High resolution solid-state n.m.r. investigation of the filler–rubber interaction: 1. High speed ^1H magic-angle spinning n.m.r. spectroscopy in carbon black filled styrene–butadiene rubber

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This present work, dealing with filler/rubber interactions, provides a new approach for investigating the behaviour of elastomeric chains (styrene–butadiene rubber, SBR) in the close vicinity of carbon black surfaces. Pulsed nuclear magnetic resonance measurements have been carried out on pure SBR, and on carbon gels obtained by solvent extraction of the carbon black filled elastomers. The initial concentration of carbon black in the filler/rubber mixtures was varied between 20 and 100 parts per hundred parts by weight (phr). The high resolution proton spin-spin relaxation time, T_2, has been measured for each of the individual resonance species belonging to the SBR chain. High resolution was achieved by rapidly spinning the sample at the magic angle. It has been observed that a very high magic-angle spinning (MAS) rate (>18 kHz) is necessary to achieve a fully resolved spectrum of SBR. However, at a spinning rate of ~ 15 kHz it is possible to avoid all of the spinning side bands and to deconvolute, unambiguously, the different resonance peaks that are present in the spectrum. In the unfilled elastomer, at temperatures much higher than the T_g, the chain segmental motions are anisotropic and deviate from true liquid-like behaviour. The adsorbed rubber chains are found to consist of loosely and tightly immobilized segments. The relative immobilization of the different protons has evidenced the methine ^1H to be much more immobilized than the aromatic or methylene species. Therefore, the olefinic part of the butadiene segment of the elastomeric chain appears to be the most affected by the carbon black surface. Moreover, T_2 is found to be independent of the filler concentration in the 30–80 phr range, and the relative concentration of the tightly bound rubber in the composite shows a maximum at a filler content of ~ 50 phr, where maximum reinforcement is normally observed. As far as the molecular dynamics is concerned, highly filled systems (>80 phr carbon black) behave differently from low and medium filled systems (<80 phr).

(Keywords: styrene–butadiene rubber; solid-state ^1H n.m.r.; filler/rubber interactions)

INTRODUCTION

The incorporation of active fillers, such as carbon black or silica, in an elastomer leads to marked improvements in the physical, mechanical and electrical properties of the elastomeric material. Therefore, the filler/rubber interaction and its effect on reinforcement are problems of remarkable scientific, technological and commercial importance. Numerous investigations have been carried out, and several reviews[1–10] and books[11,12] have surveyed and analysed the available information on the reinforcement of rubbers, particularly in the case where carbon black is used as a filler. A great deal of research effort has been dedicated to understanding the exact nature of the interactions between the filler particles and the host polymer, involving several types of experimental techniques which include dynamic mechanical[13–16], thermal expansion[17,18], sorption[19,20], sonic velocity[21], secondary ion mass spectroscopy (SIMS) analysis[22], and chromatographic measurements[23,24], etc. However, up to now interpretation of the exact nature of the filler/rubber interactions remains a vexing question.

In this respect, pulsed nuclear magnetic resonance (n.m.r.) spectroscopic techniques have also been used. Indeed, n.m.r. spectroscopy can provide direct physical evidence which is relevant to the multicomponent phase model, the extent of the layer thickness and the degree of immobilization of the rubber chains. Linewidth measurements[25–27] and the nearly equivalent T_2 measure-

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ments[28–42] are, by far, the most sensitive n.m.r. parameters for filler/rubber interactions. However, up until now, only low field and low resolution n.m.r. have been applied in such investigations, and a knowledge of the chemical shifts or site-specific information is still lacking in this area. Thus, it is reasonable to expect that the achievement of high resolution by solid-state n.m.r. techniques and relaxation studies for each chemically shifted species will contribute to a further in depth understanding of the polymer/filler interactions.

In this present investigation, the motional heterogeneity of carbon black filled styrene–butadiene rubber (SBR) materials has been examined by a proton pulsed n.m.r. technique. The spin-spin relaxation times, T_2s, have been determined for each individual proton resonance species from the Fourier-transformed free induction decay (FID) spectra. This work is aimed at gaining further integrated in depth information on the more detailed aspects of the rubber/carbon black interactions.

EXPERIMENTAL

Materials

The elastomer involved in this study, which was used without further purification, was a commercially available styrene–butadiene rubber, SBR 1500, where the chains contain random sequences of the two monomers. Its main characteristics are as follows: molecular weight $= 140\,000\ \mathrm{g\,mol^{-1}}$; Mooney viscosity, $M_{L1+4}(100°C) = 52$; styrene/butadiene molar ratio (as determined from liquid-state ^{13}C n.m.r. spectra) = 11/89; polybutadiene moiety microstructure (calculated from liquid-state ^{13}C n.m.r. spectra), 1,4 *trans* = 77%, 1,4 *cis* = 11.5%, and 1,2 vinyl units = 11.5%.

The carbon black used as the filler was a SAF grade (Corax N110, Degussa), with an elementary particle diameter and specific surface area, respectively, of 19 nm and $145\ \mathrm{m^2\,g^{-1}}$. Its elemental analysis yielded: C = 97.76, H = 0.46, O = 0.47, S = 0.41 and N = 0.26%. The pH of an aqueous slurry was 8.1.

