

Application of NMR Spectroscopy to the Characterization of Elastomer/Filler Interactions

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SYNOPSIS

Proton spin-spin relaxation time measurements have been performed at 300 and 400 MHz on bound rubber-filler mixes resulting from the solvent extraction of silica-filled and silica-filled-modified polybutadiene, on the one hand, and of carbon black-filled and carbon black-filled-modified styrene butadiene rubber, on the other hand. Two relaxation times are observed for all samples. They are ascribed to the occurrence of tightly and loosely bound rubber components, respectively. The effect of the grafting modification of the fillers on the formation of bound rubber and its two components is discussed. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

In most of their industrial applications, elastomers are used as composite materials. They are indeed often filled with various finely divided solids such as carbon blacks or silicas, the incorporation of which in the matrix is associated with an improvement of the properties of the corresponding polymers (e.g., improved abrasion and tear resistance, and tensile strength). This process is termed reinforcement. Among the various mechanisms that have been identified for participating in reinforcement (modification of the conformation of macromolecular chains, breaking up of the so-called secondary structure of the filler, alignment of the chains and filler aggregates upon straining of the sample, etc.¹), those implying the absorption or the dissipation of mechanical energy have a prominent place.

In this connection, a qualitative illustration for interpreting modulus change of an elastomer upon filler blending was proposed some 30 years ago by Payne²: A hydrodynamic or strain amplification effect and the structure of the filler or the existence of interaction, particularly of the filler/elastomer type, all play a part in this modulus increase. If these

interactions take place primarily at the rubber/filler interface, they are, nevertheless, felt in a certain volume of matrix surrounding the filler particles, the so-called interphase. In this volume, which is associated with the formation of bound rubber, one can expect the mobility of the elastomeric chains to be strongly hindered by the presence of the solid surface.^{3,4} Moreover, since the ability of a filler to interact with polymeric chains depends on its surface reactivity, any modification of the chemistry of the surface should be followed by an evolution of the mobility of the chains in the interphase. In this respect, solid-state NMR appears to be a tool of choice for its characterization and thus can provide a way of gaining further insight in the understanding of rubber/filler interactions.

For this purpose, high-resolution solid-state NMR was used for the characterization of reinforced elastomers, and, particularly, of the rubber/filler interphase, by study of bound rubber (quantification, examination of polymer/filler interactions, molecular dynamics, etc.) using either ¹³C-NMR (magic-angle spinning or cross-polarization and decoupling) or ¹H-NMR (*T*₂ relaxation times). These techniques were applied to polybutadiene/silica or to SBR/carbon black samples. The effect on the interphase of a surface modification of the filler by grafting of well-characterized alkyl chains was checked.

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EXPERIMENTAL

Materials

Two silicas and one carbon black were used:

- A fumed silica, Aerosil 200 = A (Degussa; $A_S = 200 \text{ m}^2/\text{g}$, as provided by the supplier).
- A precipitated silica, Zeosil 175 MP = P (Rhône-Poulenc; $A_S = 175 \text{ m}^2/\text{g}$, as provided by the supplier).
- A reinforcing thermal carbon black, Corax N110 = N (Degussa; $A_S = 143 \text{ m}^2/\text{g}$, as provided by the supplier).

To selectively modify the solids, we took advantage of the reactivity of their surface functional groups, either silanols in the case of silicas or carboxylic acids in the case of carbon black. Esterifications were thus performed with two alcohols: methanol (C_1) and hexadecanol (C_{16}) (Prolabo, reagent grade).

Two elastomers were blended with the fillers:

- 1,4-Polybutadiene = BR ($M_n = 10^5 \text{ g mol}^{-1}$, 1–2 links < 2%).
- Styrene butadiene copolymer = SBR (SBR 1500, Büna Hüls; styrene = 23.5%, $ML_{4,100} = 48$).

Preparation of the Modified Fillers

Esterification with Methanol

In a typical experiment, 20 g of *silica or carbon black*, dried for 24 h at 110°C, was dispersed into a large excess of methanol (100 mL) in a 2 L autoclave. After heating at 200°C for 2 h, the reaction medium was rapidly cooled down and the silica separated by centrifugation. After drying under vacuum, first at room temperature, then at 150°C for 6 h, the samples (identified as AC_1 and PC_1 , respectively) were characterized by elemental analysis to determine their grafting ratios.

