References and Notes

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An NMR Investigation of the Interaction between Carbon Black and *cis*-Polybutadiene

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ABSTRACT: T_1, T_2, and $T_{1\rho}$ NMR measurements from −130 to +100 °C are reported for samples of carbon black filled *cis*-polybutadiene of widely different preparative histories in which the type of carbon black and the loading are systematically controlled. An asymmetric ESR signal is observed in the unfilled rubber which has been traced to the presence of paramagnetic impurities. At temperatures well in excess of T_g, motional freedom of liquid character is not achieved in the unfilled system in keeping with observations in other elastomers. T_g is unchanged with the introduction of the filler. The T_2 data are consistent with the existence of a region of tightly bound rubber molecules in the immediate vicinity of the filler in addition to a loosely bound component. In the context of the Pliskin-Tokita analysis, the thickness of the bound layer decreases as the specific surface area of the carbon black increases, which probably derives from the increased tendency of the finer carbon blacks to agglomerate. A model for the filled elastomer which elaborates upon existing ideas is presented and discussed.

The use of carbon black to enhance the physical properties of elastomers is a well-documented phenomenon.[1–4] Much attention has focussed upon the nature of the interaction between the filler particles and the host polymer through several types of experiment which include free volume, thermal expansion,[5,6] dynamic mechanical,[7–9] sonic velocity,[10] and magnetic resonance methods.[11–23] The significant contribution of nuclear magnetic resonance (NMR) which is of specific interest in this paper will be reviewed briefly.

Line width[11–13] and nearly equivalent T_2[15–23] measurements are by far the most sensitive of the NMR parameters to the carbon black–rubber interaction. Typically T_2 for the methine carbon in solid polyisoprene above the glass transition temperature T_g is reduced by a factor of the order of 5–10 in the filled system.[18,22] Proton line widths behave similarly. The proton T_2 results of Kaufman, Slichter, and Davis[15] on high *cis*-polybutadiene (*cis*-PB) and an ethylene–propylene–diene terpolymer (EPDM) demonstrate the presence of three distinct regions in the filled rubber as characterized by the differing degrees of molecular mobility exhibited by the constituent rubber chains: a region of unbound rubber which displays mobility above T_g comparable to the pure gum, bound rubber in an outer shell around the carbon black which is somewhat less mobile, and an inner shell of tightly bound rubber which experiences very limited motion on the T_2 time scale ($\sim 10^{-4}$ s). Similar behavior has been observed by Nishi[23] in swelling experiments on filled natural rubber.

By contrast, the addition of carbon black has little effect upon the position or magnitude of the observed T_1 minimum. Waldrup and Kraus[14] report a shift of at most 4 °C to higher temperatures in the position of the T_1 minimum in filled SBR rubber. Schaefer's ^{13}C results[18] show that the individual carbon T_1 magnitudes in polyisoprene are not noticeably affected by the addition of carbon black. Nuclear Overhauser enhancement factors (NOEF's) are equally insensitive to the incorporation of the filler.[18,20] The fact that the T_1 decay is exponential in both the filled and unfilled systems is central to the argument of Waldrup and Kraus[14] against a region of severely restricted mobility; it might be expected that a second, longer T_1 component characteristic of the bound region should be observed. In this respect the T_1 data appear, at first sight, to be in conflict with the T_2 interpretation discussed above although some workers have reported the presence of two T_1 components.[17] In these considerations no account has been taken of the conditions necessary for the resolution of two T_1 components[24] or of the effects of spin diffusion.

More generally, the amount of bound rubber depends in an important way upon the surface activity and specific surface area of the carbon black particles.[1,2,9] Pliskin and Tokita[9] have derived the following expression for the fraction of apparently bound rubber, BR, defined as the volume of insoluble polymer divided by the volume of polymer in the composite:

$$\mathrm{BR} = \Delta R_0 f \left\{\frac{\phi\rho A}{1-\phi}\right\} + G \tag{1}$$

ΔR_0 is the average thickness of the bound rubber layer, f is the fraction of the total surface area exposed to the soluble gum, ϕ is the volume fraction of carbon black in the composite, ρ and A are the density (1.85 g/cm^3)[1,2] and specific surface area of the carbon black particles, respectively, and G is the fraction of insoluble gel. A plot of BR vs. $\phi\rho A/(1-\phi)$ is linear for a wide range of commercially available carbon blacks and rubbers[9,23] and the slope of the line provides ΔR_0 the parameter of interest.

A closer inspection of the data used in these plots, however, indicates a more subtle dependence of ΔR_0 upon the carbon black used. This viewpoint gains support from the observation that ΔR_0 values determined from modulus data decrease with an increase in the specific surface area of the carbon blacks.[9] It has been suggested that this observation may relate to the ability of the various carbon blacks to disperse uniformly throughout the composite.[9]

In this paper we report the results of a comprehensive NMR study on filled *cis*-polybutadiene which attempts to gain further insight into these more detailed aspects of the rubber–carbon black interaction. Rotating frame relaxation data

Table I
Characterization of the Various Carbon Blacks

Type	N_2 (BET) surface area, m^2/g	Av EM diameter, nm	Mineral oil absorption, cm^3/g	Apparent specific vol at 734 psi, cm^3/g
SRF	30.3	61-100	0.75-0.90	1.20-1.35
GPF	29.3	51-55	0.95-1.05	1.30-1.40
FEF	43.4	40-48	1.15-1.45	1.40-1.70
HAF	83.5	26-30	1.20-1.40	1.45-1.60
ISAF	104.3	20-25	1.25-1.45	1.45-1.75

Table II
Details of Sample Preparation

Sample code No.	Carbon black filler	Loading, phr	Mixing temp, °C
1	None	0	
2	None	0	
3	Statex (GPF)	100	84
4	Statex (GPF)	90	84
5	Statex (GPF)	80	84
6	Statex (GPF)	70	84
7	Statex (GPF)	60	84
8	Statex (GPF)	50	84
9	Statex (GPF)	40	84
10	Statex (GPF)	30	84
11	Statex (GPF)	20	84
12	Regal (SRF)	50	89
13	Statex (GPF)	50	86
14	Philblack A (FEF)	50	100
15	Statex R (HAF)	50	71
16	Vulcan 6 (ISAF)	50	79
17	Vulcan 6 (ISAF)	50	

complement T_1 and T_2 data on samples of widely different preparative histories in which the type of carbon black and the loading are systematically controlled. Our experimental results are used to complement existing ideas in the formulation of a plausible model for the filled rubber system.

