

¹³C and ²⁹Si Solid-State NMR of Rubber–Silica Composite Materials

Roberto Simonutti,[†] Angiolina Comotti,[†] Fabio Negroni,[‡] and Piero Sozzani^{*,†}

Department of Materials Science, Milan University, via Emanuela 15, 20126 Milano, Italy, and
Pirelli Coordinamento Pneumatici, viale Sarca 222, 20126 Milano, Italy

Received October 13, 1998

The polymer–silica interaction in elastomeric materials composed of 1,4-*cis*-polyisoprene rubber and silica was studied by magic angle spinning NMR. The relaxation times in the hydrogen domain are informative about phases at the nanometer scale when a spin propagation phenomenon, due to strong dipolar couplings in the solid, prevails. However, magnetization diffusion is quenched in a rubbery phase where spin–spin relaxation rates are slow. The problem was overcome by promoting spin diffusion below the glass transition at low temperature. The interface was then observed under high-resolution conditions by the reciprocal points of view of ¹³C and ²⁹Si nuclei. In particular, a fast transfer of magnetization from the polymer to the silica surface was observed by cross-polarization dynamics following the nonprotonated silicon atoms. Bidentate coupling agents and vulcanization promote a better interaction with the silica surface. The morphological modifications of the silica particles after processing could also be observed.

Introduction

The presence of inorganic material greatly influences the mechanical and physical properties of polymers; for example, glass fibers reinforce polymers and give them high performance. In recent years silica has been proposed as a reinforcing agent of elastomers especially for application to tires. In fact a combination of silica and a bifunctional organosilane have improved rolling resistance and wet traction with no loss in abrasion resistance.¹

Silica-filled compounds present moduli higher than those of carbon black when measured at low elongation (20–40%). In carbon black compounds, the mechanical properties are determined by the interaction between rubber and filler. In the case of silica, filler–filler and rubber–filler interactions must be taken into account.

In this work, for the first time, ¹³C and ²⁹Si magic-angle spinning (MAS) NMR was used for obtaining a detailed description, at a microscopic level, of the interaction between 1,4-*cis*-polyisoprene and silica. We took a similar approach to that applied to macro defect free composites^{2,3} (MDF) made by vinyl alcohol/vinyl acetate copolymer and calcium silicate or aluminate. Proton $T_{1\rho}$ and T_1 relaxation times, measured by transferring the magnetization to the carbon or silicon atoms, demonstrated an intimate mixing of the polymer and inorganic phases.

Silica and modified silica materials have been intensively studied using different solid-state NMR tech-

niques. Maciel et al. demonstrated the possibility of describing the silica surface by measuring, with ²⁹Si cross-polarization (CP) MAS, the ratio between the different kinds of silicon atoms, sometimes using silylation as a probe.^{4–9} Fyfe et al. proposed the use of ²⁹Si MAS without CP and long recycle delay to obtain a quantitative description of the silica particles.¹⁰ More recently the importance of the relaxation parameters has been highlighted in CPMAS experiments, resulting in a better description of the silica structure.^{11–14}

There are few examples concerning the NMR characterization of polymer–silica composites. Polyamide-6 samples filled with glass microspheres pretreated with a coupling agent (γ -aminopropyl)triethoxysilane (γ -APS) have been studied by ¹³C and ²⁹Si CPMAS, the authors finding evidence of chemical bonding between γ -APS and Nylon 6; there was also the suggestion of chain entanglements and interpenetration of networks.^{15,16} Bifunctional epoxy resins often have γ -APS silylated silica as a filler. The mobility of the silane coupling agent onto the matrix resin interface has been charac-

- (4) Maciel, G. E.; Sindorf, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 7607.
- (5) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 4263.
- (6) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1982**, *86*, 5208.
- (7) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 1487.
- (8) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 3767.
- (9) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1983**, *87*, 5516.
- (10) Fyfe, C. A.; Gobbi, G. C.; Kennedy, G. C. *J. Phys. Chem.* **1985**, *89*, 277.
- (11) Pfeiderer, B.; Albert, K.; Bayer, E.; van de Ven, L.; de Haan, J.; Cramers, C. *J. Phys. Chem.* **1990**, *94*, 4189.
- (12) Leonardelli, S.; Facchini, L.; Fretigny, C.; Tougne, P.; Legrand, A. P. *J. Am. Chem. Soc.* **1992**, *114*, 6412.
- (13) Chuang, I.-S.; Maciel, G. E. *J. Am. Chem. Soc.* **1996**, *118*, 401.
- (14) Liu, C. C.; Maciel, G. E. *J. Am. Chem. Soc.* **1996**, *118*, 5103.
- (15) Weeding, T. L.; Veeman, W. S.; Jennekens, L. W.; Angad Gaur, H.; Schuurs, H. E. C.; Huysmans, W. G. B. *Macromolecules* **1989**, *22*, 706.
- (16) Huijgen, T. P.; Angad Gaur, H.; Weeding, T. L.; Jennekens, L. W.; Schuurs, H. E. C.; Huysmans, W. G. B.; Veeman, W. S. *Macromolecules* **1990**, *23*, 3063.

[†] University of Milano.

[‡] Pirelli Coordinamento Pneumatici.

(1) Wolf, S. *Rubber Chem. and Technol.* **1996**, *69*, 325.