Sample preparation technique

The carbon black and rubber were mixed in a Brabender Plasticorder (PLE-651), at an average temperature of 80°C, at $30\ \mathrm{rev\,min^{-1}}$ for 20 min. The carbon black loading was varied from 20 to 100 phr (*Table 1*).

To ease the analysis of the spectra and focus our interest on the elastomeric chains that are specifically interacting with the filler surface, the samples were extracted with a good solvent for the polymer, which allowed the determination of the so-called bound rubber. In a typical experiment, the SBR/carbon black composite was first cut into small pieces and 2 g of the material were loosely packed in a wire mesh case (mesh size = 200). The case was immersed in a sufficiently large amount of toluene and leaching was then carried out at room temperature for 7 days. From time to time, the solvent was changed with fresh toluene. When the leaching was complete, the carbon gel was suspended in acetone, in order to exchange the toluene with the more volatile solvent, filtered, and dried first at room temperature in air for 24 h, and then under vacuum for a further 7 days. The amount of polymer left adsorbed on the carbon black surface (bound rubber) was determined by pyrolysis. These data are reported in *Table 1*.

Table 1 Bound rubber measurement data obtained as a function of carbon black loading

Sample	Loading (phr)	m_c[a]	Φ[b]	Φ'[c]	R_B[d] (%)
P_0	0	–	–	–	–
P_{20}	20	0.166	0.09	0.59	6.65
P_{30}	30	0.230	0.13	0.52	14.15
P_{40}	40	0.285	0.17	0.49	24.00
P_{50}	50	0.333	0.20	0.49	27.20
P_{60}	60	0.375	0.23	0.49	31.40
P_{70}	70	0.411	0.26	0.52	32.75
P_{80}	80	0.444	0.29	0.47	45.20
P_{90}	90	0.473	0.31	0.47	52.70
P_{100}	100	0.500	0.34	0.49	51.50

[a] Mass fraction of carbon black in composite
[b] Volume fraction of carbon black in composite
[c] Volume fraction of carbon black in carbon gel
[d] Amount of bound rubber in composite

N.m.r. methods

^{1}H n.m.r. measurements were performed using a Bruker MSL 300 NMR spectrometer, operating at 300 MHz. The sample was placed in a fused zirconia rotor (4 mm in diameter) which was fitted with a Kel-F cap, and then spun at the magic angle, with rates varying from 0 to 18 kHz. The spin-spin relaxation, characterized by the relaxation time T_2, was determined for both the unfilled SBR and the solvent-extracted carbon gels. The radiofrequency (RF) pulse sequences used in these experiments were, respectively, acquisition of free induction decay (FID) after a 90° pulse, and spin-echo following a $90°–\tau–180°$ sequence[43].

From the complex FID time signal, $F(t)$, information about each resonance species was extracted through Fourier transformation (frequency spectrum $F(\omega)$) of the acquired FID. The spin-echo experiment for each sample was repeated with different delay times. The lineshape change with the total evolution period, t_d, inherently contains molecular information of the sample being studied. The evolution of the intensity, or the area under the peak, of each signal as a function of time allowed determination of the transverse relaxation time, or rate. The composite peaks were deconvoluted by using 'Linesim', a Bruker-supplied Pascal program for simulating n.m.r. lineshapes in solids. An Aspect 3000 computer was used to run both the lineshape simulation and curve fitting programs.

RESULTS AND DISCUSSION

Effect of magic-angle spinning rate on high resolution

Figure 1 shows the Fourier transformed proton n.m.r. spectra of pure SBR, obtained at different spinning rates. Free induction decays were acquired after a 90° pulse of $4\ \mu$s (dead time $= 15\ \mu$s, pulse repetition time = 8 s). The top spectrum of *Figure 1* illustrates that in the absence of spinning, the linewidth is relatively broad (2.5 kHz), although the outline of several peaks can be perceived. The principal static anisotropic interactions that broaden the n.m.r. spectrum of protons in a polymer are the result of both spin dipolar interactions (major portions of these interactions occur among the protons themselves) and chemical shift anisotropy (c.s.a.). Magic-angle spinning (MAS) can remove any kind of solid-state interactions that display a $(3\cos^2\theta - 1)$ dependence[44–48], where θ is