Experimental Section

Sample Materials. A linear high *cis*- (>96%) polybutadiene (Shell Carifex BR 1220) of density 1.01 g cm^{-3} was used exclusively in this study. An uncalibrated GPC trace indicated a fairly broad molecular weight distribution. It is realized of course that the subsequent mastication process will significantly alter the initial molecular weight distribution.[1] With samples 3-16, carbon blacks, described in Table I,[25] were incorporated into the rubber in an internal mixer in ambient atmosphere. Specific details of sample preparation are listed in Table II. In the case of sample 17 the carbon black was intimately mixed with the rubber dissolved in Naptha and the composite extracted by evaporation at room temperature. The preparation of 4-11 involved the progressive dilution of the 100 phr masterbatch (No. 3) to achieve the desired loading. As a final stage in preparation, all samples were subjected to 30 passes through the nip of a cold two-roll mill. The composite samples were prepared several months before NMR measurements were carried out to ensure equilibration of the bound rubber.[1] The bound rubber component was obtained from each filled rubber composite by extraction with hot toluene under an atmosphere of nitrogen in a Soxhlet extractor. The extraction procedure was continued until there was negligible further loss of weight with time. Each quoted bound rubber value is the mean of four extractions with an estimated error of ±15%. (The extracted samples are identified by the letter E attached to the appropriate code number in Table II.)

The purified version of the bulk rubber (No. 2) was prepared by dissolving the rubber as received (No. 1) in hexane for 3 days, precipitating out the purified rubber by the addition of CH_3OH, and drying under vacuum for a further 4 days. This procedure removed the bulk of trace catalysts from the rubber as received.

All samples were sealed under vacuum in sample tubes suitable for NMR study.

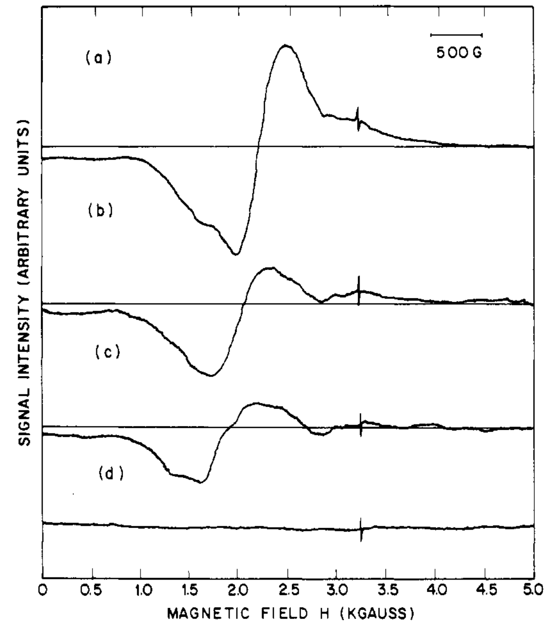

Figure 1. First derivative anisotropic ESR spectra for *cis*-polybutadiene recorded at room temperature. The sharp resonance corresponds to a DPPH marker. (a) Sample 1 as received; orientation in magnetic field unknown. (b) Oriented at 45° to (a). (c) Oriented at 90° to (a). (d) Purified rubber sample 2.

Data Acquisition and Analysis. A Bruker Spectrometer operating at a resonant frequency of 40 MHz provided T_1, T_2, and $T_{1\rho}$ (H_1 = 10 G) data. The spectrometer was equipped to control sample temperatures to ±1 °C. The duration of a 90° pulse and recovery time were $\sim$2.5 and 7 μs, respectively. The solid–echo sequence,[26] 90°-τ-90° (90° phase shift), provided an approximation to the complete free induction decay from which T_2 was computed as $t_{1/2}/\ln 2$ where $t_{1/2}$ is the time for the signal to decay to half its peak value.[27] Longer T_2's were determined by a spin–echo method which employed the 90°-τ-180° sequence.[28] An earlier paper has treated in detail the analysis of multicomponent T_2 decays.[29] $T_{1\rho}$ was determined from the 90°-90° phase shift spin locking method[30] while a 90°-τ-90° pulse sequence provided T_1 relaxation times.[28]

The electron spin resonance spectra reported in this paper were recorded on a Bruker ESR spectrometer operating conventionally at X-Band frequencies.