(2) Comotti, A.; Simonutti, R.; Sozzani, P. *Chem. Mater.* **1996**, *8*, 2341.

(3) Comotti, A.; Simonutti, R.; Sozzani, P. *J. Mater. Sci.* **1997**, *32*, 4237.

terized by following, under different conditions,¹⁷ the ²⁹Si cross-polarization rates. Blum et al. studied the mobility of the coupling agent in the presence of the polymer matrix using the ²H NMR technique.¹⁸ Ford and co-workers measured a few relaxation parameters from the point of view of both ¹³C and ²⁹Si nuclei, in a poly(methyl methacrylate)–silica composite where the silica particles were covered by a suitable coupling agent. From the relaxation data they proposed the existence of a layer of dangling chains at the interphase between the polymer matrix and the silica grains.¹⁹ In all these studies the silica surface was strongly modified due the presence of the coupling agent; in fact, the silane content is not negligible with respect to the silica. Zumbulyadis et al.²⁰ studied a system containing only poly(vinyl alcohol) and silica. In this example, the authors were able to demonstrate the proximity of the polymer backbone to the silica surface. In our work the polymer–silica composites were studied before and after vulcanization and in the presence as well as in the absence of the coupling agent.

Experimental Section

Materials. 1,4-*cis*-Polyisoprene (PI) was purchased from Goodyear (NATSYN RNS-7477; *cis* content, 97%). The fumed silica was Cab-O-Sil HS-5 from Cabot Corp. (surface area 325 m²/g); the precipitated silica was Ultrasil VN3 from Degussa (surface area 175 m²/g). Bis(triethoxysilylpropyl)tetrasulfane (TESPT) was purchased from Degussa. Though high-resolution ¹³C NMR showed the presence of a mixture of silanes of different sulfuric chain lengths, TESPT was used without purification.

The samples were prepared by mechanical mixing for about 30 min in a roll mill mixer. The temperature was kept at 70 °C to avoid any curing reactions. All the samples contained sulfur and accelerator cure systems. The composition of the samples was as follows: sample A, 300.0 g of PI, 141.4 g of Ultrasil VN3, 6.7 g of sulfur, 6.0 g of stearic acid, 15.0 g of ZnO, 2.1 g of *N-tert*-butyl-2-benzothiazylsulfenamide; sample B, 300.0 g of PI, 141.4 g of Ultrasil VN3, 15.0 g of TESPT, 6.7 g of sulfur, 6.0 g of stearic acid, 15.0 g of ZnO, 2.1 g of *N-tert*-butyl-2-benzothiazylsulfenamide; sample C, 300.0 g of PI, 141.4 g of Cab-O-Sil HS5, 6.7 g of sulfur, 6.0 g of stearic acid, 15 g of ZnO, 2.1 g of *N-tert*-butyl-2-benzothiazylsulfenamide. Samples A_v, B_v, and C_v respectively correspond to the vulcanized samples of A, B, and C. Vulcanization was carried out at 160 °C for 12 min (sample A) or 8 min (sample B and C).

Solid-State NMR. High-resolution ¹³C and ²⁹Si MAS NMR spectra were collected at 75.5 and 59.6 MHz, respectively, on a MSL300 Bruker instrument operating at a static field of 7.4 T. A MAS Bruker probe was used with 7 mm ZrO₂ rotors; the spinning speed ranged between 2 and 4.5 kHz. Low temperature experiments were made using a Bruker cooling system, in which only bearing flux is cooled. Temperatures ranged between 203 and 298 K, and the stability was ±1 K. All the experiments were made using a high-power proton decoupling (DD) field of 15 G. The 90° pulse for carbon was 4 μs, the 90° pulse for silicon was 6 μs, and the 90° pulse for proton was 6 μs. CPMAS experiments were performed with a delay time of 4–10 s and a contact time ranging from 1 to 18 ms. ¹³C CPMAS experiments were run by collecting 200–400 scans. ²⁹Si CPMAS experiments were run by collecting 10 000–20 000 scans (for Cab-O-Sil, 80 000 scans). ¹³C single pulse excitation

MAS (SPE MAS) experiments were run using a recycle delay of 8 s; quantitative ²⁹Si SPE MAS experiments were done using a recycle delay of 100 s, and 2000–3000 scans were collected.

Proton relaxation times in the rotating frame $T_{1\rho}(^1\text{H})$ were measured indirectly by varying the duration of a ¹H spin-lock period before a fixed ¹H → ¹³C cross-polarization contact period.³ For each relaxation measurement, 13 spectra at 203 K were run. $T_{1\rho}(^1\text{H})$ values were calculated using a nonlinear least-squares fitting routine.

The resolution for carbon was checked on glycine (width at half-height = 22 Hz). Crystalline polyethylene (PE) was taken as an external reference at 33.63 ppm from tetramethylsilane (TMS).²¹ The resolution for silicon was checked on Q₈M₈ sample (trimethylsilyl ester of octameric silicic acid, Si₈O₂₀H₈). Q₈M₈ sample was also used as the second standard, assigning the ²⁹Si chemical shift of the trimethylsilyl groups to +11.5 ppm from TMS.²²

Results and Discussion

¹³C MAS NMR of PI/Silica Compounds. The observation of the ¹³C nucleus under MAS condition is considered the most valid technique for studying polymers and polymer composites by solid-state NMR, so we applied it to see the effect of silica on the polymer's spectroscopic properties.