Esterification with Hexadecanol

In a typical experiment, 30 g of filler, previously dried for 24 h at 110°C, were added to 300 g of hexadecanol in a 2 L round-bottom flask equipped with a stirrer, a thermometer, and a condenser. The reaction mixture was heated at 200°C for 2 h while stirring. After reaction, the silica was separated from the excess alcohol either through a prolonged extraction (24 h) with chloroform or by dilution of the reaction

medium with chloroform followed by centrifugation and a series of four washings with a toluene/chloroform mixture (3/2 v/v). Before any analysis, the samples (identified as AC_{16} , PC_{16} , and NC_{16} , respectively) were dried under vacuum at 130°C.

Characterization and Properties of Modified Fillers

Modified fillers were characterized by determination of their esterification ratios. For this purpose, elemental analysis, gravimetry (pyrolysis), and radiochemistry were used. In the case of carbon black, the results were also controlled by titration (potentiometry) of the remaining surface functional groups. The surface properties of the solids were assessed previously from the determination of their surface free energy (dispersive and specific components) as measured by inverse gas solid chromatography.^{5,6}

Filler/Rubber Systems: Preparation of the Samples

Nonmodified and modified fillers were blended with the elastomers according to a method previously described.⁷ In a typical compounding procedure, a dispersion of filler (previously dried for 24 h at 110°C) into 200 mL benzene was added to a 200 mL rubber/benzene solution of known concentration (2 wt %). After gently stirring the resulting mixture for 24 h, the solvent was evaporated on a rotary evaporator under reduced pressure and the filled elastomers were dried at 80°C under vacuum for 24 h. The filler content of each sample was 100 phr. The resulting elastomer/filler blends were identified as ABR, AC_1BR , $AC_{16}BR$, PBR, PC_1BR , $PC_{16}BR$, NSBR, and $NC_{16}SBR$. Bound rubber samples resulted from a prolonged benzene extraction of the composites at room temperature. It was thus possible to get rid of the elastomer that was not irreversibly adsorbed on the surface of the solid. After drying under vacuum

Table I Grafting Ratios of the Modified Fillers

Samples	Grafting Ratios (Chain/nm ²)
AC_1	2.92 ± 0.40
AC_{16}	1.43 ± 0.03
PC_1	8.69 ± 0.09
PC_{16}	2.33 ± 0.02
NC_1	0.52 ± 0.01
NC_{16}	0.83 ± 0.01

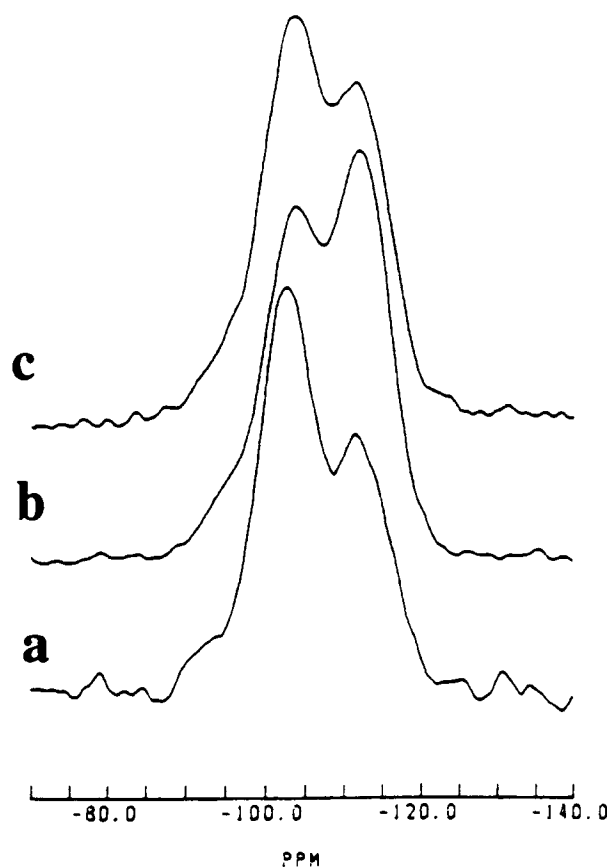


Figure 2 ^{29}Si MAS/CP spectra of initial and modified silica/elastomer blend: a-PBR, b-PC₁BR, c-PC₁₆BR. The peak at -100 ppm is related to single silanol and that at -110 ppm to siloxane.

for 48 h, the samples were submitted to elemental analysis or were pyrolysed (gravimetry) for determination of the amounts of bound rubber. The resulting samples were identified as ABRE, AC₁BRE, AC₁₆BRE, PBRE, PC₁BRE, PC₁₆BRE, NSBRE, and NC₁₆SBRE.