Results and Discussion

Unfilled Polybutadiene Results. Prompted by the report of a permanent assymetric free radical ESR signal in pure masticated SBR rubber,[31] a preliminary experiment was performed to ascertain if stable free radicals were present in the bulk polybutadiene as received. The presence of free radical species might well complicate the interpretation of the NMR data.[32] In fact, the assymetric ESR signal presented in Figure 1 was obtained. As with the signal observed in SBR by Ellis and Baugher,[31] the spectrum displayed marked anisotropy as a function of sample orientation in the magnetic field. The agents most probably responsible for the ESR signal are

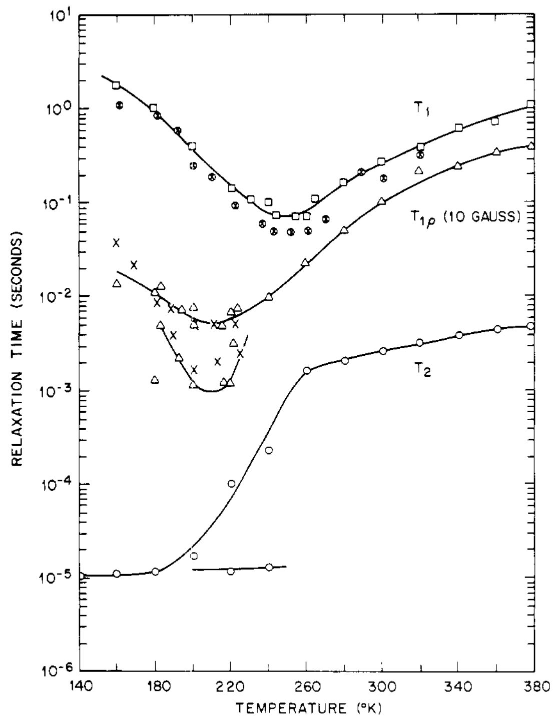

Figure 2. T_1 (□), $T_{1\rho}$ (△), and T_2 (○) data as a function of temperature for *cis*-polybutadiene (No. 1). The T_1 and $T_{1\rho}$ data for the purified material (No. 2) are denoted by ⊗ and ×, respectively.

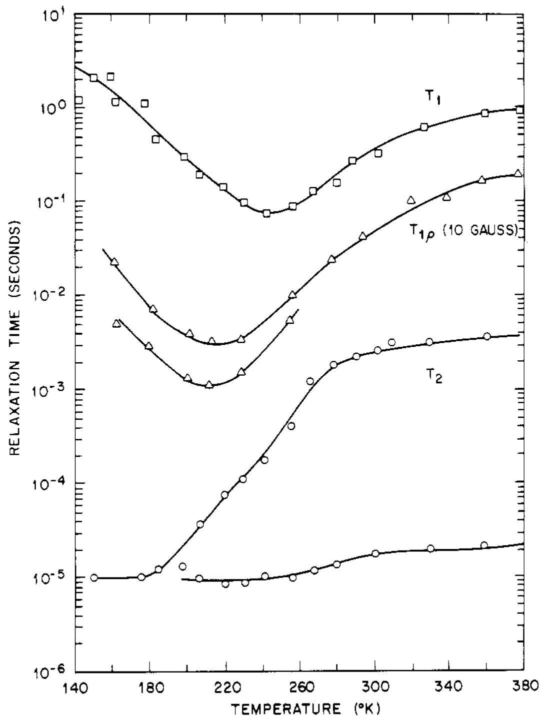

Figure 3. T_1 (□), $T_{1\rho}$ (△), and T_2 (○) data as a function of temperature for sample 8.

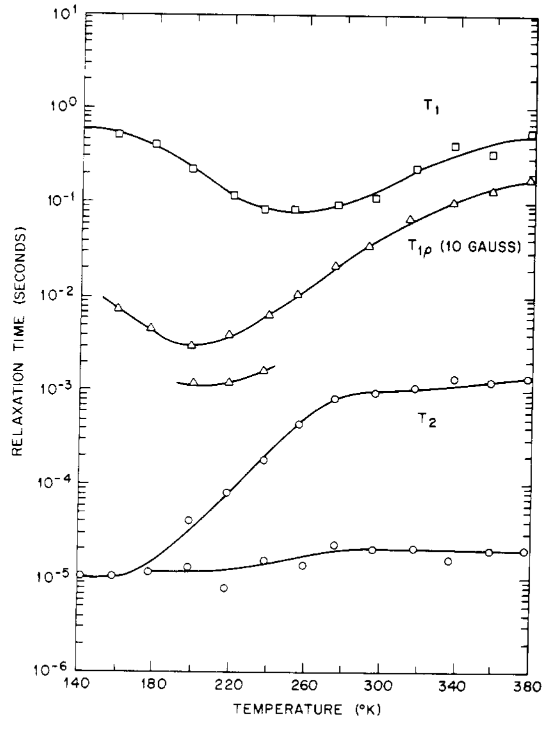

Figure 4. T_1 (□), $T_{1\rho}$ (△), and T_2 (○) data as a function of temperature for sample 8E.

paramagnetic impurities in the rubber,[31] incorporated either as a short stop in the rubber synthesis or possibly the Zeigler-Natta, cobalt complex catalyst used in the polymerization process. This viewpoint is supported by the fact that the purification procedure, which removed the bulk of such impurities, drastically reduced the intensity of the ESR signal as shown in Figure 1d.

The NMR data for samples 1 and 2 are summarized in Figure 2. With the exception of the somewhat lower T_1 values for the purified material, which in all probability reflect a closer packing of molecules in sample 2, the insignificant differences between the two sets of data demonstrate that the free radical impurities in fact do not exert an undue influence upon the relaxation behavior in *cis*-PB.

The data are characteristic of the well documented glass–rubber transition in elastomers and are in agreement with earlier T_1 and T_2 results for *cis*-PB.[15,33] The new $T_{1\rho}$ data show up two important additional features which require comment: the nonexponential $T_{1\rho}$ behavior in the region of the minimum and, the fact that $T_{1\rho}$ and T_1 do not merge at temperatures far in excess of the glass transition temperature.

