the silica surface of one or two alkoxy groups respectively. Moreover, only a negligible amount of T^3 species is present, proving that the third alkoxy group shows a very low condensation on the silica surface, probably for steric reason.

Conclusion

An alkoxysilane able to modify silica surface was prepared by the radical addition of a mercaptoalkoxysilane onto the double bonds of a low molecular weight polybutadiene. The thiol group present in MPTS was quantitatively added to the double bonds of polybutadiene allowing the introduction of a trialkoxy group on the oligomer chain. After condensation with silanised polybutadiene, silica assumed an organophilic character, as indicated by contact angle measurements.

The silanised polybutadiene was covalently bonded on the surface of the silica particles as assessed by solid state ^{29}Si NMR, ^{13}C-NMR and ^{1}H NMR It was shown that for each trialkoxy group only one or two alkoxy groups condense on the silica surface, the third function shows very low reactivity, probably due to steric reasons.

Due to its organophilic character and to the presence of polybutadiene chains, the modified silica is expected to have better dispersion properties in elastomeric matrices; hence it could be successfully employed as reinforcing filler of tyre tread compounds.

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