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Gel-like behaviour of polybutadiene/carbon black mixtures: n.m.r. and swelling properties

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Adsorption properties of polybutadiene on carbon black aggregates are investigated from several experimental approaches: weighing, n.m.r. of protons attached to chains, and swelling of mixtures, induced by good solvents of the polymer. The observed apparent law of polymer adsorption is shown both experimentally and theoretically to obey a master curve obtained by using the reduced variable defined by the ratio M_n/Q_i (M_n is the number of average chain molecular weight and Q_i is the initial amount of polymer per gram of filler). The gel-like behaviour of bridged aggregates is observed for mixtures which are swollen by a good solvent, after eliminating free chains; the transverse relaxation process of protons attached to chains provides an insight into properties of the adsorbed layer. Copyright © 1996 Elsevier Science Ltd.

(Keywords: loaded polymer; adsorption; carbon black; polybutadiene)

INTRODUCTION

This work deals with gel-like properties observed on polybutadiene loaded with finely divided carbon black. It is considered that polymer molecules may be attached to the filler aggregates by chemical bonds even though the exact nature of these bonds is still partly unknown[1,2]. Each filler aggregate may be bridged to others by several polymer chains; such an aggregate is a rigid occupier of space and it acts as a multiple crosslink.

The purpose of this work is to investigate the phenomenon of chain adsorption on the surface of aggregates by applying several experimental approaches to carbon black/polybutadiene mixtures.

(i) The first one is based on measurements of the fraction of bound polymer obtained after washing mixtures, using good solvents of polybutadiene.
(ii) The analysis of the relaxation process of the transverse magnetization of protons attached to polymer molecules provides the second approach.
(iii) The gel behaviour of network structures, formed by mineral aggregates connected to one another by chains, is considered in the third approach. Mixtures can be swollen when carbon black concentrations and chain lengths have suitable values; the analysis of the swelling effect gives an insight into structures of these networks.

The evolution of the fraction of bound polymer, observed by varying both the chain molecular weight and the initial carbon black concentration, is analysed in the third section of this paper. The attempt to detect directly the presence of monomeric units on the carbon black surface was based on the observation of the transverse magnetic relaxation of protons; this attempt is discussed in the fourth section. The section after that concerns local constraints exerted on monomeric units in the adsorbed layer, considering the transverse magnetic relaxation of protons attached to the polymer. The swelling effect was observed to give evidence for the bridging of aggregates; this is described in the penultimate section.

EXPERIMENTAL

All solvents (toluene, n-heptane, cyclohexane and carbon tetrachloride) were obtained from Prolabo (normapur grade) and used without further purification. Mixtures were prepared and kindly supplied by the 'Manufacture Michelin'. The chain microstructure of polybutadiene was characterized by the following contents: 8% (w/w) monomeric units in the vinyl conformation, 38% (w/w) in the *cis*-1,4 conformation and 54% in the *trans*-1,4 conformation. Three number average molecular weights were considered: 7×10^4, 12×10^4 and $17 \times 10^4\,\mathrm{g\,mol^{-1}}$. The polydispersity index was equal to 1.05. The specific area of carbon black, bought from Cabot, was $115\,\mathrm{m^2\,g^{-1}}$ (N 220). Mixtures (1 g) were kept in a good solvent (100 ml) of polybutadiene during one week to extract the loosely bound part of polymer and free chains; the solvent was renewed three times. Proton relaxation functions were observed by using a CXP Bruker spectrometer operating at 60 MHz. Relaxation curves were carefully determined from free induction decays over a time interval going from 0 to about 100 μs and then from Hahn spin-echoes for longer times. Pseudo-solid spin-echoes were formed by applying the $[90°/x\text{-}\tau\text{-}180°/x\text{-}\tau\text{-}90°/y(\text{-}\tau_1\text{-}180°/x\text{-}\tau_1\text{-}180/\text{-}x)_n]$ pulse sequence to the spin system[3]. Swelling effects

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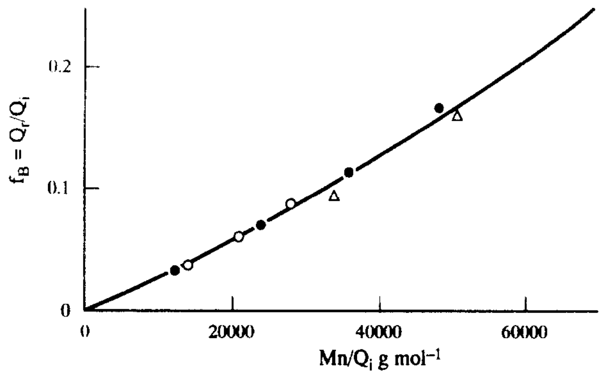

Figure 1 Fraction of bound polybutadiene; the master curve is obtained by using the M_n/Q_i variable. $M_n = 17 \times 10^4$ g mol^{-1} (△); 12×10^4 g mol^{-1} (●); 7×10^4 g mol^{-1} (○)

were characterized from weighing. The swelling ratio, hereafter called Q_m, was defined as $Q_m = (Q_r/\rho_p + V_{sol})/Q_i/\rho_p$ (ρ_p is the pure polymer density); V_{sol} is the solvent volume in the mixture per gram of carbon black, Q_r is the specific residual amount of adsorbed polymer and Q_i is the initial specific amount of polymer in the mixture; values of Q_i considered in this study are 2.5, 3.33, 5 and 10 g g^{-1}. HVHP Millipore filters were used to extract polymer molecules from mixtures.