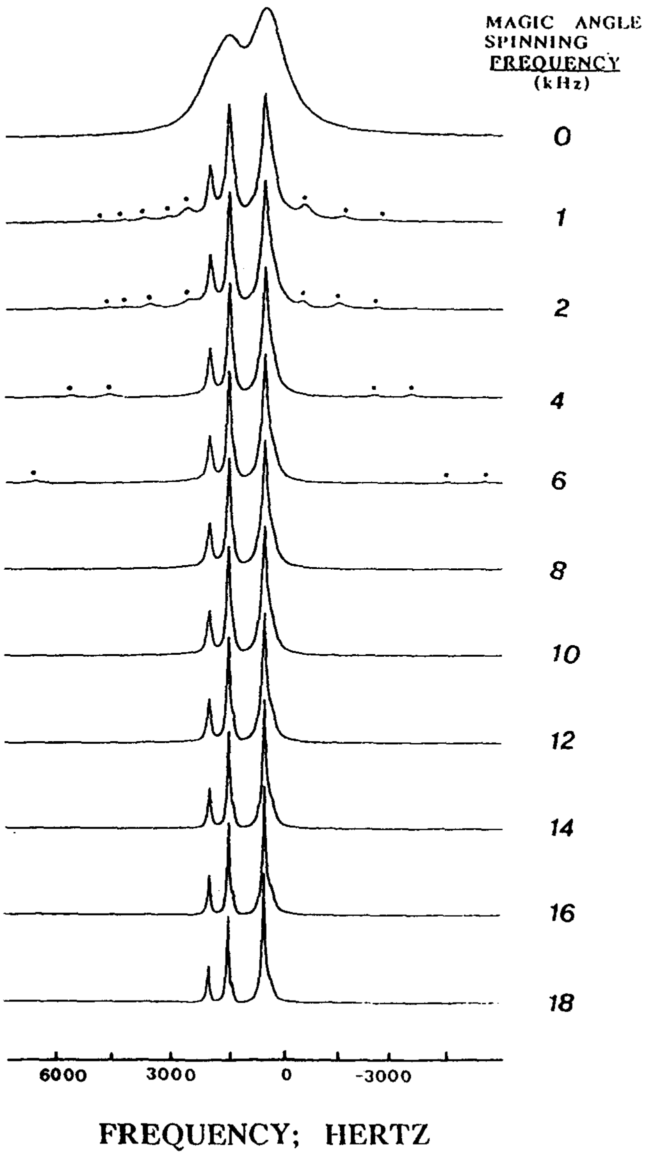


Figure 1 Effect of spinning frequency on resolution in the proton n.m.r. spectra of pure SBR: FID was obtained by a 90° pulse and acquisition technique; ● represents side bands

the angle that the internuclear vector makes with the external magnetic field. In addition to spin dipolar interactions and c.s.a., MAS can also remove or reduce other broadening effects, such as those resulting from bulk magnetic susceptibility variations, which is an important factor for filled elastomers[49,50]. However, the spinning rate required to reduce or remove these broadening effects are different for homogeneous and inhomogeneous interactions[51].

The 1 kHz spectrum of *Figure 1* depicts that, when spinning the sample at such a low rate, the inhomogeneous resonance results in a spectrum that has central bands flanked by a series of sidebands. With a progressive increase in the spinning rate, the sideband intensities decrease and depart from the central band, leaving the narrow separated major peaks. Nevertheless, even at 18 kHz, all of the possible proton peaks are not well separated. However, at 15 kHz (a steady sample spinning rate which is routinely possible with the probe) the spectrum allows a complete, unambiguous deconvolution of all of the types of proton resonance species by computer simulation. This is true not only for the unfilled SBR, but also for the carbon gel samples. It was very useful to be able to use computer generated peaks to fit the experimentally obtained spectra as a way of clearly observing the possible components which contribute to the composite spectrum. *Figure 2* shows a typical experimental spectrum, simulated individual peaks and the composite spectrum for gum SBR, at a MAS frequency of 18 kHz. The experimental spectrum can be fitted well with six different components, namely a single peak associated with aromatic protons, two lines relating to the protons carried by unsaturated carbons, and three bands relating to those carried by the saturated carbons. The proton chemical shift information and the assignment of the different components are given in *Table 2*. However, throughout this work we will consider only the major bands, a, b and e, at 7.057, 5.335 and 1.960 ppm, associated with the aromatic, methine and methylene protons, respectively. Tetramethylsilane (TMS) was used as an external reference for the primary standard, with H_2O being used as a secondary standard[52]. The variation of the linewidth, $\nu_{1/2}$ (full width at the peak half-height), of the three kinds of protons as a function of the frequency, Ω, of the sample rotation at the magic angle, is shown in *Figure 3* for pure SBR. In agreement with the evolution evidenced in *Figure 1*, $\nu_{1/2}$ appears to decrease very rapidly with Ω for each of the species, up to a spinning rate of 2 kHz. Above this value, the decrease is slow and asymptotic in nature. Therefore, it was assumed that a spinning frequency of 15 kHz would allow us to obtain spectral lines which were sharp enough for an accurate analysis.

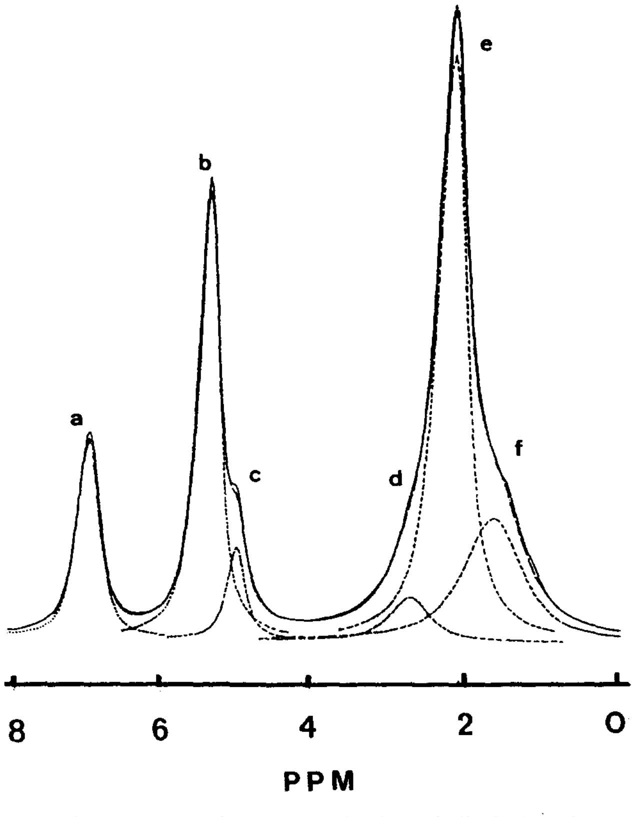
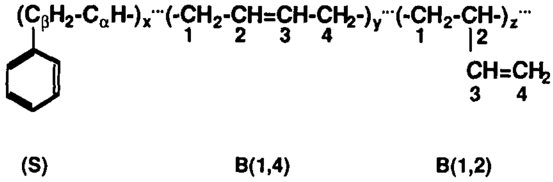