NMR Measurements

The ^{13}C -NMR spectra were taken on an NMR spectrometer from Bruker (Karlsruhe, Germany; Model CXP100) operating at 25.14 MHz in a magnetic field of 2.3 T. The spectrometer was equipped with a double-bearing probe head allowing rotation of the sample at the magic angle ($54^\circ 44'$) at a spinning rate of 4 kHz and irradiation at both the proton and the rare nuclei. Measurements can be made with (MAS/CP) and without (MAS) cross-polarization. The ^1H spectra were taken on Bruker CXP300 and MSL400 spectrometers operating at 300 and 400 MHz, in magnetic fields of 7 and 9.33 T, respectively. Specially designed probe heads, without a proton probe signal, were used (type HP WB73A Sol 5 mm

^1H VIN Bruker). One pulse sequence ($t_{\pi/2} \approx 1.1 \mu\text{s}$, repetition rate 5 s) followed by a Fourier transform gave the absorption spectrum. Depending on the temperature range, spectra evince a broad line and a resolved or unresolved two peak massif. The latter is attributed to the methyl and methylene groups, respectively. This observation is possible because of the high-frequency measurement utilized. The proton spin-spin relaxation times (T_2) and the fraction of each component were determined by decomposition of the absorption spectrum. T_2 were calculated by taking into account the type of the best decomposition (Lorentzian or Gaussian).

RESULTS AND DISCUSSION

The modification of silicas or carbon black resulted from the reaction of their surface functional groups (either silanol or carboxylic acids) with alcohols according to methods previously devised.^{8,9} The highest degrees of modification attained are reported in Table I.

The consequences of the alkoxylation reactions performed on the surface reactivity of the fillers and on their elastomer-reinforcing ability were assessed previously⁸⁻¹⁰ by determination of the surface free energy of the solids and by examination of the rheological properties of filler suspensions in liquid hydrocarbons, such as squalene, used as a model of natural rubber. It appeared that the surface grafting is associated with a decrease of the ability of the fillers to exchange strong interactions with the surrounding medium. It was indeed shown that C₁₆-modified carbon black, or silica as well, have very

Table II Silica/Elastomer Samples—Elastomer Content

Samples	Monomer Unit ($\text{nm}^{-2} \pm 0.1$)
ABR	15.0
AC ₁ BR	27.6
AC ₁₆ BR	34.0
PBR	26.5
PC ₁ BR	24.4
PC ₁₆ BR	28.6
ABRE	3.4
AC ₁ BRE	4.9
AC ₁₆ BRE	4.1
PBRE	3.5
PC ₁ BRE	5.1
PC ₁₆ BRE	3.3

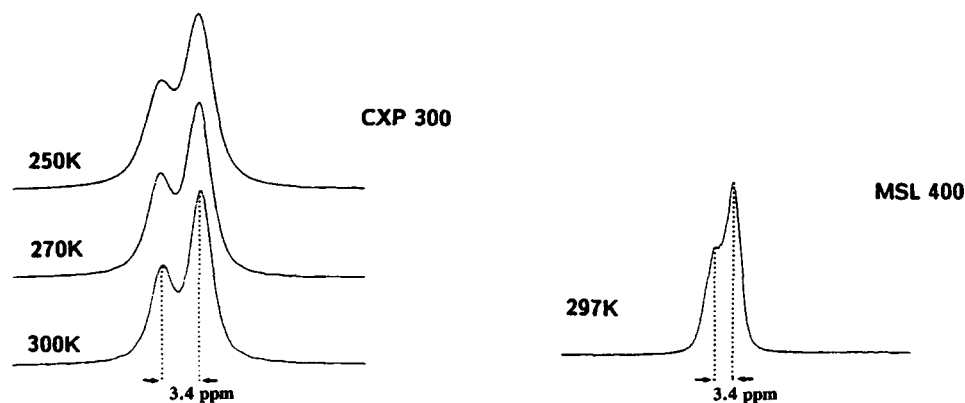


Figure 3 ^1H NMR spectra at 400 MHz and 300 MHz of polybutadiene. Resolution is better at lower frequency.

low surface free energies. Moreover, it appeared that the modifications were associated, on the one hand, with an improvement of the dispersibility of the modified fillers in hydrocarbon media and, on the other hand, with a decrease of the degree of agglomeration of the corresponding solids, their so called structure that is known to play an important role in reinforcement processes. In this respect, study of the dynamic mechanical properties of carbon black-reinforced SBR showed that the structure of the polymer/filler interphase was dependent on the surface treatment of the filler, C_{16} -modified carbon black being indeed associated with the attainment of high mobilities for the elastomeric chains participating in the interphase. Such a behavior was related to the decrease of polymer/filler interactions upon deactivation of the solid surface.⁹ To gain further information on the structure of this interphase, it was examined by solid-state NMR spectrometry.