BOUND FRACTION OF POLYMER

In this section, the mechanism of adsorption of chains on carbon black is analysed from the fraction of bound polymer measured as a function of both M_n, the chain molecular weight, and Q_i, the initial specific amount of polymer. The specific residual amount of bound polymer, Q_r, was measured after washing mixtures, using a good solvent.

Master curve

Considering several mixtures characterized by different carbon black concentrations and different chain molecular weights, the fraction of bound polymer, hereafter called f_B, was found to be represented by a single curve as a function of the ratio M_n/Q_i (*Figure 1*). Two striking features are perceived from the master curve.

(i) The fraction $f_B = Q_r/Q_i$ is nearly proportional to M_n for low values of M_n/Q_i ($M_n/Q_i <$ 24 000 g mol^{-1}); in this domain (low molecular weight or low carbon black concentration), the specific number of adsorbed polymer molecules is constant (1.8×10^{18} g^{-1}). A small deviation from a straight line is then observed for values of M_n/Q_i higher than 24 000 g mol^{-1}.

(ii) The curvature of the experimental curve reveals, by considering a constant chain molecular weight, that the specific amount of adsorbed polymer is increased when the carbon black concentration is increased. In other words, it is observed after washing of mixtures that the adsorption of polymer molecules is stabilized by increasing the filler concentration. This result is contrasted to the polydimethylsiloxane (PDMS) adsorption observed on silica; for these systems, the specific amount of adsorbed polymer is lowered by increasing the silica concentration because more and more adsorbed chains are shared by aggregates[4].

Adsorption model

The interpretation of the experimental master curve parallels the quantitative description already given to the phase diagram associated with mixtures of silica and PDMS[4]. The interpretation is based on the assumption that there exists an elementary interaction which can be established between any monomeric unit and the carbon black surface. It is not necessary to specify the nature of this elementary interaction which occurs on sites.

Sites of elementary interaction. The total specific number of sites of elementary interaction located on the carbon black surface and which participate in the polymer binding process after washing a mixture is called $\mathcal{N}_c$.

Polymeric bifunctional units. It is assumed that one polymer molecule can bridge two aggregates, only; therefore, each polymer molecule is considered as a bifunctional unit which can interact with the carbon black surface. The specific initial number of polymeric functions is thus equal to $2Q_i/M_n$. The average number of monomeric units involved in the binding of one chain is called $\psi(N)$; N is the average number of skeletal bonds in one chain. Therefore, the average specific number of binding sites of chains is $\mathcal{N}_c/\psi(N)$. For silica/PDMS mixtures, the average number of contact points of one chain with the silica surface has been shown both experimentally and theoretically to be $\psi(N) \simeq N^{1/2}$; this result is related to the Gaussian statistics of chains in a melt[5].

State of a mixture. For a given mixture observed after washing, there is a fraction ϕ_p of polymeric functions which are involved in the polymer adsorption process. Correspondingly, the specific number of binding sites of chains, occupied on the carbon black surface, obeys the equation:

$$2Q_i\phi_p\mathcal{A}/M_n = \mathcal{N}_c/\psi(N) \quad (1)$$

where $\mathcal{A}$ is the Avogadro number, and

$$\phi_p = \mathcal{B}M_n/Q_i \quad (2)$$

with

$$\mathcal{B} = \mathcal{N}_c/2\psi(N)\mathcal{A} \quad (3)$$

The $\mathcal{B}$ coefficient characterizes the mechanism of polymer adsorption. The specific number of chains which bridge two aggregates is

$$\nu''_p = Q_i\phi_p^2/M_n \quad (4)$$

while the specific number of dangling chains is

$$\nu'_p = 2Q_i\phi_p(1 - \phi_p)/M_n \quad (5)$$

Finally, the interpretation is based on the assumption that chains which bridge two aggregates are not eliminated by washing a mixture, while dangling chains are partly desorbed. The specific amount of bound polymer is then expressed as