Figure 2 Experimental spectrum, simulated individual peaks, and composite spectrum obtained from proton n.m.r. spectroscopic measurements on SBR, using a sample spinning frequency of 18 kHz: (------) experimental spectrum; (-----------) composite spectrum; (– – – –) computer generated individual peaks

Table 2 Peak positions and peak assignments for the proton n.m.r. spectra of SBR



δ (ppm)	Peak	Assignment
7.057	a	C_6H_5(S)
5.335	b	H_2(B 1,4)+H_3(B 1,4)+H_3(B 1,2)
4.941	c	$2H_4$(B 1,2)
2.441	d	$1H_2$(B 1,2)+$1H_\alpha$(S)
1.960	e	$2H_1$(B 1,4)+$2H_4$(B 1,4)
1.412	f	$2H_1$(B 1,2)+$2H_\beta$(S)[a]

[a] Also contains a contribution from small quantities of impurities present in SBR

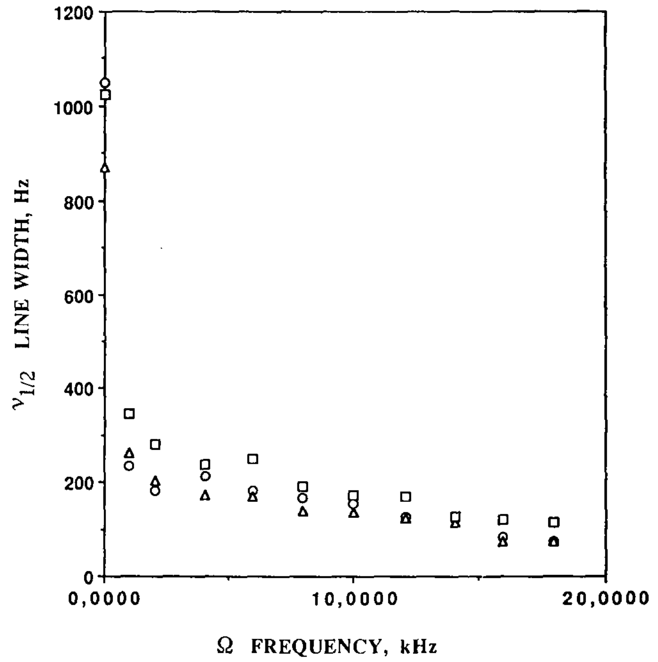


Figure 3 Dependence of the linewidth of the different kinds of proton species present in the n.m.r. spectrum of pure SBR on the frequency of sample rotation at the magic angle: (○) aromatic protons; (Δ) methine protons; (□) methylene protons

Effect of filler concentration on individual relaxation times for each resonance species, as observed by the spin-echo method

The spin-echo method was used to measure spin-spin relaxation times for both the gum and the extracted carbon gels. The delay time, τ, was in the 10 μs–10 ms range. All spectra were deconvoluted into their different components by using computer simulated peaks. The spin-spin relaxation time, T_2, was calculated from a determination of the time constant of the decay curve, which was obtained by plotting the signal intensity (calculated from the area under each individual spectrum) as a function of t_d ($t_d = 2\tau$), the total delay time between the $\pi/2$ pulse and the maximum echo amplitude[53]. The T_2 values for the individual components of the multi-component system were obtained by a computer fitting of each curve thus obtained on the basis of a non-linear, least-squares fitting programme (i.e. 'Simfit', a Bruker-supplied Pascal program).

Figure 4 shows plots of the peak area, $M(t)$ *versus* the total evolution delay, t_d for the aromatic protons of gum SBR and five extracted carbon gels. Similar curves are obtained for the methine and methylene protons. The experimental data seem to fit well with the sum of two exponential decay functions, corresponding to short (s)