The glass transition of 1,4-*cis*-polyisoprene and 1,4-*cis*-polyisoprene/silica compounds is detected by DSC and DMA at –48 °C and it is known that 1,4-*cis*-polyisoprene shows different properties above and below this transition temperature. Therefore, we collected our ¹³C solid-state NMR spectra under various conditions: room and low temperature.

The main reason for studying a “rubber” at very low temperatures was the fact that spin diffusion is promoted in the polymer matrix. It is known that in rigid solids and for strongly coupled nuclei, such as ¹H and ¹⁹F, magnetization can propagate between regions by a flip–flop mechanism, thereby offering information complementary to that given by microscopy. Spin diffusion in polymers is quenched when a macromolecule undergoes fast isotropic molecular motion plus rapid local translation diffusion, a state that occurs in a “rubber” far above glass transition or in the liquid state. Such motions are typified by weak dipolar couplings and correspondingly long T_2 spin–spin relaxation times. In a regime with these molecular dynamics, spin diffusion experiments are precluded; thus, we searched for conditions where the polymer was rigid enough for spin propagation to travel reasonably long distances within the polymer.

The solid-state SPE ¹³C NMR spectrum of PI as recorded at room temperature (Figure 1) shows five narrow signals (full width at half-maximum of about 10–12 Hz) corresponding to the five different carbon atoms of the monomeric unit.²³ A short ¹³C T_1 relaxation time (just a few seconds) was measured for all the signals. These relaxation data suggest that at room temperature the polyisoprene is in the extreme narrowing limit, an observation consistent with the behavior of most polymers at about 80 K above the glass transition. The spectra of the nonvulcanized composites, PI

(17) Hoh, K. P.; Ishida, H.; Koenig, J. L. *Polym. Compos.* **1990**, *11*, 121.

(18) Gambogi, J. E.; Blum, F. D. *Macromolecules* **1992**, *25*, 4526.

(19) Joseph, R.; Zhang, S.; Ford, W. T. *Macromolecules* **1996**, *29*, 1305.

(20) Zumbulyadis, N.; O'Reilly, J. M. *Macromolecules* **1991**, *24*, 5294.

(21) Earl, W. L.; VanderHart, D. L. *J. Magn. Res.* **1982**, *48*, 35.

(22) Lippmaa, E.; Mägi, M.; Samoson, A.; Engelhardt, G.; Grimmer, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 4889.

(23) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*, Academic Press: San Diego, 1988; p 373.

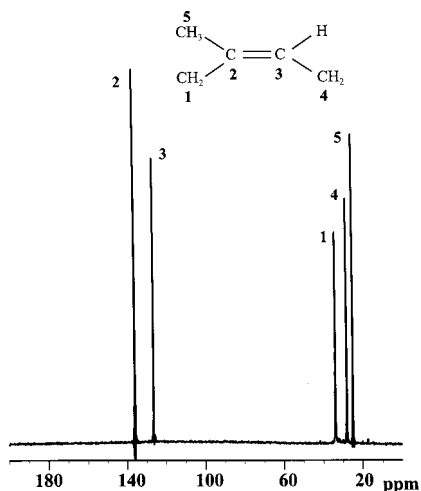


Figure 1. 75.5 MHz ^{13}C MAS spectrum of polyisoprene at room temperature. A recycle delay of 8 s was applied.

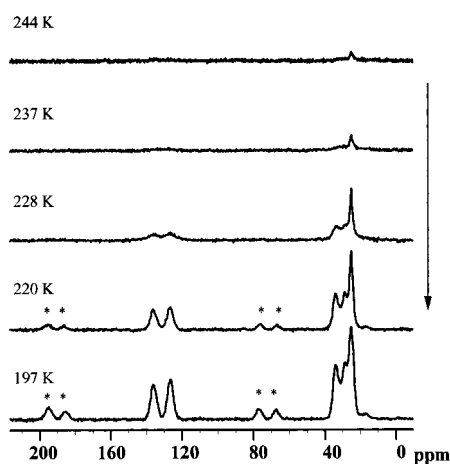


Figure 2. 75.5 MHz ^{13}C CPMAS spectrum of polyisoprene at variable temperatures ranging from 244 K to 197 K. The peaks marked with an asterisk correspond to spinning speed sidebands.

with silica VN3 (sample A), PI with silica VN3 and TESPT (sample B), and PI with silica Cab-O-Sil (sample C), (spectra not shown) present the same features and again there is no broadening of the peaks. Thus the presence of the filler particles does not visibly modify the T_2 relaxation times of the bulk polymer. To identify a less mobile part of PI possibly associated with the interface, cross-polarization experiments (with a few milliseconds of contact time) were run on both PI and the composites. No signal was present at room temperature with 400 scans; only after 10 000 scans a spectrum was obtained (not shown), but the appearance of this spectrum was the same of the SPE spectrum, indicating that no specific information about the interface was collected.