$$Q_r = Q_i\phi_p^2 + 2\beta\phi_p(1 - \phi_p)Q_i \quad (6)$$

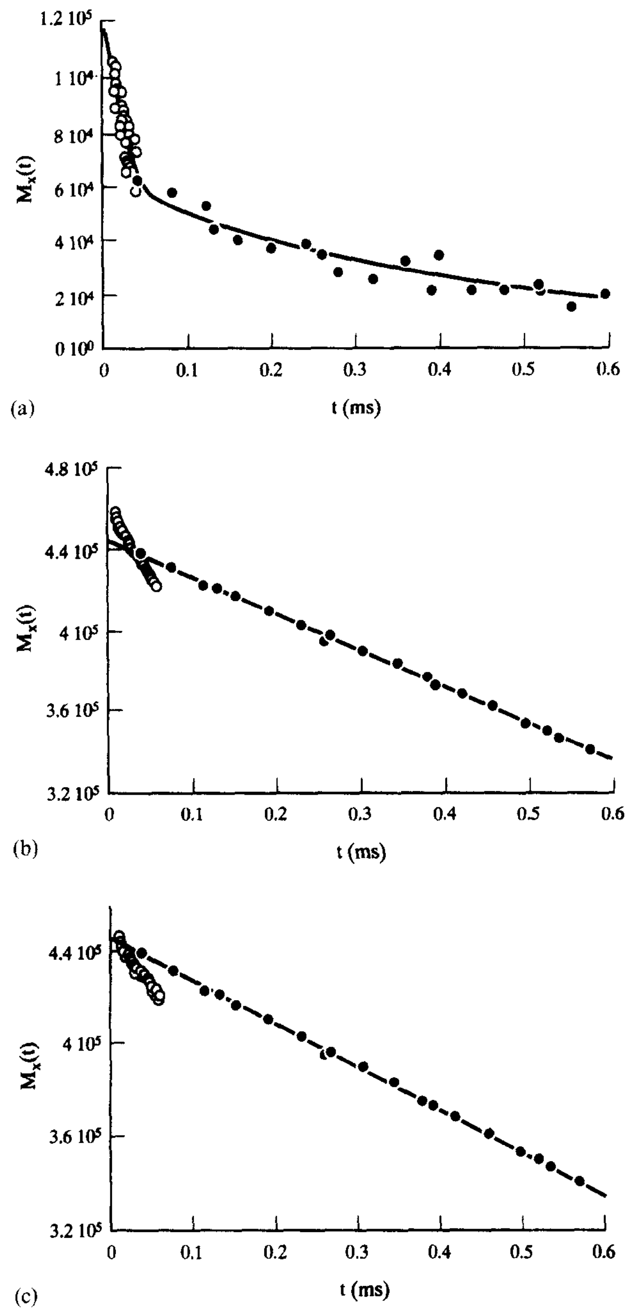

Figure 2 Proton transfer relaxation curves: (○) free industion decay; (●) spin-echoes (continuous lines through data drawn for convenience). (a) Organic impurities on carbon black; (b) polybutadiene/carbon black mixture observed after washing: $M_n = 17 \times 10^4\,\mathrm{g\,mol^{-1}}$; $Q_i = 2.5\,\mathrm{g\,g^{-1}}$ and $Q_r = 0.54\,\mathrm{g\,g^{-1}}$; (c) polybutadiene/carbon black mixture (the relaxation curve of organic impurities was subtracted)

$1 - \beta$ is the fraction of desorbed dangling chains, and

$$f_B = (1 - 2\beta)\mathscr{B}^2\left(\frac{M_n}{Q_i}\right)^2 + 2\beta\mathscr{B}\frac{M_n}{Q_i} \qquad (7)$$

This equation fits the master curve with $\beta = 0.35$ and $\mathscr{B} = 4 \times 10^{-6}\,\mathrm{g^{-1}}$ (*Figure 1*). It is worth emphasizing that equation (7) applies to all concentrations and to all molecular weights, except for short chains ($M_n = 7 \times 10^4\,\mathrm{g\,mol^{-1}}$ and $Q_i = 10\,\mathrm{g\,g^{-1}}$). This equation describes the apparent law of polybutadiene adsorption on carbon black. The main feature about equation (7) concerns the independence of $\mathscr{B}$ coefficient with respect to the chain molecular weight; consequently, $\psi(N)$ is independent of N, contrary to the case of silica/PDMS mixtures where $\psi(N)$ was proportional to $N^{\frac{1}{2}}$. An estimate of the density of sites where polybutadiene chains are strongly bound is derived from the numerical value of $\beta\mathscr{B}$; this density is about $4.2 \times 10^{-2}\,\mathrm{nm^{-2}}$. Such a low value is presumably due to the washing effect. It is supposed that, before washing mixtures, the actual law of adsorption obeys Gaussian statistics; it should be analogous to that observed on silica/PDMS mixtures: the number of contact points of one chain with the filler surface should be proportional to $M_n^{1/2}$. However, in the case of silica/PDMS mixtures, contact points are well defined because they result from the formation of hydrogen bonds between monomeric units and silanol groups which cover the silica surface; the strength of the filler/monomeric unit interaction is nearly uniform on the surface of aggregates. These mixtures are contrasted to polybutadiene/carbon black systems where there is a broad distribution of enthalpies of adsorption of monomeric units[6]. Consequently, the enthalpy of solvent/surface interaction may be stronger than some of the enthalpies of adsorption, and the washing of mixtures yields a partial elimination of adsorbed chains from the layer.

CONCENTRATION OF FIXED MONOMERIC UNITS

In this section, the attempt to observe directly monomeric units fixed on the surface filler is described. The n.m.r. approach, applied to the search for contact points of polymer molecules with the carbon black surface, was based on the simple following property, already used successfully for the observation of adsorbed monomeric units in silica/PDMS mixtures[7]. The proton magnetic relaxation of fixed monomeric units, characterized by a rate of $\sigma_B \simeq 10^5\,\mathrm{rad\,s^{-1}}$, can be easily discriminated from the proton relaxation of units which pertain to loops or to dangling chains; this relaxation is characterized by a rate $\sigma_L \simeq 10^3\,\mathrm{rad\,s^{-1}}$. The n.m.r. approach was applied in the following way.

(i) The proton relaxation of hydrogenated organic impurities fixed on the carbon black was first recorded before attempting to observe fixed monomeric units. The corresponding relaxation curve is illustrated in *Figure 2a* where both the free induction decay (open symbols) and Hahn spin-echoes are reported (black symbols); there was no effect of temperature increase on this magnetic relaxation.

(ii) Relaxation curves were then recorded on several mixtures, after removing all free chains. One of these curves is illustrated in *Figure 2b* with $M_n = 17 \times 10^4\,\mathrm{g\,mol^{-1}}$, $Q_i = 2.5\,\mathrm{g\,g^{-1}}$ and $Q_r = 0.54\,\mathrm{g\,g^{-1}}$. The proton magnetization associated with polybutadiene chains is represented, without any ambiguity, by black points. The relaxation curve drawn from black symbols can be extrapolated to $t = 0$; the intersection resulting from the extrapolation does not correspond to the whole magnetization which is actually observed.