The observation of nonexponential character in the vicinity of the $T_{1\rho}$ minimum may well result from the broad distribution of molecular weights in the rubber or may indicate the presence of ordered and disordered regions. Connor has made similar observations in atactic polystyrenes.[34] The lack of convergence in $T_{1\rho}$ and T_1 even at high temperatures indicates that the molecular motions do not satisfy the extreme narrowing condition and cannot be described in terms of a single correlation time. This aspect of molecular motional behavior has received detailed attention by several workers in the description of their ^{13}C, ^{1}H, and NOEF data on elastomers above the glass transition temperature.[19,21,22,35–38]

Filled Polybutadiene Results. Complete NMR data were recorded for samples 8, 8E, 16, and 16E for which the carbon black fillers were of very different character (see Table I). Figures 3 and 4 which present the results for samples 8 and 8E, respectively, also provide an adequate description of the T_1 and $T_{1\rho}$ response for 16 and 16E; the high-temperature plateau for the longer T_2 component, however, was somewhat lower in the 16 and 16E materials, respectively. When compared with the unfilled rubber data (Figure 2) there were insignificant differences in the T_1 and $T_{1\rho}$ response of samples 8 and 16 but three important aspects of the T_2 data are of note: (i) the presence of a short T_2 component in the filled material over the complete temperature range, (ii) the increase in the

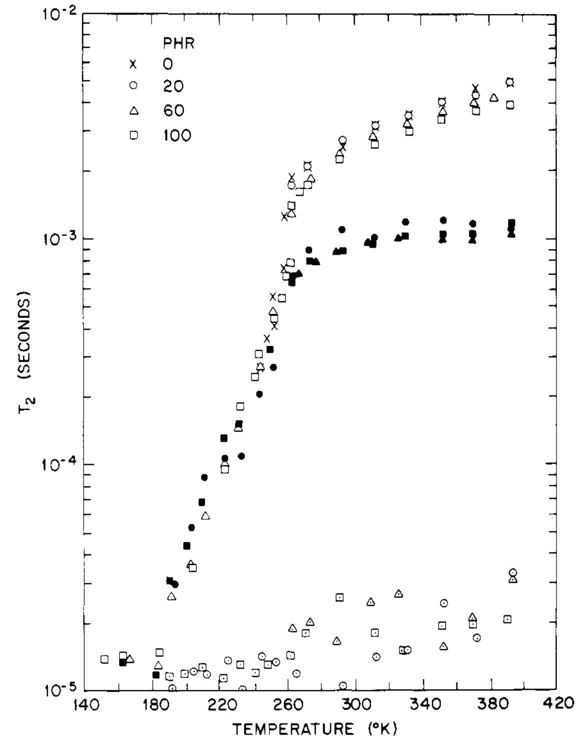

Figure 5. T_2 data as a function of temperature for various carbon black loadings. The open symbols relate to the composite sample; the filled symbols relate to the long T_2 component of the extracted sample; the symbols with dots correspond to the short T_2 component of the extracted material.

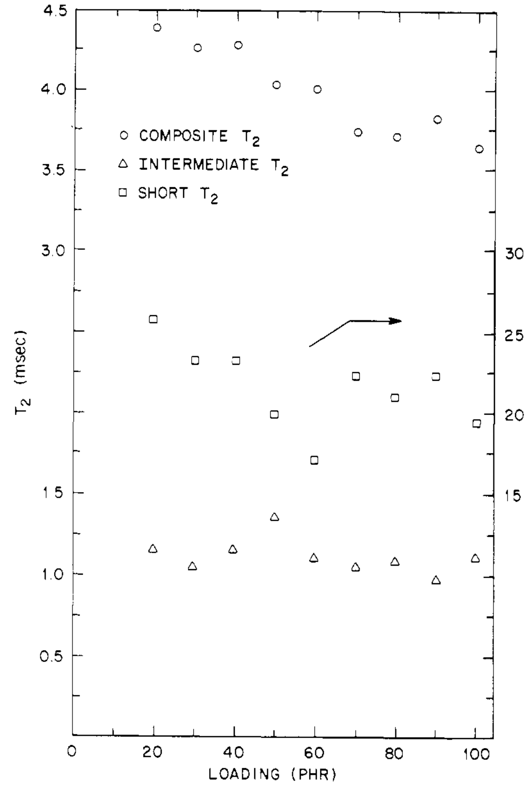

Figure 6. Plateau T_2 magnitudes of Figure 5 plotted as a function of carbon black loading.

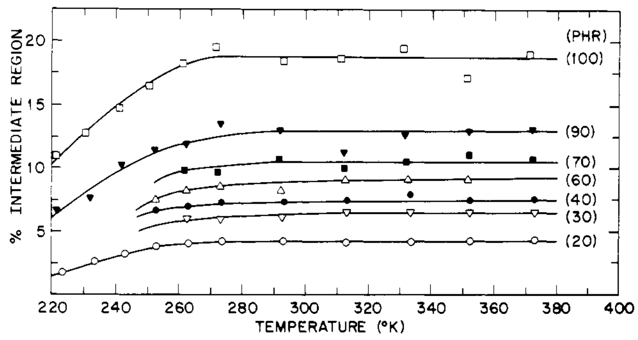

Figure 7. Relative amounts of the loosely bound intermediate region plotted as a function of temperature for various carbon black loadings.

magnitude of this short T_2 value with increase in temperature, and (iii) the reduced plateau levels achieved by the long T_2 component in the filled material.

With the extracted materials, 8E and 16E, it was just possible to resolve two $T_{1\rho}$ components in the vicinity of the minimum and this fact, coupled with the relatively small sample volume following the extraction procedures, imposed a limitation upon the accuracy of these data points. As a result it was difficult to ascertain with certainty the effects of the filler on the $T_{1\rho}$ minimum. In the T_1 data there was a slight increase in the magnitude and substantial broadening of the minimum while the high-temperature T_2 plateau was further reduced as compared with either the unfilled rubber or the composite unextracted material.