Thus, to increase the dipolar interactions within the polymer and the sensitivity to the presence of the filler, ^{13}C CPMAS spectra were performed at low temperature. Figure 2 shows ^{13}C CPMAS spectra of pure PI at the reported temperatures. At 244 K the peak of the methyl group starts to appear. At lower temperatures all the carbons of the monomeric unit are detectable; the large anisotropy of the carbon atoms of the double bond is reflected by the presence of a few orders of spinning sidebands, which could not be averaged by the magic

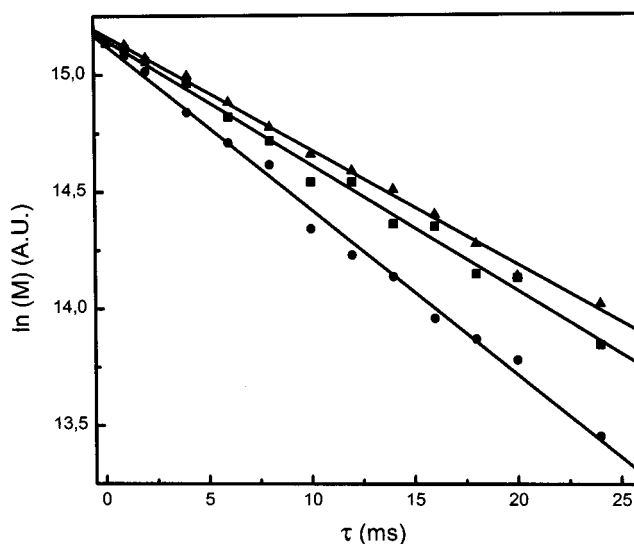


Figure 3. Proton $T_{1\rho}$ relaxation times measured at 197 K observed from the ^{13}C spectra of polyisoprene (●), PI/VN3 compound (sample A) (■), and PI/Cab-O-Sil (sample C) (▲).

angle rotation at 4500 Hz. The intensity of the sidebands reveals a different anisotropy on the two unsaturated signals. The variable temperature ^{13}C CPMAS spectra of the composite show the same trend, and no significant difference in temperature dependence was found; in fact, the compounds present nearly the same glass transition as the pure polymer.

Techniques should be adopted which can be sensitive to extended domains of the material. A measurement of the degree of compatibility between organic and inorganic phases of materials has already been obtained by analyzing the relaxation times in the hydrogen domain, as indirectly detected, via cross polarization, by the high-resolution signals of silicon-29 and carbon-13. The example studied was a high glass transition temperature polymer (poly(vinyl alcohol)) interacting with calcium silicates at room temperature. We have demonstrated that spin propagation can cross heterogeneous interfaces.^{2,3}

If the domains are large enough, the detected relaxation times are those associated with each domain present; but if the domains are small, the magnetization has time to equilibrate. Then, the relaxation time should be the average of the intrinsic relaxation processes in the two regions. Domain extensions of a few nanometers are defined by the proton $T_{1\rho}$ for times of a few milliseconds. Several papers report detailed theoretical and practical descriptions of this matter,²⁴⁻²⁶ so no further details are given here.

Figure 3 shows the decay of the proton magnetization in the rotating frame (by transfer of magnetization to ^{13}C), for the pure polymer and the composite materials at 197 K. The reported measurements are averaged over the exponential fit of each signal; all the peaks present the same relaxation behavior, indicating no bias due to local environment.

(24) McBrierty, V. J.; Packer, K. J. *Nuclear Magnetic Resonance in Solid Polymers*, Cambridge University, Cambridge, 1993.

(25) VanderHart, D. L. *Makromol. Chem. Macromol. Symp.* **1990**, *34*, 125.

(26) Dickinson, L. C.; Yang, H.; Chu, C. W.; Stein, R. S.; Chien, J. C. W. *Macromolecules* **1987**, *20*, 1757.

At 197 K the proton $T_{1\rho}$ relaxation times of pure 1,4-*cis*-polyisoprene samples show just one exponential component of about 13 ms. The composites with precipitated VN3 (sample A) and fumed Cab-O-Sil silica (sample C) show longer relaxation times (about 20 ms) at 197 K, evidencing the effect of the silica particles. At 197 K, below the glass transition of the polymer, the motions are intrinsically hindered, and thus we suggest that the relaxation rate is reduced (measured from the ^{13}C) by the spin diffusion phenomenon between the polymer and the silica surface. Anyway, the relaxation rate can be partly affected by different chain mobilities.

If one considers the spin diffusion coefficient for PI below the glass transition to be of the same order as the polyethylene value, then the distances traveled by proton magnetization in 20 ms reach about 15 nm; thus, the phase extension of the polymer matrix, where magnetization travels without interaction with the silica particles, is estimated to be smaller than this value of 15 nm. This is clear indication of well-dispersed composites.

The different silica particles, fumed versus precipitated, do not affect the relaxation measurement; this indicates that the polymer, within these given phase dimensions, is intimate with the silica to the same extent.

^{29}Si MAS NMR of PI/Silica Compounds. Two kinds of silica powders (VN3 and Cab-O-Sil) obtained by different methods (see experimental Section) were studied. Surface area was measured by BET and was 175 and 325 m^2/g .