(iii) Finally, the relaxation curve obtained after subtracting a suitably weighted organic impurity signal is shown in *Figure 2c*; the amplitude of the resulting curve, determined at $t = 0$, corresponds to the whole magnetization which is detected. Consequently, it is

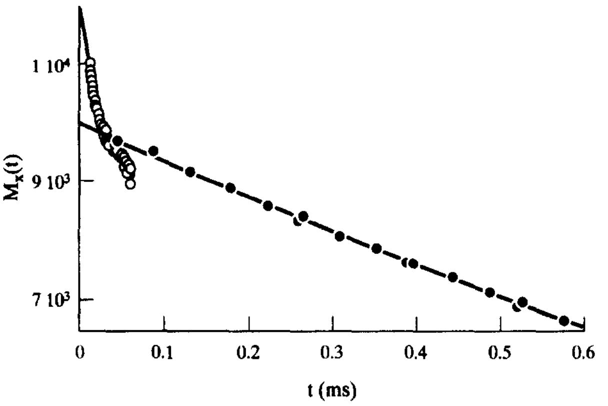

Figure 3 Natural rubber/carbon black (N 347) mixture observed after washing: $Q_i = 2.0\,g\,g^{-1}$ and $Q_r = 0.8\,g\,g^{-1}$ (continuous lines through data drawn for convenience)

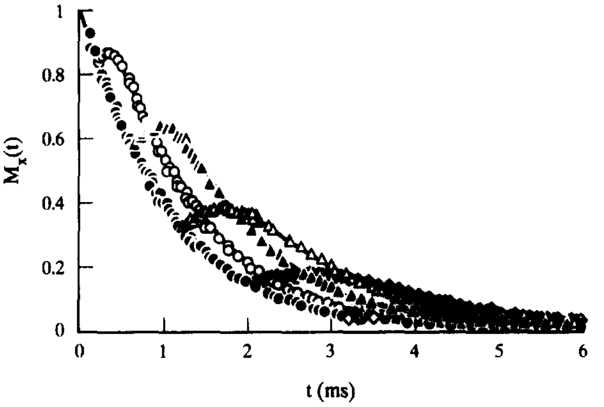

Figure 4 Pseudo-solid spin-echoes observed from a washed polybutadiene/carbon black mixture: $M_n = 12 \times 10^4\,g\,mol^{-1}$, $Q_i = 2.5\,g\,g^{-1}$ and $Q_r = 0.4\,g\,g^{-1}$ (continuous lines through data drawn for convenience)

considered that no fixed monomeric units are detected although the presence of an adsorbed layer is proved from weighing or from the observation of a swelling effect.

To prove that this n.m.r. approach is not questioned, mixtures formed from natural rubber and another carbon black (N 347) were also considered, with a specific amount of polymer, Q_i, equal to $2\,g\,g^{-1}$; the presence of fixed monomeric units was easily observed after subtracting the suitably weighted relaxation curve of organic impurities located on the surface of carbon black (*Figure 3*). The specific amount of bound natural rubber was $Q_r = 0.8\,g\,g^{-1}$ and the fraction of fixed protons was found to be equal to 0.11; this result is in agreement with already reported data[8]. From this study, it is concluded that adsorbed monomeric units of polybutadiene are not detected; taking the n.m.r. sensitivity into consideration ($\gtrsim 2\%$), the number of fixed monomeric units is smaller than about $10^{-3}\,nm^{-2}$.

ADSORBED LAYER PROPERTIES

It is now established, without any ambiguity, that the transverse relaxation of protons observed in high polymers or in gels is primarily sensitive to non-isotropic rotations of monomeric units resulting from topological constraints exerted on chain segments[3]. The presence of constraints is detected as a residual tensorial interaction of nuclear spins attached to monomeric units.

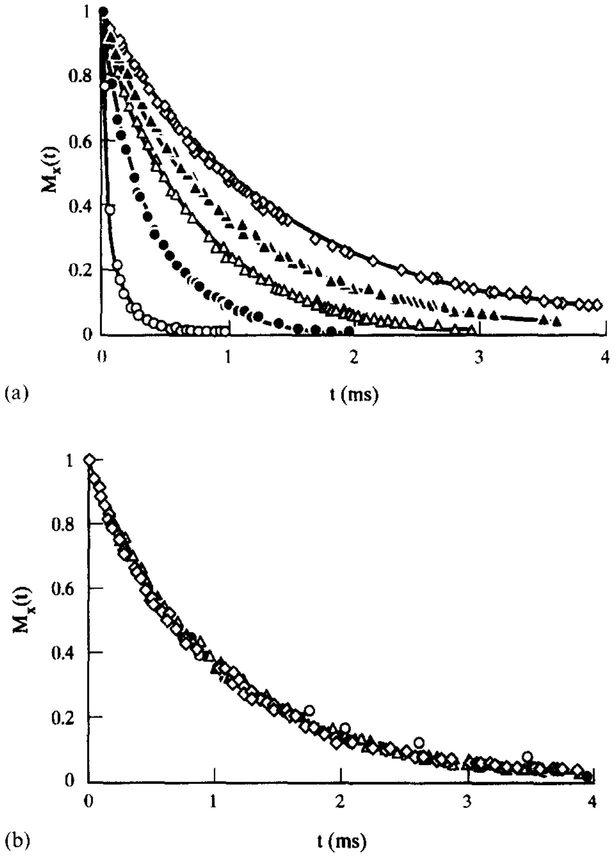

Figure 5 Effect of temperature variations on the transverse relaxation of protons attached to polybutadiene in the adsorbed layer: $M_n = 12 \times 10^4\,g\,mol^{-1}$, $Q_i = 2.5\,g\,g^{-1}$ and $Q_r = 0.4\,g\,g^{-1}$ (relaxation curves drawn from Hahn spin-echoes). (a) −56°C (○), −31.6°C (●), −3°C (△), 28°C (▲) and 80°C (◇); (b) superposition of relaxation curves obtained by applying suitable factors to time scales