The overall NMR data for samples 8E and 16E reflect a change, with the introduction of filler, in the distribution of correlation times describing the segmental motions toward longer correlation times.[19,37] The effect is undetected in No. 8 and 16 because of the dominant presence of a large amount (~80%) of unbound rubber. The leveling off in T_1 for sample 8E at low temperatures is typical of the free radical or impurity controlled relaxation effects[39] already observed in some filled elastomers.[14]

The T_2 behavior in the filled materials is in broad agreement with the results of Kaufman et al.[15] and Nishi.[23] However, the increase in the value of the short T_2 with temperature indicates that the tightly bound layer is not completely immobilized over the complete temperature range. Motions of a limited nature appear to set in at temperatures which roughly correspond to those at which the loosely bound molecules attain their full motional vigor (Figures 3 and 4) indicating a tight coupling between the two regions. We shall defer further more detailed consideration of the tightly bound layer to a later section of the paper.

Dependence of Bound Rubber Content on Carbon Black Loading. T_2 measurements, the most informative of the NMR parameters, were recorded over a wide temperature range for a series of samples in which the carbon black loading was varied from 20 to 100 phr (samples 3–11). Representative plots are presented in Figure 5. The T_2 plateau dependence on carbon black above T_g is more evident in Figure 6 where T_2 plateau values at temperatures in the region of 360–380 K are plotted as a function of loading for the composite material, the outer bound region, and the tightly bound region, respectively. T_2 for the composite material decreases essentially linearly with increase in loading while T_2 for the loosely bound rubber is independent of loading within the limits of experimental error. The apparent downward trend in the short T_2 with increased loading is somewhat fortuitous in view of the scatter in the data (Figure 5) and is by no means typical of other selected temperature regions. The decrease in the composite T_2 with loading reflects an increase in the relative amounts of the two shorter T_2 components contributing to the composite T_2 signal rather than to a decrease in their magnitudes. This is clear from Figure 7 which illustrates the

Table III
Data Relating to the Bound Rubber Content as a Function of Loading

Sample No.	Loading, phr	m_c[a]	ϕ[b]	ϕ'[c]	γ[d]	BR,[e] % Inner region	BR,[e] % Outer region	ΔR_T, Å[f]	ΔR_I, Å[f]
3	100	0.50	0.35	0.70	0.20	4.7	18.7	80.3 ± 20.0	16.0 ± 5.6
4	90	0.47	0.33	0.75	0.21	3.4	13.0	61.5 ± 15.4	12.9 ± 4.5
5	80	0.44	0.30	0.78	0.15	1.8	10.3	52.0 ± 13.0	7.8 ± 2.7
6	70	0.41	0.27	0.74	0.22	2.9	10.4	66.4 ± 16.6	14.6 ± 5.1
7	60	0.38	0.25	0.75	0.19	2.1	9.0	61.4 ± 15.4	11.7 ± 4.1
8	50	0.33	0.21	0.77	0.23	1.8	6.2	55.6 ± 13.9	12.8 ± 4.5
9	40	0.29	0.18	0.71	0.16	1.5	7.6	76.4 ± 19.1	12.2 ± 4.3
10	30	0.23	0.14	0.67	0.20	1.6	6.4	90.6 ± 22.7	18.1 ± 6.3
11	20	0.17	0.10	0.69	0.16	0.8	4.2	83.0 ± 20.8	13.3 ± 4.7

[a] m_c = mass fraction of carbon black in composite. [b] ϕ = volume fraction of carbon black in composite. [c] ϕ' = volume fraction of carbon black in extracted bound rubber. [d] γ = fraction of short T_2 component in bound rubber. [e] BR = percentage bound rubber in composite. [f] ΔR_T, ΔR_I = thickness of the total and inner bound layers, respectively.

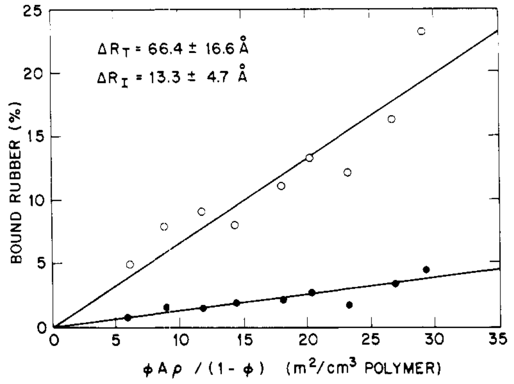

Figure 8. Pliskin–Tokita plot (see text) for samples 3–11. ΔR_I and ΔR_T are the thicknesses of the inner (●) and total (○) bound layers, respectively.

variation with loading of the intensity of the intermediate or loosely bound region as a function of temperature. The intensities increase with loading and are independent of temperature above 270 K which in fact corresponds to the temperature at which the magnitudes of T_2 begin to level off (Figure 5).

Table III contains the various parameters of interest for this series of samples. The bound layer thicknesses were computed according to the formula of Pliskin and Tokita (eq 1).[9] The parameter BR of their formalism has been interpreted, respectively, as the volume percent of bound rubber in the inner layer computed from the intensity of the short T_2 component and the total bound rubber determined from the unextractable rubber content. The respective plots of $\phi A\rho/(1-\phi)$ vs. BR are shown in Figure 8. The lines are constrained to pass through the origin, that is $G = 0$, and f is set equal to unity on the basis of earlier work on *cis*-PB by Pliskin and Tokita.[9] The quoted accuracies for ΔR are based upon the following principal sources of error in the dependent parameters: BR, ±15%; A, ±10%;[1,2] and γ, ±10%.[29]

It is evident from Figure 8 that the Pliskin–Tokita formula is reasonably obeyed for the inner tightly bound layer as well as the total layer. The inner layer accounts for about ⅕ of the total layer thickness which is comparable to observations in natural rubber.[23] The total layer thickness ΔR_T = 66.4 ± 13.3 Å is in reasonable agreement with the value of 74.7 ± 3.2 Å computed by Pliskin and Tokita.[9]