The single pulse excitation (SPE) MAS spectra of VN3 and Cab-O-Sil samples are reported in parts c and a of Figure 4 with the respective deconvolution; 100 s of recycle delay was applied to ensure a complete relaxation of the silicon nuclei. In the VN3 silica spectrum, two peaks are easily recognized: one peak, at -103 ppm, is attributed to silicon atoms that have one hydroxyl group, $(\text{Si}-\text{O})_3\text{Si}-\text{OH}$ (single silanol, called Q^3),²² and the other at -113 ppm is due to silicon atoms without hydroxyl groups, $\text{Si}(\text{Si}-\text{O})_4$ (called Q^4). The peak at -93 ppm, related to the presence of geminal silanols, $(\text{Si}-\text{O})_2\text{Si}-(\text{OH})_2$ (called Q^2), is not shown by SPE MAS experiments, because of its low abundance. Q^3 and Q^2 species are present at the surface of the silica particle; thus, the intensity ratio $(\text{Q}^3 + \text{Q}^2)/\text{Q}^4$ is related to the surface area of the silica. In the Cab-O-Sil SPE MAS spectrum (Figure 4a) the two peaks, Q^3 and Q^4 , are blurred; the deconvolution makes it possible to separate the resonances. The line width of peaks in the Cab-O-Sil is nearly twice that of VN3 silica. This can be explained by the fact that Cab-O-Sil is synthesized at high temperature and then rapidly cooled, thus producing highly strained Si–O–Si bond angles with a spreading out of the chemical shifts.¹⁴ Cab-O-Sil presents the higher value of $(\text{Q}^3 + \text{Q}^2)/\text{Q}^4$, confirming the surface area obtained with BET measurements.

Parts d and b of Figure 4 show the ^{29}Si CP MAS spectra of VN3 and Cab-O-Sil. The CP technique generates signals from those silicon atoms that are dipolar-coupled to hydrogens. The spectra are not quantitative, and since the signal response decreases rapidly with increasing distance from the hydrogens, the relative intensities of the Q^n resonances become weaker as n

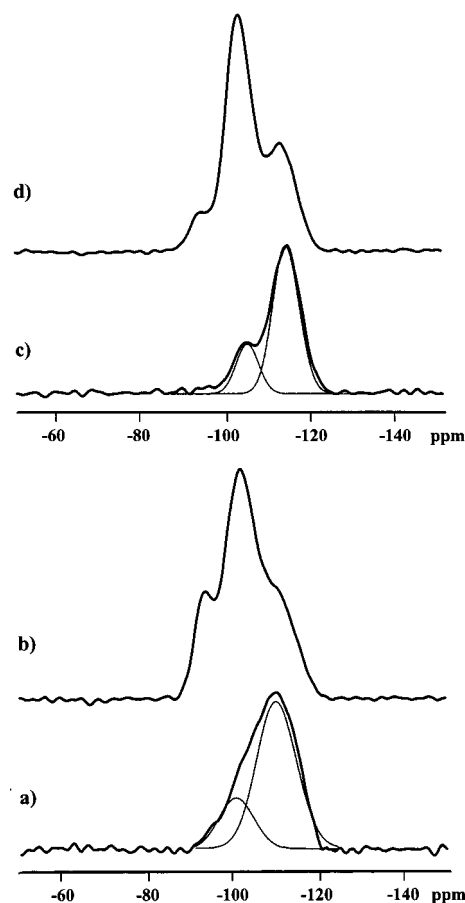


Figure 4. (a) 59.6 MHz ^{29}Si SPE MAS spectrum of Cab-O-Sil silica with a relaxation delay of 100 s; (b) 59.6 MHz ^{29}Si CP MAS spectrum Cab-O-Sil silica with a contact time of 3.5 ms; (c) 59.6 MHz ^{29}Si SPE MAS spectrum of VN3 silica with a relaxation delay of 100 s; (d) 59.6 MHz ^{29}Si CP MAS spectrum of VN3 silica with a contact time of 3.5 ms. The spectra were performed at room temperature.

increases, especially for $n = 4$. The Q^4 signal is thus only due to the Q^4 silicons close to the surface.

Cab-O-Sil has a very high Q^2/Q^3 ratio, indicating an high number of edges; in fact, there are reports that in fumed silica the chain structure dominates.

We also wished to exploit the sensitivity of the $^1\text{H} \rightarrow ^{29}\text{Si}$ cross-polarization technique to changes in the proton density at the silica surface; in fact, if the polymer comes close to the surface of the silica particle (at a scale of tenths of nanometers), a large number of protons could become a source of magnetization for the silicon nuclei at the interface.

Therefore, to demonstrate that the protons of the polymer matrix of the silica/PI compound can transfer magnetization to silica under cross-polarization conditions, we recorded the ^{29}Si CP MAS spectra of compounds with 3.5 ms of contact time and compared the Q^3/Q^4 intensity ratio in the compounds with that of pure silica.