Initial and modified silica/elastomer blends were analyzed using ^{13}C -MAS/CP NMR. Spectra of modified silicas show the presence of alkoxy chains (Fig. 1). Two peaks at 27.7 and 129.6 ppm were attributed to the $-\text{CH}_2-$ and $-\text{HC}=\text{CH}-$ of the polybutadiene rubber, respectively. The peak at 50 ppm was attributed to $\text{CH}_3-\text{O}-$.¹¹ For C_{16} -modified silicas, a distribution of the frequencies of resonance of the methylene groups along the chain¹² was observed.

Influence of the alkoxy chain grafting on silica was observed using ^{29}Si -MAS/CP. Three peaks at -90 , -100 , and -110 ppm were attributed, respectively, to geminal, single silanols, and siloxane groups.¹³ After reaction of silanols with alkoxy chains, they are similar to the siloxanes, from an NMR point of view. As a result, it can be observed in Figure 2 that the intensity of the peak of the single silanols decreases proportionally to the amount that has reacted.

Filler/Rubber Composite-Evolution of Bound Rubber with Surface Treatment of the Filler

Initial and modified fillers were blended (100 phr) with elastomers (either BR with silicas or SBR with carbon blacks). In Tables II and III are reported the amounts of polymer in each sample, expressed in equivalent monomer unit per unit surface area of the silica filler, as assessed from carbon content determined by elemental analysis or expressed as the fraction of rubber incorporated in the blend and unextractable by solvent. When an uncured filler/

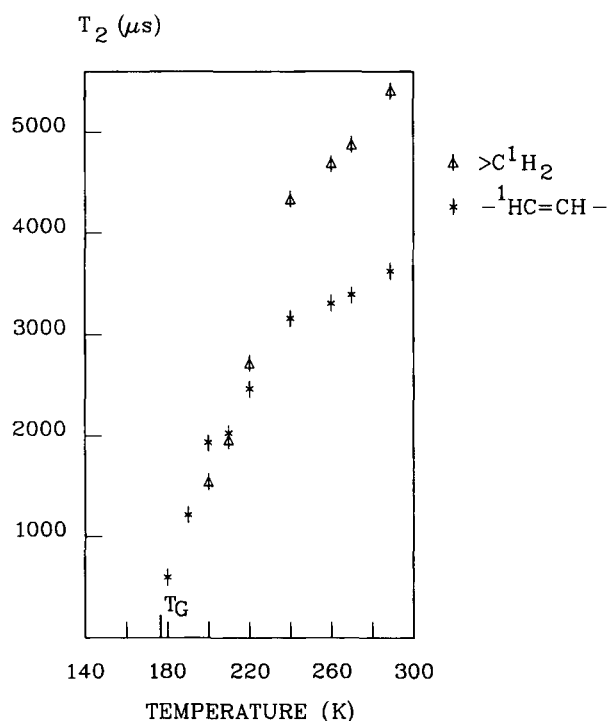


Figure 4 Temperature dependence of ^1H spin-spin relaxation times for polybutadiene at 400 MHz (duty cycle: 5 s, $t_{\tau/2} = 1.1 \mu\text{s}$, sweep width 125 kHz).