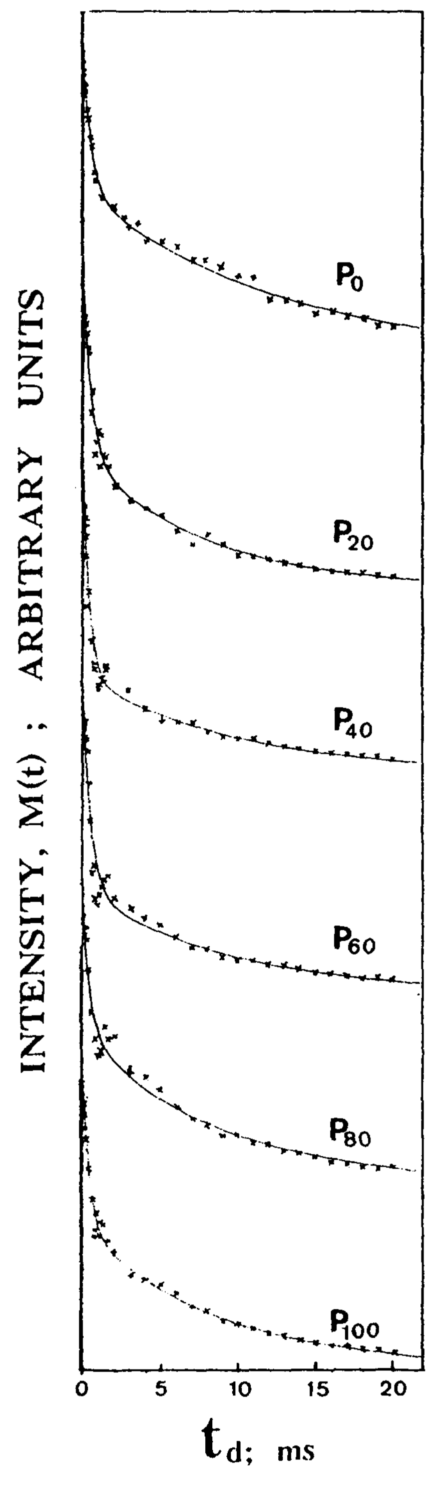


Figure 4 Plots of the transverse magnetization relaxation functions for aromatic protons of unfilled SBR and SBR chains adsorbed on carbon black; six typical compositions are shown, with the solid lines giving the double exponential fit of the experimental data resulting from spin-echo measurements

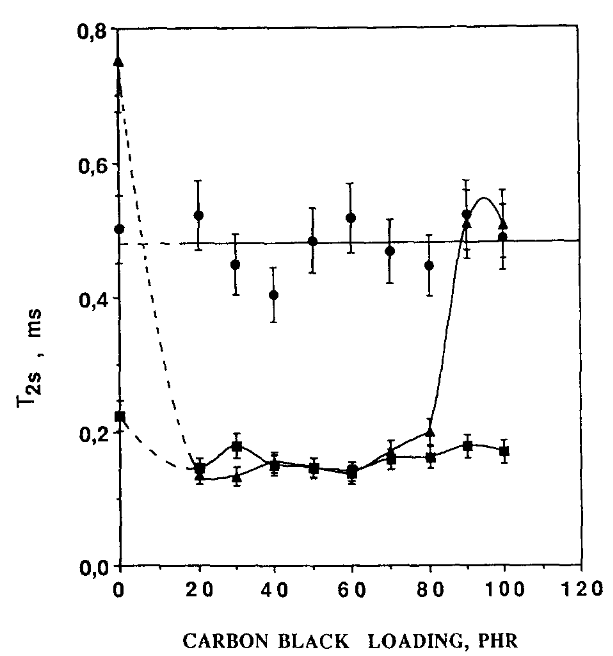


Figure 5 The effect of carbon black filler concentration on T_{2s} for different kinds of proton species in carbon gels: (●) aromatic protons; (▲) methine protons; (■) methylene protons

and long (l) relaxation times, respectively. Therefore, one can write:

$$M(t) = N_s \exp(-t_d/T_{2s}) + N_l \exp(-t_d/T_{2l})$$

where t_d is the total evolution delay, N_s and N_l are the fractions of the rubber in the two respective regions and T_{2s} and T_{2l} are the spin-spin relaxation times of the corresponding components.

The evolution of T_{2s} and T_{2l} with filler loading are shown in *Figures 5* and *6*, respectively. It is important to note that the relaxation characteristics of the different kinds of proton species cannot be compared between themselves, because each one has its own characteristic relaxation process. It has been observed that at least two components are necessary to simulate the magnetization decay curve for each kind of proton of pure SBR (P_0). Therefore, it appears that the SBR chain consists of two types of domains, which are characterized by two different basic relaxation functions. Topological constraints, created by physical entanglements or physical and chemical interactions, induce a restriction of the conformational fluctuations of the chain backbones. The pseudo-solid behaviour of the spins in pure SBR is associated with the temporary network structure which characterizes any high-molecular-weight polymer. This has been discussed in detail by Cohen-Addad and coworkers[54,55]. Folland and coworkers[56–60] extensively investigated this phenomenon by pulsed n.m.r. studies, using pure polydimethylsiloxanes and *cis*-polyisoprenes having a wide range of molecular weights.