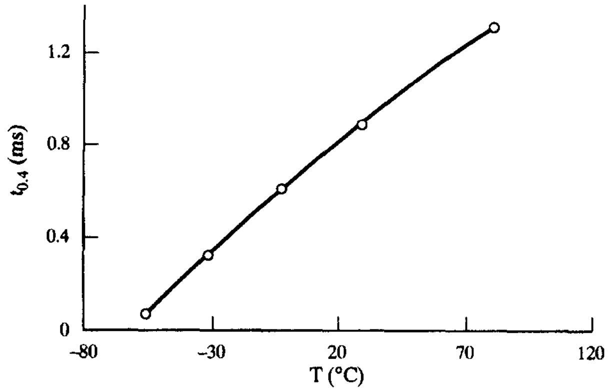

Figure 6 Variation of the $t_{0.4}$ time interval as a temperature function

Effect of temperature variations

The evidence for a residual tensorial interaction is given by forming pseudo-solid spin-echoes[3]; these are illustrated in *Figure 4*. They were recorded from a washed mixture ($M_n = 12 \times 10^4\,g\,mol^{-1}$; $Q_r = 0.4\,g\,g^{-1}$ and $Q_i = 2.5\,g\,g^{-1}$); the observation of well defined echoes indicates the presence of fixed monomeric units even though their concentration is too low to be detected

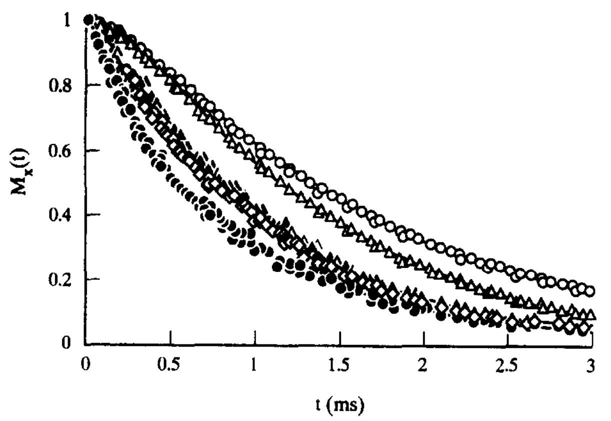

Figure 7 Effect of chain length variation on the transverse relaxation of protons attached to polybutadiene in the absorbed layer after washing ($Q_i = 3.30\,g\,g^{-1}$): $M_n = 7 \times 10^4\,g\,mol^{-1}$, $Q_r = 0.18\,g\,g^{-1}$ (●); $M_n = 12 \times 10^4\,g\,mol^{-1}$; $Q_r = 0.35\,g\,g^{-1}$ (◇) and $M_n = 17 \times 10^4\,g\,mol^{-1}$, $Q_r = 0.5\,g\,g^{-1}$ (▲). Pure polymer: $M_n = 7 \times 10^4\,g\,mol^{-1}$ (○) and $17 \times 10^4\,g\,mol^{-1}$ (△). Relaxation curves drawn from Hahn spin-echoes (continuous lines through data drawn for convenience)

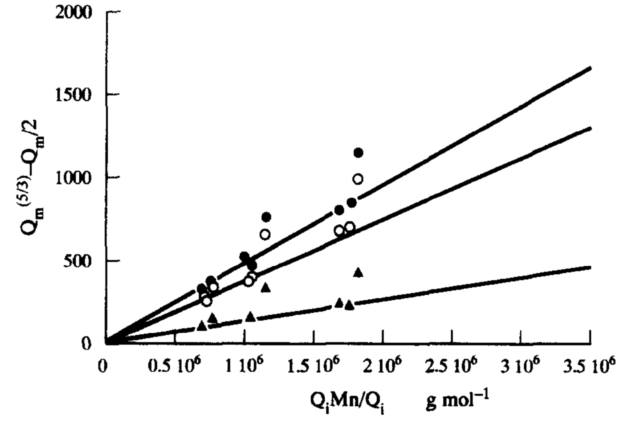

Figure 8 Representation of the primary swelling effect as a master curve. Swelling agent: (▲) n-heptane; (○) cyclohexane; (●) carbon tetrachloride

directly. Considering a given washed mixture ($M_n = 12 \times 10^4\,g\,mol^{-1}$ and $Q_i = 2.5\,g\,g^{-1}$), relaxation curves were recorded as a function of temperature, from −56 to 80°C (*Figure 5a*). Relaxation curves were found to obey a property of superposition by applying suitable factors to time scales (*Figure 5b*). Such a property means that the mechanism of magnetic relaxation is invariant; the relaxation rate is associated with a single physical property which corresponds to more and more deviation from isotropic rotations of monomeric units induced by lowering the temperature of the mixture, until the glass transition temperature is reached. Variations of the time interval ($t_{0.4}$) corresponding to 40% of the amplitude of the relaxation curve are reported, as a temperature function, in *Figure 6*. This thermal behaviour parallels that observed for pure polybutadiene[9]. The temperature evolution of local anisotropy of monomeric unit rotations in the adsorbed layer is similar to that observed in pure polybutadiene.