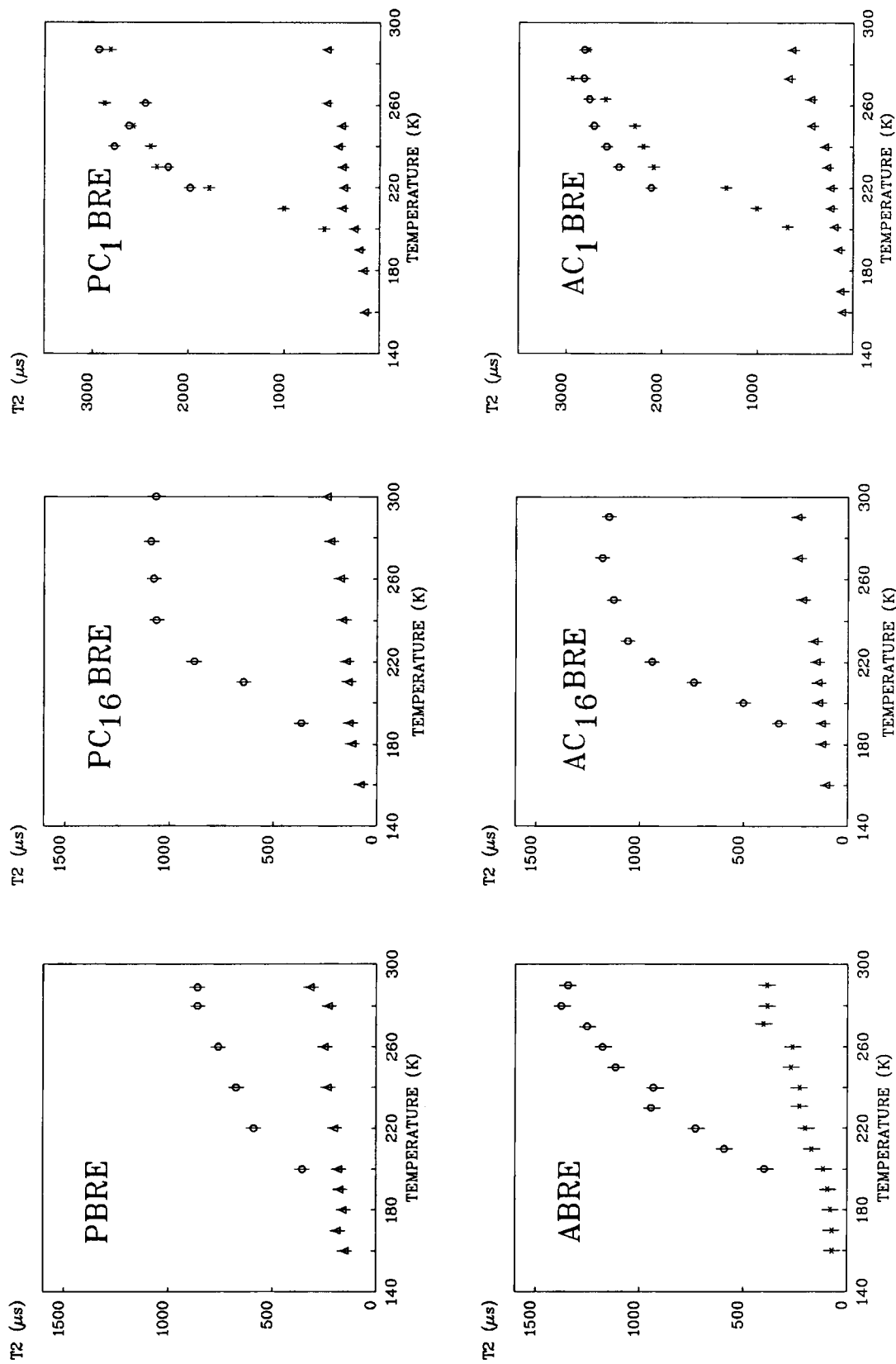


Figure 5 Temperature dependence of ^1H spin-spin relaxation times for bound rubber in silica-filled and silica-modified-filled PBRE, PC₁₆BRE, AC₁₆BRE measured at 400 MHz, ABRE, AC₁BRE, PC₁BRE measured at 300 MHz. Note that for AC₁BRE and PC₁BRE it is possible to decompose the line into its two components and to calculate two spin-spin relaxation times.

elastomer blend is submitted to solvent extraction for an extended period of time, only part of the polymer can be recovered, even with a very good solvent for the rubber. This quantity of unextractable elastomer adhering to the filler is known as bound rubber. Its evaluation can allow an estimation of the interactions the elastomer is able to exchange with the filler. In Table II we report the amount of bound rubber corresponding to the different samples. It appears that solvent extraction is associated with an important decrease of the amount of rubber in each sample. One notes, however, that only small differences are observed between unmodified and esterified fillers, particularly with samples A containing silica, which after alkoxylation yield slightly higher bound rubber values. This observation was not interpreted but could be in relation with the aging of polybutadiene during the prolonged extraction of the samples, a process associated with the cross-linking of the elastomer, which thus would become unextractable. The samples have been analyzed by NMR spectrometry to control the results yielded by the measurement of bound rubber.

Temperature Dependence of Spin-Spin Relaxation Time of Bound Rubber

Silica-Polybutadiene

Figure 3 shows the spectra of polybutadiene observed at different temperatures and frequencies. The separation between the methyl and methylene groups is clearly noted. Nevertheless, the resolution decreases at 400 MHz, which was not observed at lower frequency. Figure 4 points out the temperature dependence of spin-spin relaxation time (T_2). At low temperature, the T_2 for both methyl and methylene groups are short enough to prevent their separation. Above 220 K, this is possible and distinct values can be assigned. The origin of this difference, also observed in other polymers like polystyrene,¹⁴ is attributed to different micro-Brownian motion of the chemical groups inside of the polymer backbone.