The results obtained for the T_2 relaxation times from the carbon gels may be summarized as follows. The T_2 for each kind of proton is found to consist of at least two components. This kind of motional heterogeneity in the carbon gels (obtained from different filled elastomeric systems) has also been observed by many other investigators by low field, low resolution n.m.r. studies. Kaufman *et al.*[27], using carbon black filled high *cis*-polybutadiene and ethylene-propylene-diene terpolymer, demonstrated the presence of three distinctly different phases in the filled rubber, as characterized by the different degree of mobility exhibited by the constituent rubber chain. These were identified as a tightly bound region (highly immobilized rubber layer around active fillers), an outer annular region of loosely bound rubber, and free materials having dynamics which were identical to those of an unfilled rubber. This was further confirmed through n.m.r. investigations by O'Brien *et al.*[36] on carbon black filled *cis*-polybutadiene, and by Ito *et al.*[41] on silica filled polyisoprene and polybutadiene composites. Similar behaviour has also been observed by Nishi[35] in swelling experiments carried out with filled natural rubber. O'Brien *et al.*[36] have developed a generalized and comprehensive model for the filler/elastomer interaction that satisfactorily accounts for their n.m.r. observations and also for those from a variety of experiments by many other investigators. According to their model, and irrespective of the kind of interaction, few of the elements (either the molecule or a segment of the molecule) which are close to the carbon black surface are in a highly constrained configuration. Loosely folded chains, chain ends and loosely tied molecules, which are outside the limits of the low-mobility region, will be capable of undergoing extensive motions. This model, however, has not yielded, until now, information about the site-specific nature of the filler particle/polymer matrix coupling. The T_2 values (*Figure 5*) obtained for our carbon gels appear to provide valuable indications in this respect for the SBR/carbon black systems. In such a case, different T_{2s} behaviours are noticed, depending on the type of proton which is being considered. In the 20–100 phr filler concentration range under consideration, the aromatic and methylene protons have T_{2s} values which are only slightly different from those of pure SBR, which suggests that they result from the immobilization only associated with physical entanglements. However, methine protons exhibit much shorter T_{2s} values than

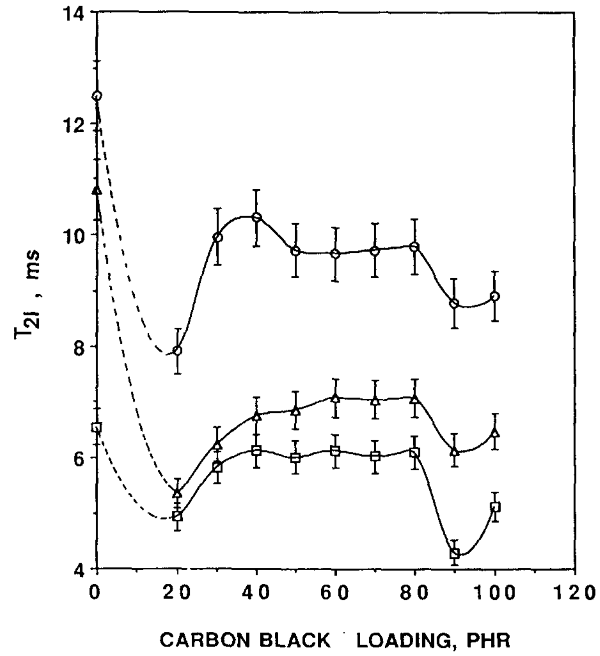


Figure 6 The effect of carbon black filler concentration on T_{2l} for different kinds of proton species in carbon gels: (○) aromatic protons; (△) methine protons; (□) methylene protons

those of pure SBR (P_0). These observations clearly indicate that the olefinic part of the butadiene segment of the SBR polymer chain is the most significantly affected by the presence of the filler. This part of the polymer chain seems to exchange a specific kind of interaction with the carbon black surface, the exact nature of which is still unknown. Although the variation of the filler concentration between 20 and 80 phr exerts no significant effect on the T_{2s} values of methine protons, their mobility, however, increases sharply above 80 phr. Such a behaviour has still to be interpreted.

It is interesting to note that the observed T_{2s} values for carbon gels are much higher (120–550 μs) than those obtained by earlier investigators (10–25 μs)[35,36,41,42]. It is worth mentioning, however, that these investigators worked with low resolution n.m.r. under static conditions, in which case the homonuclear dipolar interaction is very strong. Consequently, the magnetization decay is very fast. In the present case, a high spinning rate suppresses most of the dipolar interactions and c.s.a. However, magnetization decay remains controlled by molecular dynamics and becomes relatively slow.

The T_{2l} values (*Figure 6*) for all of the different kinds of proton species show qualitatively identical behaviour. They are virtually constant over the 30–80 phr range. Below 30 phr and above 80 phr, they exhibit T_{2l} values which are comparatively lower and hence display less mobility. This result may be interpreted as follows. Although at 20 phr, an infinite cluster of particles (i.e. a 3-dimensional mesh-like network) is formed, the mesh size of the gel remains very large. Therefore, the chemical potential of the free chain in the state of maximum swelling is significantly low. Consequently, polymer chains which are not strongly linked to the carbon black surface can be easily desorbed when the sample is solvent extracted. Thus, in low filled systems, only strongly adsorbed polymer chains remain in the sample after extraction. It is clearly seen from *Table 1* that the P_{20}-extracted sample contains a larger amount of filler (59%) than the other carbon gels (values varying between 47 and 52%). This results in a small increase in the T_{2l} value as the filler loading is increased from 20 to 40 phr. The mesh size of the swollen carbon gel progressively decreases with increases in the filler loading and desorption of the less strongly adsorbed molecules is also successively reduced. The mesh size decrease of the carbon gel with increases in the filler loading was indeed directly observed by Ban *et al.*[61] using high resolution electron microscopy. Cohen-Addad and Ebengou also made similar observations in the case of silica-siloxane rubber blends[62]. The experimental results (*Table 1*) show that the desorption effect is constant in those composites where the filler loading varies between 40 and 80 phr (P_{40} to P_{80}). Thus, all of these have virtually identical T_{2l} values for each kind of proton species. Above the 80 phr level, the relaxation time decreases for all of the protons. As is the case for T_{2s}, such a behaviour has still to be interpreted. Finally a correlation can be obtained between the rubber fraction, N_s, and the filler loading (*Figure 7*). Indeed, the N_s relative proportion progressively increases with the filler loading up to 50 phr (the concentration at which a maximum reinforcement is normally observed). Beyond that level, N_s decreases with further increases in the filler loading up to the 80 phr level. As previously mentioned, highly filled samples (90 and 100 phr) cannot be compared with the others because they have significantly different T_{2s} and T_{2l} values. It was, nevertheless, unexpected to find that ~40% of the chains in the pure rubber exhibit a reduced mobility. Such a result remains, for the moment, unexplained and should deserve further investigation.