Dependence of Bound Rubber Content on Type of Carbon Black. For the series of samples loaded to 50 phr with various carbon blacks the high-temperature T_2 plateau values

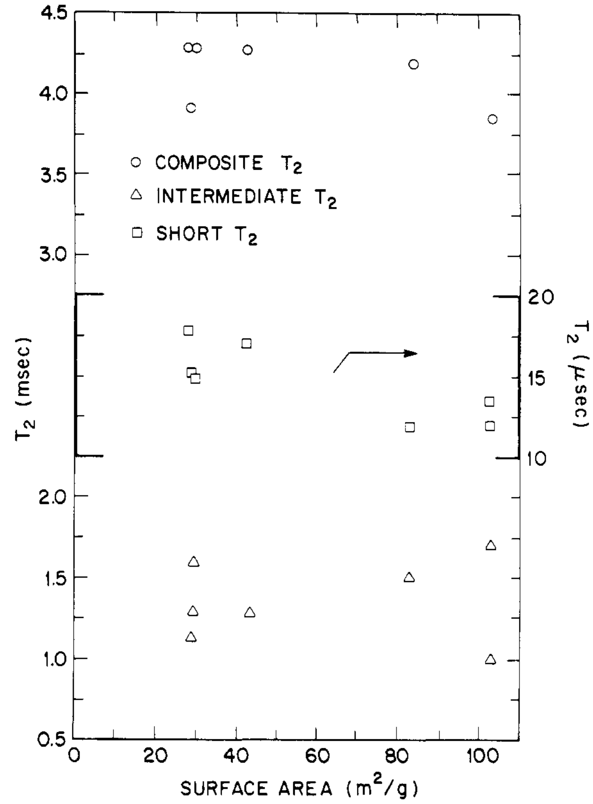

Figure 9. Plateau magnitudes of Figure 9 plotted as a function of carbon black surface area.

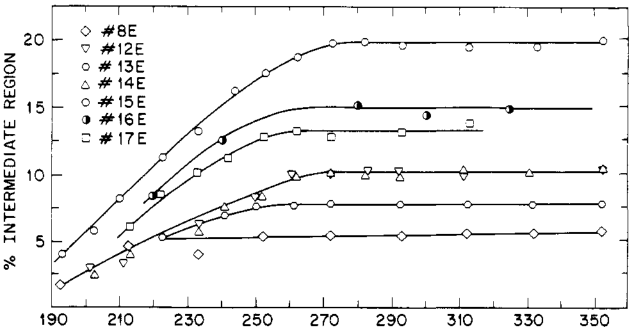

Figure 10. Relative amounts of the loosely bound intermediate region as a function of temperature for the samples indicated on the diagram.

Table IV
Data Relating to the Bound Rubber Content as a Function of Carbon Black Type

Sample No.	Carbon black (50 phr)	ϕ'	γ	BR, % Inner region	BR, % Outer region	ΔR_T, Å	ΔR_I, Å
12	SRF	0.67	0.21	2.9	10.1	86.2 ± 21.6	19.2 ± 6.7
13	GPF	0.73	0.21	2.1	7.7	67.2 ± 16.8	14.4 ± 5.0
8	GPF	0.77	0.23	1.8	6.2	54.9 ± 13.7	12.3 ± 4.3
14	FEF	0.67	0.22	2.9	10.1	60.2 ± 15.1	13.4 ± 4.7
15	HAF	0.54	0.13	2.8	19.6	53.9 ± 13.5	6.7 ± 2.3
16	ISAF	0.60	0.15	2.7	15.3	34.7 ± 8.7	5.2 ± 1.8
17	ISAF	0.64	0.13	2.0	13.4	29.7 ± 7.4	3.9 ± 1.4

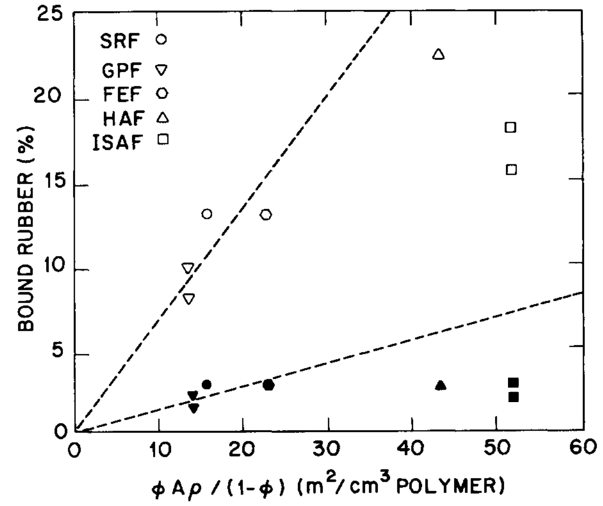

Figure 11. Pliskin–Tokita plot with surface area A as the carbon black variable. The dashed lines are the loci of Figure 8 which are included for comparison.