Effect of molecular weight variations

Furthermore, the thickness of the adsorbed layer was expected to increase when the polymer molecule is lengthened because the specific number of binding sites of chains is nearly constant according to equation (7). The chain molecular weight, in mixtures, was varied while the initial filler concentration was kept constant; the, relaxation curves recorded after washing were found to lengthen upon increase of the molecular weight (*Figure 7*). Consequently, the thicker the adsorbed layer, the lower the degree of anisotropy of rotations of monomeric units. This result is contrasted to that observed for pure polymers where the proton relaxation curve is usually shortened, because the lifetime of entanglements is lengthened when the polymer molecular weight is increased.

To conclude this section, it may be worth emphasizing that the transverse relaxation of protons, attached to polybutadiene, is fully governed by residual dipole/dipole interactions; the partial average of interactions results from non-isotropic rotations of monomeric units. In no case can correlation times be derived from the relaxation process of the transverse magnetization, which behaves like in a solid.

SWELLING EFFECT OF MIXTURES

The swelling effect was studied to prove the existence of a network structure; this was necessarily formed by bridging carbon black aggregates to one another although fixed monomeric units were not detected by n.m.r.

Primary swelling

Mixtures were washed, using a given good solvent, and the swelling ratio was measured prior to any drying. The analysis of experimental results was based on the mean field approach to the swelling effect of polymeric gels, proposed by Flory[10]. The search for a master curve led to representation of the physical quantity ($Q_m^{5/3} - Q_m/2$) as a function of the reduced variable Q_iM_n/Q_r (*Figure 8*). The Q_m swelling ratio was measured by using three good solvents of polybutadiene/carbon tetrachloride, cyclohexane and n-heptane. Straight lines were obtained for each solvent; experimental points corresponding to shortest chains ($M_n = 70\,000\,g\,mol^{-1}$) and values of Q_i equal to 3.33 or $5\,g\,g^{-1}$, were not expected to be on straight lines because they correspond to the formation of clusters rather than to the presence of gels. The slope of each straight line depends on the excluded volume parameter, which reflects the strength of the polymer/solvent interaction; carbon tetrachloride is usually considered as a better solvent of polybutadiene than is n-heptane or cyclohexane. The empirical equation derived from *Figure 8* reads

$$Q_m^{5/3} - Q_m/2 = \kappa Q_i(Q_r/M_n)^{-1} \qquad (8)$$

where κ is probably a complicated constant which depends on the connectivity of the network structure; the $Q_i(Q_r/M_n)^{-1}$ expression represents the number of bound chains per unit mass (or unit volume) of polymer in the mixture, prior to any washing. This result shows that the network structure is formed in the presence of free chains which act as a swelling agent; the effect of swelling must be described within Gaussian statistics. Free chains are then removed from mixtures by washing, using a good solvent; they are simply replaced by solvent

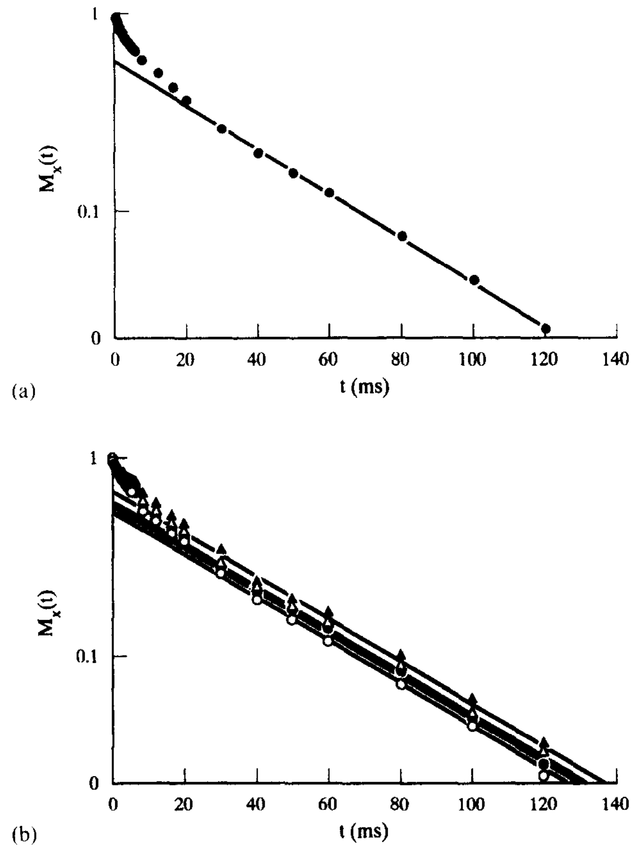

Figure 9 Proton transverse relaxation curves observed on mixtures in a state of primary swelling (relaxation curves drawn from Hahn spin-echoes): (a) semi-logarithmic representation for $M_n = 12 \times 10^4\,\mathrm{g\,mol^{-1}}$ and $Q_i = 2.5\,\mathrm{g\,g^{-1}}$ (the swelling agent is CCl_4); (b) effect of variations of the initial specific amount of polymer: (○) $Q_i = 2.5\,\mathrm{g\,g^{-1}}$; (●) $Q_i = 3.3\,\mathrm{g\,g^{-1}}$; (△) $Q_i = 5\,\mathrm{g\,g^{-1}}$; (▲) $Q_i = 10\,\mathrm{g\,g^{-1}}$