Figure 5 presents the temperature dependence of the spin-spin relaxation time of the bound rubber, in silica-filled and silica-filled-modified polybutadiene rubber. At low temperature, the T_2 of all the samples are equal to about 50 μ s and remain almost constant up to the glass transition temperature of the elastomer (≈ 177 K, as measured by DCS). Above this temperature, the spectra clearly show two phases, as observed by Ito et al.¹⁵ These authors have attributed the difference of mobility to tightly (short T_2) and loosely (long T_2) bound rubber phases. Moreover, they have shown that the relax-

ation times increased with decreasing silanol group concentration on the silica surface.

This effect can be easily observed for the loosely bound rubber. Indeed, the spin-spin relaxation times are ordered as follows for the precipitated silica samples:

$$\text{PBRE} < \text{PC}_{16}\text{BRE} < \text{PC}_1\text{BRE} < \text{BR}$$

and for the fumed silica composites:

$$\text{ABRE} \approx \text{AC}_{16}\text{BRE} < \text{AC}_1\text{BRE} < \text{BR}$$

These behaviors thus appear to be independent of the nature of the silica. As mentioned above for BR, measurements done at 400 MHz give smaller spin-spin relaxation time values than those performed at 300 MHz (Fig. 6).

For the tightly bound rubber fraction in the composite (Fig. 7), another phenomenon appears to be significant. The spin-spin relaxation times decrease as follows:

$$\text{PC}_1\text{BRE} > \text{PBRE} \approx \text{PC}_{16}\text{BRE}$$

and

$$\text{AC}_1\text{BRE} > \text{ABRE} \approx \text{AC}_{16}\text{BRE}$$

These results can be interpreted in terms of active sites on the silica surface that are shielded by the grafted layer. As mentioned in Table I, the number of grafted methyl groups is much higher than that of hexadecyl chains. Consequently, the shielding is

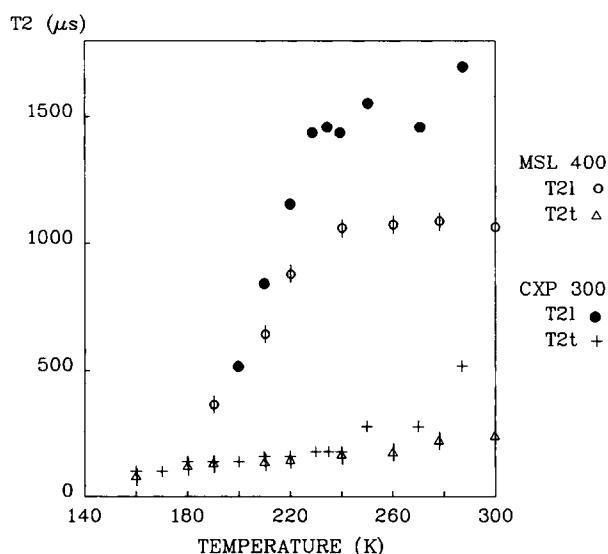


Figure 6 Temperature dependence of ^1H spin-spin relaxation times for bound rubber in a PC_{16}BRE , at 400 MHz (ϕ Δ) and 300 MHz (\bullet $+$).