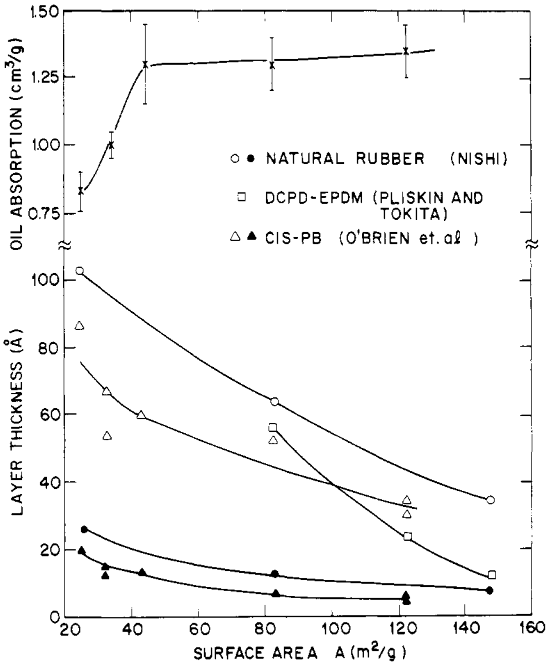

Figure 12. Computed layer thicknesses plotted as a function of surface area A for the three sets of data indicated. The X's denote the dependence of mineral oil absorption upon A.

do appear to depend upon the type of carbon black used. Figure 9 shows the plateau behavior as a function of the specific surface area, A. The composite T_2 decreases with increasing surface area while the intermediate T_2, characteristic of the loosely bound region, is essentially independent of A within experimental error. There is also some evidence of a decrease in the short T_2 as A is increased. The temperature dependence of the intensity of the intermediate T_2 component is portrayed for the various carbon blacks in Figure 10. It is evident from this figure and Table IV that the amount of bound rubber increases with surface area as observed earlier.[1,9] An exception to this general trend, however, is the HAF loaded sample which exhibits a greater bound rubber content than the ISAF loaded rubber although the surface area is smaller. It is interesting to note that the two samples, 16 and 17, each loaded with ISAF carbon black by different procedures exhibit roughly the same bound rubber content.

The thickness ΔR_T and ΔR_I for the total and inner bound layers, respectively, have been determined as before according to eq 1. The plot of BR vs. $\phi\rho A/(1-\phi)$ is shown in Figure 11 from which it is apparent that the mutual dependence is no longer linear. The dashed lines which represent the loci obtained from Figure 8, with loading as the variable, are included for comparison. It is evident from Figure 11 and Table IV that the calculated layer thicknesses are lower for those carbon blacks with the greater surface area. Layer thicknesses are plotted as a function of surface area in Figure 12 along with the corresponding results extracted from the data of Nishi[23] on natural rubber and of Pliskin and Tokita[9] for dicyclopentadiene–EPDM (for which the bound rubber was extracted with toluene at room temperature). There is considerable uncertainty associated with the 56.7 Å bound layer magnitude in the Pliskin–Tokita results since only two data points were available in their plot of BR vs. $\phi A\rho/(1-\phi)$. The similarity in the overall behavior of the three sets of data tends to indicate that the apparent decrease in layer thickness with increase in A is principally a carbon black phenomenon. The plot of mineral oil absorption vs. A, also included in Figure 12, lends credence to this argument for the following reason. Mineral oil absorption provides a measure of the relative structure of carbon blacks or, alternatively stated, their relative tendency to agglomerate.[40] Thus, it is much more difficult to achieve efficient dispersion of the finer carbon blacks such as ISAF by comparison with those blacks which exhibit a high degree of chain structure. The surface area available to the polymer molecules is reduced as a result of agglomeration and the parameter f in eq 1 becomes progressively smaller than unity as A is increased. If corrected A values were used in Figure 11 the plot of BR vs. $A\rho\phi/(1-\phi)$ may well be linear in support of a bound layer thickness and independent of the carbon black used.

Of course the above considerations do not take account of the relative surface activities of the carbon blacks as was the case with earlier studies.[9,23] For example, it is known that carbon blacks with higher oxygen content tend to develop more bound rubber than those with lower amounts of oxygen.[40] However, the finer carbon blacks such as ISAF have a greater percentage of oxygen than the coarse blacks[1,2] and this should enhance rather than depress the bound rubber content. We have measured the unpaired electron spin content of the various carbon blacks used in this study as a possible measure of surface activity and find no trend as a function of surface area of the black. Thus, in the absence of more detailed information about the relative surface activities it is assumed that the tendency to agglomerate is the dominant mechanism responsible for the smaller observed bound layer thicknesses as *A* is increased.

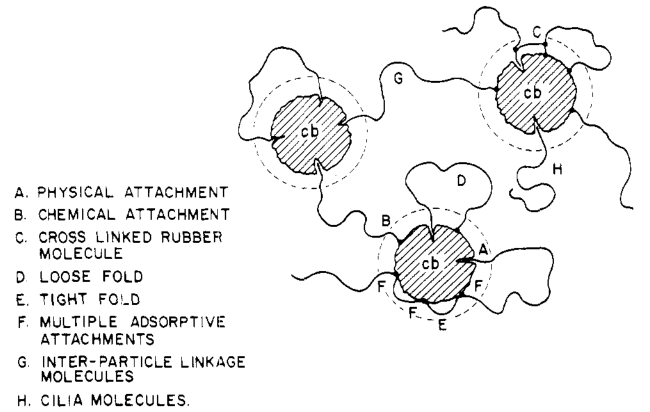

Figure 13. Diagram which illustrates the model for the filled rubber system discussed in the text; the dashed circles denote the boundaries of the tightly bound region.

The Nature of the Bound Layer. In order to understand the nature of the interaction between the butadiene and carbon black we must focus attention upon the behavior of the short T_2 which has been identified with a tightly bound layer. We recall the following important experimental facts: (i) Motions of a limited nature set in at temperatures which roughly correspond to those at which the loosely bound rubber attains its full motional vigor; there is an increase in the short T_2 of about a factor of 2. (ii) The T_2 magnitudes attained at high temperatures appear to be lower in the high surface area carbon blacks (Figure 9). (iii) The results of Nishi[23] on natural rubber show that the degree of molecular motion and the fraction of the tightly bound layer, as characterized by the short T_2, are not affected by swelling in CCl_4 at room temperature. (iv) The general observation that the interaction is both physical and chemical in nature.[1] (v) The fact that the bound rubber content increases with storage time.[40]