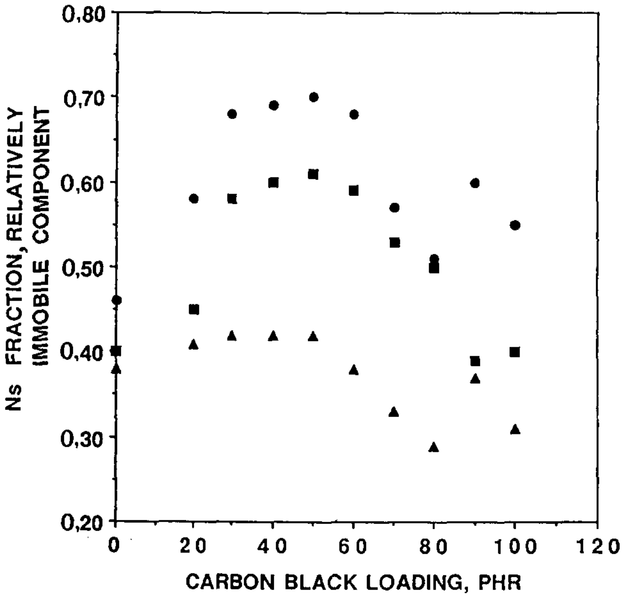


Figure 7 Effect of the filler concentration on the relative quantity of the different kinds of protons linked to the adsorbed or constrained interfacial monomer units: (●) aromatic protons; (▲) methine protons; (■) methylene protons

CONCLUSIONS

Although conventional solid-state n.m.r. studies of protons give global information on the dynamics of polymer chains, with the help of high speed, high resolution solid-state n.m.r. spectroscopy, it is possible to study the dynamics of the individual proton resonance species that are present in a polymer.

The chain segmental motions, even for pure SBR well above its T_g, are anisotropic in nature and deviate from a true liquid-like behaviour. The rubber chains adsorbed on a carbon black surface seem to consist of low and high mobility segments. The adsorption process appears to be site-specific in nature, with the olefinic part of the butadiene moieties in the SBR polymer chain being more significantly affected by the presence of the filler. Due to this adsorption, the restriction imposed on the mobility of the different kinds of resonance species is strongly dependent on their chemical nature and their intrinsic mobility. However, the exact nature of the specific interactions is still unknown. In order to understand this process more specifically, our future work should be directed to: (a) high resolution ^{13}C n.m.r. spectroscopic investigations of unfilled pure gum and filled composites, and carbon gels; (b) n.m.r. investigations of the unfilled and crosslinked systems; (c) studies of model polymer and model filled composites.