In fact, the Q^4 signals of the ^{29}Si CP MAS spectra of the Cab-O-Sil silica in compound C are relatively increased (Figure 5a) (compared to Figure 4b). When the Q^4 signals are close to the surface, they are more sensitive to the presence of additional hydrogens in the surroundings, as already demonstrated by Zumbulyadis et al. in ref 20. On comparing poly(vinyl alcohol)–silica compounds, hydrogenated and selectively deuterated,

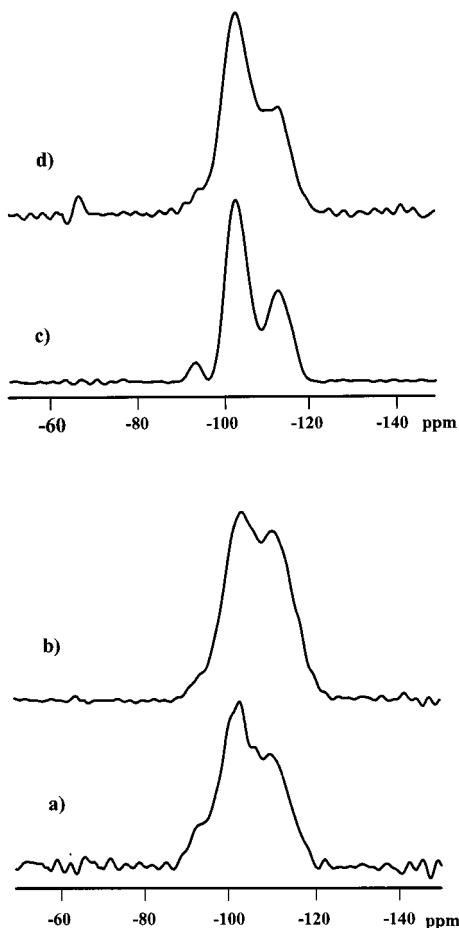


Figure 5. 59.6 MHz ^{29}Si CP MAS spectra: (a) Cab-O-Sil/PI compound after mixing (sample C), (b) vulcanized Cab-O-Sil/PI compound (sample C_v), (c) VN3/PI compound after mixing (sample A), and (d) vulcanized VN3/PI compound (sample A_v). A contact time of 3.5 ms was applied. The spectra were performed at room temperature.

those authors observed the transfer of magnetization from the polymer to the silica surface. Thus the polymer and the silica surface need to be in close proximity to justify the increase in magnetization transfer to non-hydrogenated Q^4 species in the Cab-O-Sil compound. Also, the Q^2 signal intensity of Cab-O-Sil silica in the compound is modified. We have also to take into account that the Q^2 signals are due to hydrogen-rich groups and are therefore relatively less affected by the additional hydrogen nuclei. The intensity of the Q^2 signal is reduced to half. This is probably the chemical effect of the mechanical energy applied by the mixing procedure. As Cab-O-Sil silica is endowed with a fragile structure similar to a tree, its structure may be partly modified to a more compact one, resulting in a reduction of the edges where the geminal silanol groups (Q^2) more frequently reside.

The ^{29}Si CP MAS spectrum of the VN3 silica in the compound A shows no relevant increase in Q^4 signals (Figure 5c); also, the Q^2 and Q^3 signal intensities are the same in both compound A (Figure 5c) and the pure VN3 sample (Figure 4d).

The VN3- and Cab-O-Sil-based composites show marked differences after vulcanization of the blends. In Figure 5d the effect of the treatment on VN3/PI (sample A_v) is shown; it is no more than a broadening and

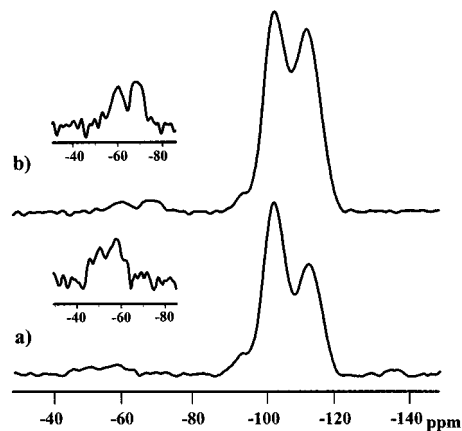


Figure 6. 59.6 MHz ^{29}Si CP MAS spectra: (a) VN3/TESPT/PI compound after mixing (sample B) and (b) vulcanized VN3/TESPT/PI compound (sample B_v). In the amplification the TESPT signals are evidenced. A contact time of 3.5 ms was applied. The spectra were performed at room temperature.

blurring of the signals. On the contrary, the Cab-O-Sil/PI vulcanized composite (sample C_v) shows a further increase in the Q^4 signal and a slight reduction of the Q^2 one (Figure 5b), following the same trend as from pure silica to simply mixed Cab-O-Sil and polymer (compare Figures 4b, 5a, and 5b). The process of heating (150 °C) and vulcanizing must have caused the polymer to approach the large and almost inaccessible surface of Cab-O-Sil; thus, the polymer mobility is reduced by topological constrains.

The increased rigidity of the polymer must also play a role. Since the sensitivity of ^{29}Si CP MAS to the closeness and properties of the polymer was apparent from previous experiments, we decided to observe, from the silicon point of view, the adhesion under forced conditions: samples containing a compatibilizer (TESPT) were prepared and characterized.

On one hand, TESPT reacts with the silica surface and on the other it takes part in the vulcanization. The structure of TESPT was established by solution NMR. The ^{13}C spectra (not shown) indicate variable amounts of sulfur atoms in a row at the center of the amphiphilic molecule. As a result, the polymer is compelled to approach the inorganic surface and to link covalently to TESPT after vulcanization. Figure 6a shows the spectrum of the sample where there was just a simple mixing of the components (sample B). Figure 5c shows substantially the same features, proving that the presence of uncured TESPT does not affect the silica surface in any significant way. After curing (sample B_v), the polymer appears to approach the surface, markedly increasing the Q^4 intensity (Figure 6b), as already described for the cured (but without compatibilizer) Cab-O-Sil silica (Figure 5b) (sample C_v).