The model chosen to describe the rubber–carbon black interaction must at least be compatible with these experimental observations. One such model, shown in Figure 13, embodies and expands upon several existing concepts on the nature of the interaction. Extensive free radical interactions must be possible in view of the preparative history of the composite materials. Many polymer free radical species are created in the mastication process by chain scission under conditions of extensive rotational and translational mobility (sample preparation is carried out at temperatures well in excess of the glass–rubber transition temperature). Thus there is ample opportunity for free radical polymer–polymer (cross-linking) and polymer–carbon black interactions (B and C on the diagram). Chemical interactions such as there have been discussed in detail by Watson.[41]

Following the suggestion by Dr. D. C. Douglass,[42] we visualize one form of physical interaction (A) as one in which the rubber molecule penetrates the porous surface of the carbon black particle. An equilibrium situation exists when the energy required for penetration is balanced by the loss of entropy of the rubber molecule. As a result, that portion of the molecule which is embedded within the pore can remain essentially rigid even at high temperatures and under severe swelling conditions. There is an obvious time dependence with this interaction in keeping with (v) above. From Figure 9 it would appear that the effect is most pronounced with the fine carbon blacks because of the persistence of the rigid T_2 value to high temperatures.

The molecular linkages, *G*, between carbon black filler particles have been discussed at some length by Blanchard and Parkinson[43,44] and elaborated upon by Bueche.[45]

The adsorption of polymers onto filler particles has been examined in detail, principally by Frisch and co-workers.[46–51] In particular the concept of multiple adsorptive attachments (F) emerges from the theory of Frisch, Simha, and Eirich[46] and it has been found in the case of polystyrene adsorption onto ISAF black that each adsorbed molecule is held at the surface by an average of 50 adsorbed segments per chain.[51]

The presence of unterminated chains or cilia (H) and folds (D, E) are of special interest in an NMR context since their motions have been quantitatively analyzed for the analogous case of a semicrystalline polymer.[52–54] A recent paper[52] has treated the fold as a worm-like chain with ends constrained to a plane crystal lamellar surface and T_2 magnitudes have been computed for each of the N elements which make up the fold. The results, which are equally valid here, show that elements close to the anchored chain ends experience, at most, motions of a very limited nature. Similar conclusions apply to those elements of the cilia molecule close to the end which is anchored.[54] Most all elements in the tightly folded configuration experience the same limits upon the motions available to them.[52] Referring to Figure 13 then, it is reasonable to assume that all molecules or portions of molecules within the confines of the tightly bound layer (dashed circles) may be characterized by a rigid or near rigid T_2. On the other hand, the theoretical calculations imply that the folds and cilia must be extremely long in order to provide T_2 magnitudes approaching those which characterize the loosely bound region.

One might expect at first sight that susceptibility variations arising from the presence of carbon black in the filled material should be considered in the interpretation of T_2 data. However, Schaefer, Chin, and Weissman[21] have concluded from their selective saturation or hole burning ^{13}C experiments on filled *cis*-polyisoprene that there is no significant line broadening due to either micro- or macroscopically inhomogenious magnetic fields associated with such susceptibility variations. Similar conclusions derive from multiple-pulse ^{1}H line narrowing experiments on *cis*-polyisoprene[22] and line width studies on polyethylene filled with iron oxide.[55]

Finally we address ourselves to the apparent difficulty in rationalizing the observation of exponential T_1 decay with the presence of a tightly bound layer. Typically, in composite materials the tightly bound layer accounts for ~2–3% and the loosely bound layer ~10–20%. These low intensities would tend to rule out the observation of a discrete T_1 component from the tightly bound region while the similarity in the T_1's from the loosely bound molecules and the unbound rubber precludes the observation of a separate component from the loosely bound layer.[24] Further, it has been often demonstrated that spin diffusion is a particularly efficient mechanism in the mutual relaxation of two coupled spin systems to produce a single exponential decay.[27,56–58] Even partial coupling of the two bound layers would be sufficient to produce a single T_1 in view of the relatively low proportion of the tightly bound material present.[58]

In summary then, the observation of a single T_1 is entirely compatible with the immobile layer in the immediate vicinity of the filler particle. Indeed the terms "immobile" and "loosely bound layers" may give the misleading impression of the existence of distinctly separate regions as exist, for example, in semicrystalline polymers. Rather, the observation of two T_2 components is more an artifact of the NMR method in its ability to distinguish between extremes in the motions experienced by different parts of a single rubber molecule.

Conclusions

Consideration of the NMR data presented in this paper in the context of previously published results leads to the following conclusions with regard to the nature of the carbon black–rubber interaction.

1. The assymetric ESR signal, observed in SBR rubber,[31] has been detected in our *cis*-polybutadiene material and is most likely due to paramagnetic impurities.

2. At temperatures well in excess of T_g, the molecular motional behavior in unfilled *cis*-PB cannot be described adequately in terms of isotropic liquid-like motions characterized by a single correlation time.[19] This result is consistent with findings from other polymers.

3. The introduction of fillers leaves T_g essentially unchanged.

4. The T_2 data are consistent with the existence of a tightly bound layer in the immediate vicinity of the filler particle in addition to a loosely bound component. The inner layer accounts for about $\frac{1}{5}$ of the total bound layer thickness.

5. In the context of the Pliskin–Tokita analysis,[9] the bound layer decreases in thickness as the specific surface area of the carbon black is increased. This observation probably derives from the increased tendency of the finer carbon blacks to agglomerate.

6. The tightly bound layer can be explained adequately in terms of the limited motions available to those segments of the polymer molecule close to the point of interaction with the carbon black particles. The analogy with fold and cilia configurations in semicrystalline polymers is made. The model proposed to describe the filled rubber system elaborates upon existing ideas and is consistent with experimental observations.

7. It has been demonstrated that the observation of exponential T_1 decay is not necessarily at odds with the existence of a tightly bound layer.

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