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REFERENCES

1 Studebaker, M. L. *Rubber Chem. Technol.* 1957, **30**, 140
2 Kraus, G. *Adv. Polym. Sci.* 1971, **8**, 155
3 Kraus, G. *Angew. Makromol. Chem.* 1977, **60/61**, 215
4 Dannenberg, E. M. *Rubber Chem. Technol.* 1975, **48**, 410
5 Medalia, A. I. *Rubber Chem. Technol.* 1978, **51**, 437
6 Medalia, A. I. and Laube, S. G. *Rubber Chem. Technol.* 1978, **51**, 89
7 Rigbi, Z. *Rubber Chem. Technol.* 1982, **55**, 1181
8 Dannenberg, E. M. *Rubber Chem. Technol.* 1986, **59**, 512
9 Wagner, M. P. *Rubber Chem. Technol.* 1976, **49**, 703
10 Nakajima, N. and Chu, M. H. *Rubber Chem. Technol.* 1990, **63**, 110
11 Donnet, J. B. and Voet, A. 'Carbon Black Physics, Chemistry and Elastomer Reinforcement', Marcel Dekker, New York, 1976
12 Kraus, G. (Ed.) 'Reinforcement of Elastomers', Wiley, New York, 1965
13 Smit, P. P. A. *Rheol. Acta* 1966, **5**, 277
14 Fujimoto, K. and Nishi, T. *Nippon Gomu Kyokaishi* 1970, **43**, 54
15 Dutta, N. K. and Tripathy, D. K. *Kautsch Gummi. Kunstst.* 1989, **42**, 665
16 Pliskin, I. and Tokita, N. *J. Appl. Polym. Sci.* 1972, **16**, 473
17 Kraus, G. and Gruver, J. T. *J. Polym. Sci. (Part A-2)* 1970, **8**, 571
18 Kraus, G., Rollman, K. W. and Gruver, J. T. *Macromolecules* 1970, **3**, 92
19 Kwei, T. K. and Cumins, C. A. *J. Appl. Polym. Sci.* 1964, **8**, 1483
20 Kwei, T. K. *J. Polym. Sci. (Part A)* 1965, **3**, 3229
21 Baccaredda, M. and Butta, E. *J. Polym. Sci.* 1962, **57**, 617
22 Ayala, J. A., Hess, W. M., Kistler, F. D. and Joyce, G. A. *Rubber Chem. Technol.* 1991, **64**, 19
23 Wang, M. J., Wolff, S. and Donnet, J. B. *Rubber Chem. Technol.* 1991, **64**, 714
24 Wang, M. J. and Wolff, S. *Rubber Chem. Technol.* 1992, **65**, 329
25 Honnold, V. R., McCaffery, F. and Mrowca, B. A. *J. Appl. Phys.* 1954, **25**, 1219
26 Takeda, M., Tanaka, K. and Nagao, R. *J. Polym. Sci.* 1962, **57**, 517
27 Kaufman, S., Slichter, W. P. and Davis, D. D. *J. Polym. Sci. (Part A-2)* 1971, **9**, 829
28 Fujimoto, K. and Nishi, T. *Nippon Gomu Kyokaishi* 1970, **43**, 465
29 Roe, R. J., Davis, D. D. and Kwei, T. K. *Bull. Am. Phys. Soc.* 1970, **15**, 308
30 Schaefer, J. *Macromolecules* 1972, **5**, 427
31 Schaefer, J. *Macromolecules* 1973, **6**, 882
32 Schaefer, J. and Natusch, D. F. S. *Macromolecules* 1972, **5**, 416
33 Schaefer, J., Chin, S. H. and Weissman, S. I. *Macromolecules* 1972, **5**, 798
34 Dybowski, C. R. and Vaughan, R. W. *Macromolecules* 1975, **8**, 50
35 Nishi, T. *J. Polym. Sci. Polym. Phys. Edn* 1974, **12**, 685
36 O'Brien, J., Cashell, E., Wardell, G. E. and McBriety, V. J. *Macromolecules* 1976, **9**, 653
37 Serizawa, H., Nakamura, T., Ito, M., Tanaka, K. and Nomura, A. *Polymer J.* 1983, **15**, 201
38 Serizawa, H., Nakamura, T., Ito, M., Tanaka, K. and Nomura, A. *Polymer J.* 1983, **15**, 543
39 Legrand, A. P., Lecomte, N., Vidal, A., Haidar, B. and Papirer, E. *J. Appl. Polym. Sci.* 1992, **46**, 2223
40 Wardell, G. E. and McBrierty, V. J. *Rubber Chem. Technol.* 1982, **55**, 1097
41 Ito, M., Nakamura T. and Tanaka, K. *J. Appl. Polym. Sci.* 1985, **30**, 3493
42 Kenny, J. C., McBrierty, V. J., Rigbi, Z. and Douglass, D. C. *Macromolecules* 1991, **24**, 434
43 Carr, H. Y. and Purcell, E. M. *Phys. Rev.* 1954, **94**, 630
44 Andrew, E. R. *Philos. Trans. R. Soc. London A* 1981, **299**, 505
45 Dec, S., Wind, R., Maciel, G. and Anthonio, F. *J. Magn. Reson.* 1986, **70**, 356
46 Langer, V., Daugaard, P. and Jakobsen, H. *J. Magn. Reson.* 1986, **70**, 472
47 Komoroski, R. A. (Ed.) 'High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk', VCH, New York, 1986, p. 19
48 Dybowski, C. R. 'Solid State NMR of Polymers', Plenum, New York, 1992, p. 1
49 Doscociliva, D. and Schneider, B. *Macromolecules* 1972, **5**, 125
50 Kentgens, A. P. M., Veeman, W. S. and VanBree, J. *Macromolecules* 1987, **20**, 1234
51 Maricq, M. M. and Waugh, J. S. *J. Chem. Phys.* 1979, **70**, 3300
52 Hayashi, S. and Hayamizu, K. *Bull. Chem. Soc. Jpn* 1991, **64**, 685
53 Sanders, J. K. and Hunter, B. K. 'Modern NMR Spectroscopy—A Guide for Chemists', Oxford University Press, Oxford, 1987
54 Cohen-Addad, J. P. *J. Phys. (Paris)* 1982, **43**, 1509
55 Cohen-Addad, J. P., Soyez, E., Viallat, A. and Queslel, J. P. *Macromolecules* 1992, **25**, 1259
56 Folland, R. and Charlesby, A. *Int. J. Radiat. Phys. Chem.* 1976, **8**, 555
57 Folland, R. and Charlesby, A. *Int. J. Radiat. Phys. Chem.* 1977, **10**, 61
58 Folland, R., Steven, J. H. and Charlesby, A. *J. Polym. Sci., Polym. Phys. Edn* 1978, **16**, 1041
59 Folland, R. and Charlesby, A. *Polymer* 1979, **20**, 207
60 Folland, R. and Charlesby, A. *Polymer* 1979, **20**, 211
61 Ban, L. L., Hess, W. M. and Papazian, L. A. *Rubber Chem. Technol.* 1974, **47**, 858
62 Cohen-Addad, J. P. and Ebengou, R. *Polymer* 1992, **33**, 379