The signals are narrower in the spectrum of Figure 6b than those of the Cab-O-Sil/PI cured samples (sample C_v), suggesting the environments of the condensation species to be better defined. The so-called T species derived from TESPT (those which contain a silicon-carbon bond) are present in the spectra at about -80 ppm (see amplification in Figure 6). Despite the unfavorable signal-to-noise ratio (TESPT content is only 3% of the total mass), one can observe on the cured sample the upfield drift of the T^n signals at higher number n .

This effect could be due to an actual condensation progress of the species and to an increased T^4 sensitivity to CP experiments, just like the Q^4 species, as already discussed. The previously mentioned surface effect of the polymer, as seen by ^{29}Si nuclei, is thus depleted by the TESPT contribution, as these nuclei are detected separately.

^{29}Si Cross-Polarization Dynamics. To have a complete description of the cross-polarization dynamics, experiments with variable contact-times were carried out on the pure silica VN3 and the sample B_v , the latter being the PI/VN3 compound vulcanized with TESPT. The cross-polarization process allows the rare spin system (^{29}Si) to come into thermal contact with the neighboring system of abundant spins (protons) by means of a radio frequency pulse sequence. In this sequence, the spin-locked (cold) system of abundant nuclei causes a large drop in the spin temperature of the rare nuclei system. Thus, there is a build up of ^{29}Si magnetization. The build up of ^{29}Si magnetization is ruled by the following equation:^{27,28}

$$M(t) = \frac{M_0}{T_{\text{SiH}}} \left\{ \exp[-t/T_{1\rho}({}^1\text{H})] - \exp[-t/T_{\text{SiH}}] \right\} \quad (1)$$

$$\frac{T_{1\rho}({}^1\text{H})}{T_{1\rho}({}^{29}\text{Si})}$$

Where $T_{1\rho}({}^1\text{H})$ is the relaxation time of the proton nuclei in the rotating frame and T_{SiH} the cross-polarization time. This equation is valid providing that the relaxation time of the silicon nuclei in the rotating frame, $T_{1\rho}({}^{29}\text{Si})$, is much larger than $T_{1\rho}({}^1\text{H})$ and T_{SiH} , a condition that is fulfilled in the case of silica. The equation describes two processes: the first exponential, with time constant $T_{1\rho}({}^1\text{H})$, is the relaxation of the proton magnetization during the CP sequence, and the other is the growth of the silicon magnetization, with the time constant T_{SiH} .

When the Hartmann–Hahn condition is fulfilled, the inverse of the cross-polarization time (T_{SiH}^{-1}) is proportional to the second moment of the dipolar coupling between the ^{29}Si and ${}^1\text{H}$ nuclei. Considering that the second moment of the heteronuclear dipolar coupling at a first approximation varies as the inverse sixth power of the proton silicon distance, the cross-polarization time (T_{SiH}) is proportional to the sixth power of the proton silicon distance.

The curves representing the fitting of the peak intensities from the variable contact-time experiments have been performed on pure silica and samples B and B_v . In Figure 7 the cross-polarization dynamics experiments of pure silica and sample B_v are reported (the experimental results for sample B are coincident with those of pure silica). The fitting was done according to the eq 1. The derived values of T_{SiH} and M_0 , together with the independently determined $T_{1\rho}({}^1\text{H})$ values, are reported in Table 1. The $T_{1\rho}({}^1\text{H})$ values were obtained by another experiment, monitoring the intensity of the proton magnetization through cross-polarization to ^{29}Si after a variable spin-lock period. For what concerns the pure silica, the T_{SiH} and $T_{1\rho}({}^1\text{H})$ values are of the