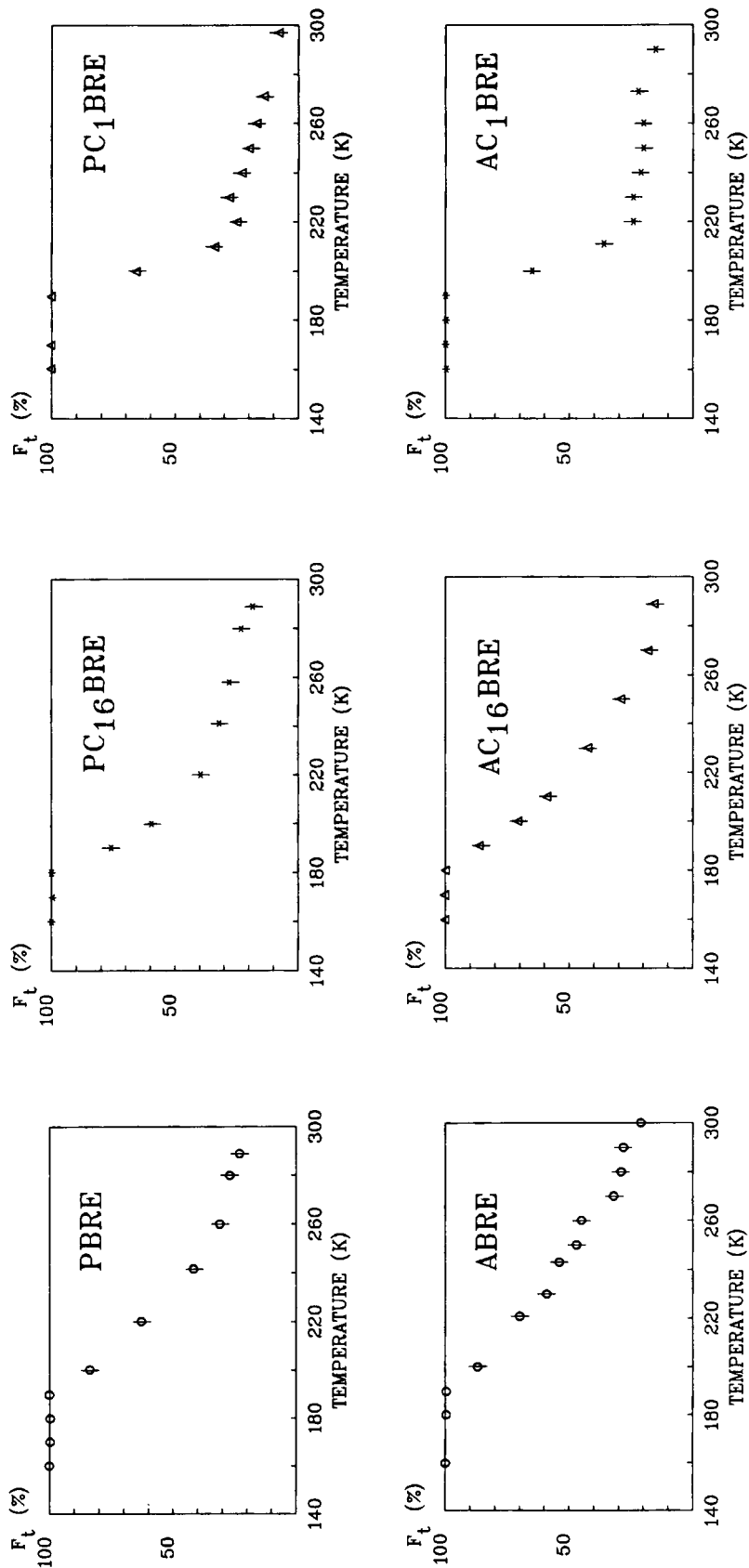


Figure 7 Tightly bound rubber fraction as a function of the temperature. PBRE, PC₁₆BRE, AC₁₆BRE measured at 400 MHz; ABRE, AC₁BRE, PC₁BRE, measured at 300 MHz.