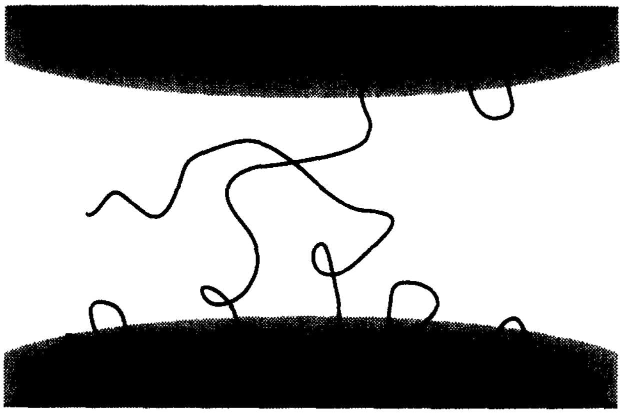

Figure 10 Schematic representation of washed mixtures in a state of primary swelling

molecules which induce a swelling effect because of their strong interaction with polymer molecules. The swelling effect can be considered as a simple three-dimensional expansion of mixtures.

N.m.r. evidence for polymeric bridging

Proton transverse relaxation curves were recorded from swollen mixtures; they were found to exhibit two well defined parts (*Figures 9a* and *b*). The fast decay was assigned to monomeric units which pertain to loops while the long part was associated with protons attached

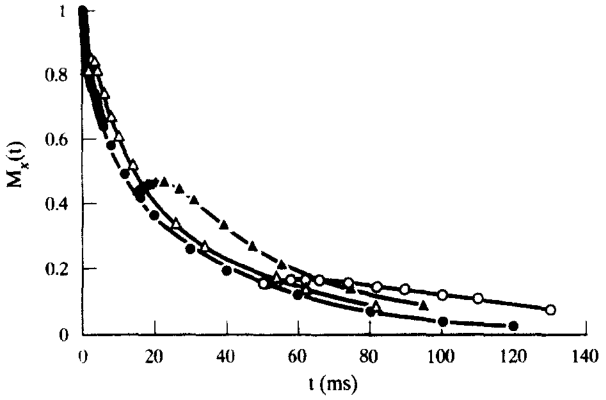

Figure 11 Pseudo-solid spin-echoes formed to prove that polymer chains undergo topological constraints due to adsorption: state of primary swelling ($M_n = 12 \times 10^4\,\mathrm{g\,mol^{-1}}$; $Q_i = 2.5\,\mathrm{g\,g^{-1}}$; the swelling agent is CCl_4) (continuous lines through data drawn for convenience)

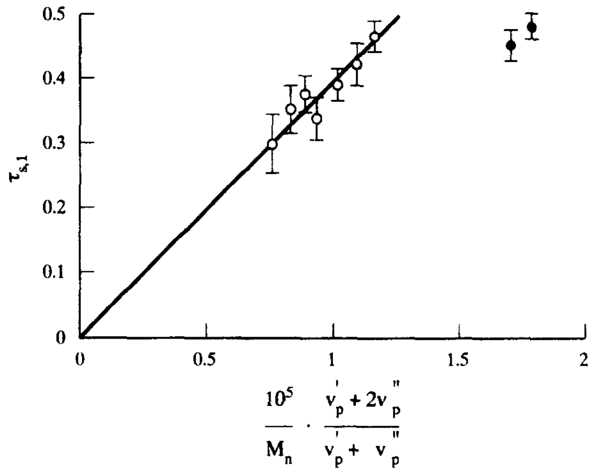

Figure 12 Variation of the fraction of monomeric units which participate in the binding process as a function of the fraction of dangling and bridging chains

to polymer bridges (*Figure 10*). Pseudo-solid spin-echoes were formed to prove that, even in the presence of solvent, polymer chains are submitted to topological constraints due to the adsorption effect (*Figure 11*). Long delays can be described by exponential time functions

$$M^{L}_{X}(t) = \exp(-t/T_{L,1}) \tag{9}$$

where the $T_{L,1}$ time constant ($\simeq$41 ms) is independent of both chain molecular weight and the carbon black concentration in mixtures; the numerical value of $M^{L}_{X}(o)$, the amplitude of the long decay, yields the fraction of protons participating in the formation of loops; let $\tau_{S,1}$ denote this fraction, which is expressed in accordance with the model of adsorption proposed in the third section.