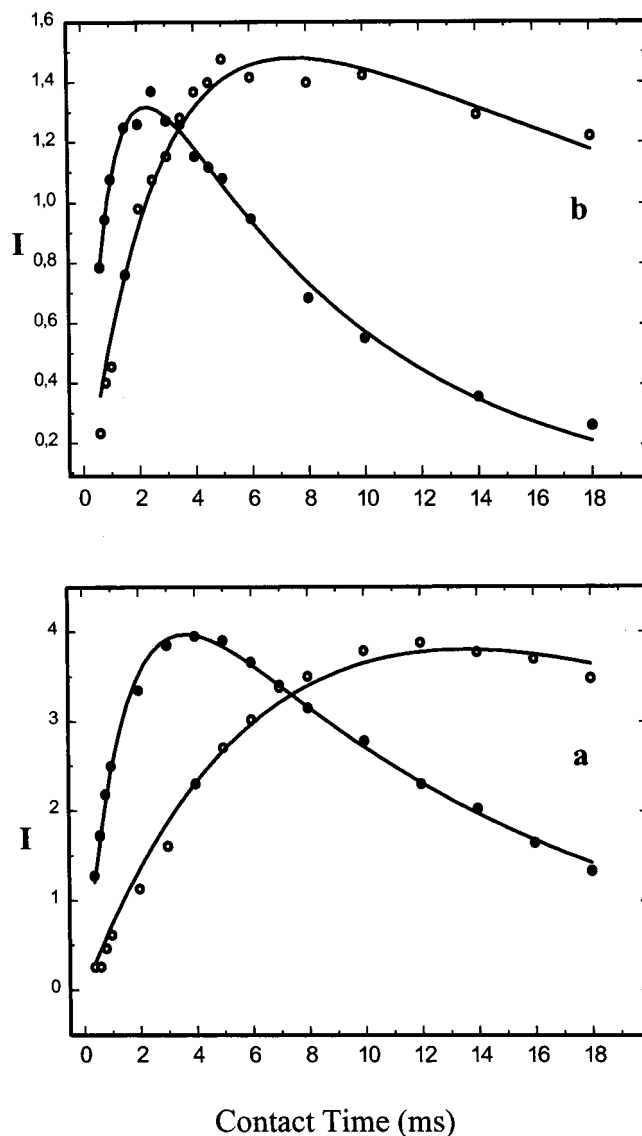


Figure 7. Variable contact time ^{29}Si CPMAS and nonlinear least-squares fitting for (a) VN3 silica and (b) PI/VN3 + TESPT vulcanized (sample B_v): Q^3 , filled dots; Q^4 , empty dots. The spectra were performed at room temperature. The results for PI/VN3 + TESPT before vulcanization (sample B) are coincident with those of VN3 silica within the experimental errors.

Table 1. ${}^1\text{H}$ – ^{29}Si Cross-Polarization Dynamics in Pure VN3 and in Vulcanized VN3/TESPT/PI Compound (sample B_v)

sample	peak	T_{SiH} (ms)	$T_{1\rho}({}^1\text{H})$ (ms)	magnetization (%)
VN3	Q^3	1.5 ± 0.1	26.7	46
	Q^4	8.0 ± 0.1	23.5	54
VN3/TESPT/PI (sample B_v , vulc)	Q^3	0.9 ± 0.1	2.0	51
	Q^4	2.3 ± 0.2	2.1	49

same order of magnitude as those reported by Maciel^{13,14} and Zumbulyadis.²⁰ In the sample B_v , a dramatic change in the cross-polarization dynamics is visible, the T_{SiH} of Q^4 in the compound is less than one-third the value of pure silica, and the Q^3 peak presents the same behavior, though less pronounced. The relaxation time $T_{1\rho}({}^1\text{H})$ in sample B_v is reduced with respect to that of pure silica and of the sample B. Thus, it is evident that after vulcanization the protons of the polymer interact

(27) Mehring, M. Principles of High-Resolution NMR in Solid. In *NMR Basic Principles and Progress*; Springer: Berlin, 1983; Vol.12.

(28) Veeman, W. S.; Mass, W. E. J. R. *NMR Basic Principles and Progress*; Springer: Berlin, 1994; Vol. 32, p 129.

with the surface of the silica grain via a spin diffusion process.

In addition, the relevant reduction of T_{SiH} in the cross-polarization dynamics study, for the Q^4 peak is a stringent demonstration of the proximity of the polymer protons within a few angstrom of the silica surface. In fact, as reported, T_{SiH} is proportional to the sixth power of the proton–silicon distance, thus a reduction to one-third of the initial value means that in the composite the average distance between Q^4 silicons and the closest protons, mainly due to PI, is at least 20% shorter than Q^4 silicons and protons in pure silica.

Conclusions

We believe the present approach to be of interest in the general field of reinforced rubber characterization by nuclear magnetic resonance. We first utilized this approach to investigate glassy polymers at room temperature in which spin propagation was fast^{2,3} and then went on to investigate rubbers. The main problem to be overcome was the inefficiency of spin propagation in rubbery polymers. The conditions of strong coupling among hydrogen nuclei, thus allowing spin diffusion, was found at 197 K. At this temperature we were able to demonstrate extended interaction and good dispersion of the particles in the polymer.

The present case applies NMR to a system composed by polyisoprene and finely dispersed silica, but we believe it can be extended to other soft polymers and to

a large variety of filler particles. The resonances of ^{13}C , ^{29}Si , and ^1H were exploited to identify the interacting surface from the points of view of both the polymer and the inorganic filler. The propagation of the magnetization in the hydrogen domain was demonstrated to be efficient at low temperatures and to cross the heterogeneous interfaces between the polymer and the filler.

Local information about the silica–polymer interface was obtained in detail (about 1–2 nm) by cross-polarization experiments in the silicon domain. Polymer protons can transfer the magnetization to the silicon-29 nuclei, showing the larger or reduced tightness of the adhesion of the polymer to the silica surface. As it was expected, the presence of a bidentate molecule (TESPT present at 3% concentration in the compound), reacting with the polymer by sulfur bridges and with the silica surface by condensation, increases the closeness of the hydrophobic polymer chains to the hydrophilic inorganic surface, thus demonstrating adhesion. The vulcanization procedure enhances magnetization transfer also due to the increased rigidity of the polymer at the interface. It is worthwhile noting that the silicons of TESPT and the degree of condensation can be detected separately from the silica surface silicons.

Acknowledgment. We want to thank Dr. G. Giuliani for sustaining the research project and the CNR PF MSTA II for financial support.

CM9807539