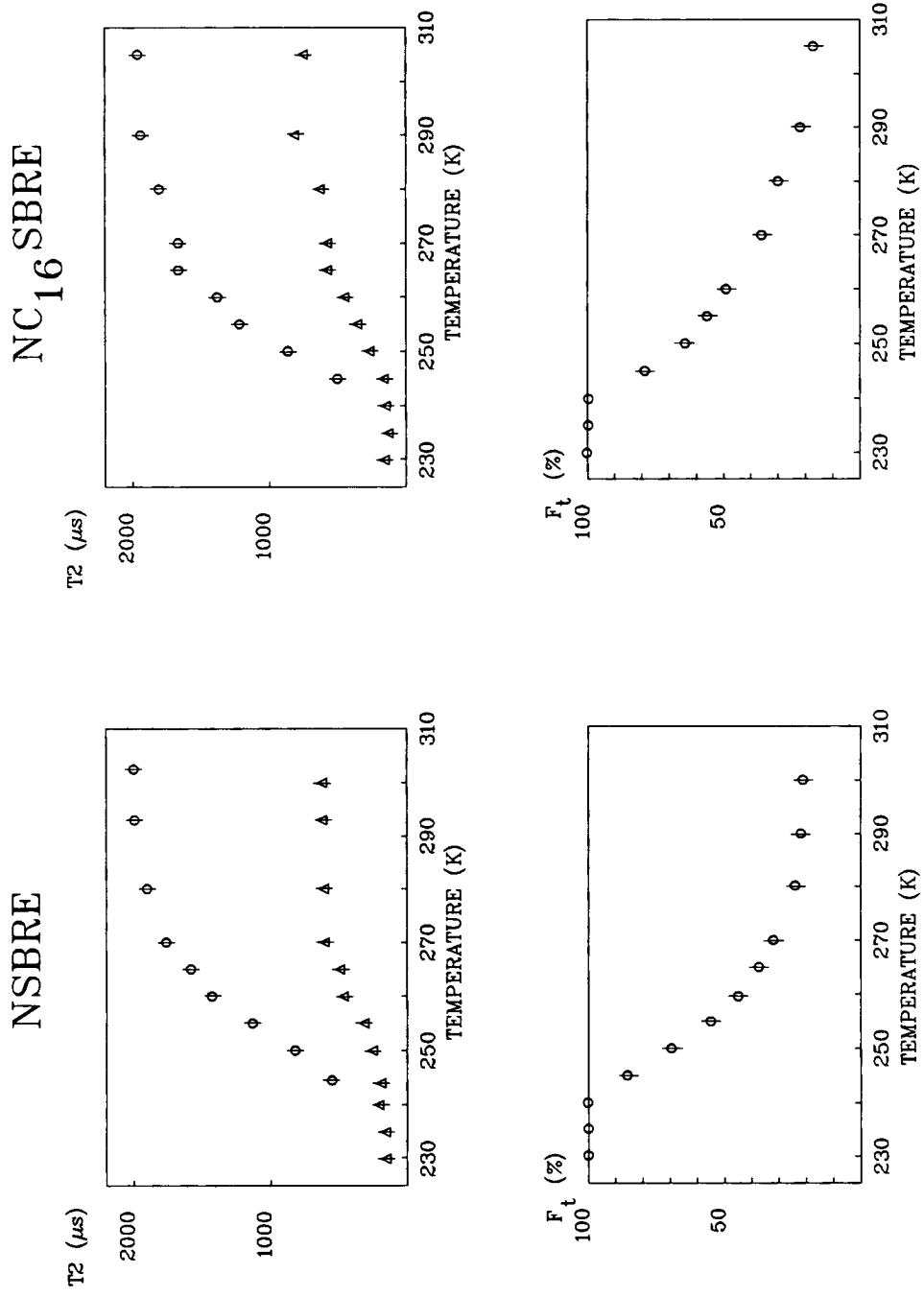


Figure 8 Temperature dependence of ¹H spin-spin relaxation times at 300 MHz and tightly bound rubber fraction for styrene butadiene rubber.

more efficient for the former than for the latter. Elastomer/filler interactions can be controlled by the type of molecule that is retained to selectively modify the silica surface and particularly by its ability to react with the surface silanols.

Carbon Black–Styrene Butadiene Rubber

Consequences of the surface modification of carbon black on the elastomer/filler interphase were analyzed using $^1\text{H-NMR}$ spectroscopy. $^{13}\text{C-MAS/CP}$ could not be used to provide information on the corresponding composites due to the conductivity of the carbon black that detunes the probe head. Such a process is, however, not observed when the concentration in the polymer is high enough.¹⁶

Temperature dependence of the spin–spin relaxation times for styrene butadiene rubber and the tightly bound rubber fraction are shown on Figure 8. Contrarily to the silica-filled samples, carbon black composites are less sensitive to the shielding effect resulting from the grafting modification. Such a result can be in relation with the much more complex surface chemistry of carbon blacks and with the distribution of their surface active groups as well.

CONCLUSION

Incorporation of fillers (silica, carbon black) in elastomers (BR, SBR) is associated with the formation of bound rubber, which results from interactions taking place between the surface of the solid and the polymer. These interactions are expected to be dependent on the surface reactivity of the solid and thus should affect the mobility of the polymer chains in the vicinity of the solid particles. Solid-state NMR spectroscopy appears in this respect to be well suited for monitoring the polymer/filler interphase and to follow its evolution vs. solid surface reactivity. It was thus shown, in agreement with previous works, that bound rubber has two components: a tightly and a loosely held phase. The modification of the filler surface reactivity by grafting of alkyl chains (methyl, hexadecyl) is associated with a change in the distribution of the two bound rubber components, which is particularly evidenced in the silica polybutadiene composites. In such a case, the influence of the grafting reaction can be

understood in terms of efficiency, i.e., number of surface active sites still available after modification. The smaller this number, the smaller is the tightly held bound rubber component. Carbon black/SBR composites appear to be less sensitive to the effect of the surface deactivation.

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