(i) It is considered that the specific number of binding sites of chains, on the carbon surface, is constant;
(ii) the number of elementary interactions of monomeric units per binding site of chain is ψ; it is independent of N. Then,

$$\tau_{S,1} = \gamma(2\nu''_p + \nu'_p)\psi M_m/(\nu'_p + \nu''_p)M_n \tag{10}$$

where M_m is the molar mass of one monomeric unit, and γ accounts for the actual number of monomeric units

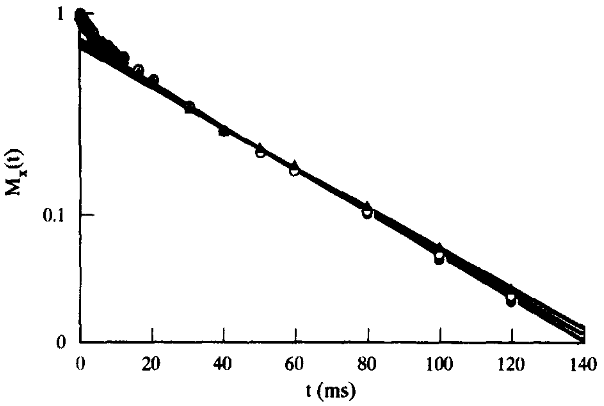

Figure 13 Proton transverse relaxation observed on washed mixtures in a state of secondary swelling: $M_n = 12 \times 10^4\,g\,mol^{-1}$; (▲) $Q_i = 2.5\,g\,g^{-1}$; (●) $3.3\,g\,g^{-1}$; (○) $5\,g\,g^{-1}$ (relaxation curves drawn from Hahn spin-echoes)

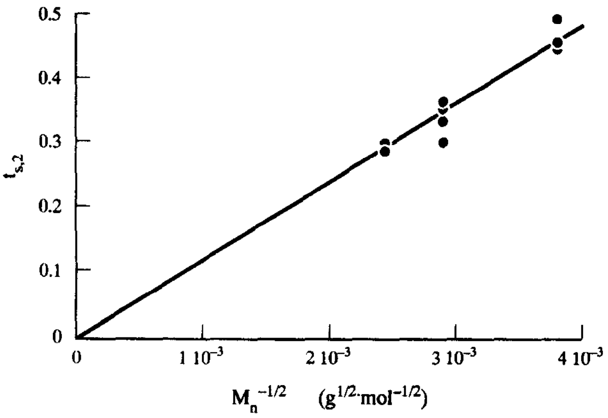

Figure 14 Variations of the fraction of monomeric units which participate in the chain binding process, in mixtures in a state of secondary swelling

involved in one chain contact with the filler surface; ν_p'' and ν_p' are calculated from equations (4)–(6). The $\tau_{S,1}$ fraction, derived from n.m.r. measurements, is represented in *Figure 12* as a function of the variable defined by $10^5(2\nu_p'' + \nu_p')/(\nu_p' + \nu_p'')M_n$. A straight line was drawn through experimental points; mixtures which consist of short chains ($M_n = 70\,000\,g\,mol^{-1}$) and carbon black concentrations corresponding to values of Q_i equal to 3.3 and $5\,g\,g^{-1}$ are not expected to obey equation (10) because they contain only clusters. The experimental value of the slope is 800; consequently, it is considered that there are about 800 monomeric units as observed from n.m.r. which are affected by one chain contact with the mineral filler surface. The linear dependence of the n.m.r. parameter $\tau_{S,1}$ is observed to be in agreement with equation (10); this result reinforces the adsorption model.

Secondary swelling

Mixtures were dried after swelling and then they were swollen again. Considering a given mixture, the new swelling ratio, Q_m^*, was found to be smaller than Q_m. Therefore, a secondary state of swelling was obtained, it resulted from an effect of secondary polymer adsorption, which occurs in the dry state. Proton transverse relaxation curves were recorded on mixtures in a secondary swelling state (*Figure 13*). They exhibit two well defined parts; the long relaxation tail can be represented by an exponential time function, characterized by a time constant $T_{L,2} = 35\,ms$. The fraction of protons which pertain to loops is called $\tau_{s,2}$; it was found to be a function of $M_n^{-1/2}$ (*Figure 14*). This result implies that the number of contact points of one chain with the carbon black surface is proportional to the square root of the total number of bonds in one polymer molecule. This is in agreement with results observed on silica/PDMS mixtures[4]; consequently, it is assumed that the dependence of the n.m.r. parameters $\tau_{s,2}$ on $M_n^{-1/2}$ shows that the secondary adsorption process, which occurs after drying, results from the presence of aggregates fully immersed in a molten polymer. It is considered that polymer chains recover Gaussian statistics in the dry state.

CONCLUSIONS

The law of adsorption of polymer molecules on the surface of mineral fillers immersed in a melt or in concentrated solutions is closely related to the statistical framework which is applied to the description of chain properties[11]. It implies the existence of a mean number of contact points of chains with the filler surface, which is expressed as a function of the total number of skeletal bonds in one chain. The formation of loops and trains in the adsorbed layer can occur when the enthalpy of adsorption of one monomeric unit is slightly higher than the thermal energy, at room temperature.

The study of the law of adsorption of polybutadiene chains on the surface of carbon black comes up against two main difficulties. The first one concerns the elimination of loosely bound chains which results from the washing of mixtures; consequently, the law of polymer adsorption which is established is only apparent. This law shows that the specific number of sites which are involved in the mechanism of chain binding is nearly constant.

The second difficulty arises from the number of monomeric units fixed on the filler surface; this number is too small to be detected directly from n.m.r. in the case of the polymer considered in this study (low *cis*-polybutadiene). However, chain segments which participate in the formation of loops, in the adsorbed layer, can be well differentiated from monomeric units that pertain to segments which bridge aggregates, by fully swelling mixtures; then, the effect of swelling is to induce very different relaxation rates of protons.

Furthermore, the existence of an adsorbed layer is clearly evidenced from weighing while the existence of a network is well detected from the analysis of the effect of swelling. An estimate of the number of chains which bridge two aggregates is given within a mean field approximation and by assuming that a fraction of dangling chains is eliminated by the presence of a solvent.

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