Electron Spin Resonance Studies of Spin-Labeled Polymers. 10. Polyethylene Containing Ketone Side Groups

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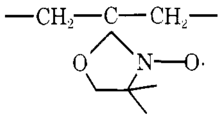
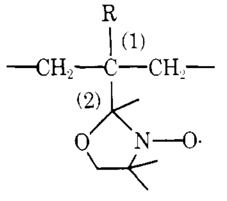
ABSTRACT: Two low-density polyethylenes containing 2% copolymerized methyl vinyl ketone and methyl isopropenyl ketone respectively were spin labeled by converting a small fraction of ketone groups to oxazolidine-*N*-oxyl radicals. Spin concentrations were ≤ 1 per 10^5 monomer units. Correlation times were measured by analysis of the ESR spectra of the polymers in the solid state and in solution. In solid polymer at 220–330 K relaxation with an activation energy of 25.1 kJ mol^{-1} was attributed to the β process. The results support the conclusions from a previous study of polyethylene in which the oxazolidine-*N*-oxyl label was rigidly held with respect to the main chain. In the present case the spin labels show faster and possibly more isotropic motion in both the solid state and solution.

In part 8 of the present series[1] we studied the relaxation processes in low density polyethylene by the spin-labeling technique. The polymer contained 0.5% copolymerized carbon monoxide (PE/CO) and was spin labeled at the ketone group with a dimethyl oxazolidine-*N*-oxyl radical (I). Subsequent experiments, which are reported here, are concerned with two other low-density polyethylenes, one containing 2% copolymerized methyl vinyl ketone (PE/MVK) and the other 2% methyl isopropenyl ketone (PE/MIPK). Both polymers were treated following the synthesis given previously[1] to yield pendant oxazolidine-*N*-oxyl radicals (II).


I



II

R = H for PE/MVK
R = CH_3 for PE/MIPK

In structure II the oxazolidine-*N*-oxyl radical should have greater motional freedom with respect to the main chain than in I where the ring is rigidly fixed with the axis of the *z* component of the hyperfine tensor parallel to the extended chain direction.

The results described here show that in the bulk polymer the motion of II is slightly more rapid and possibly more isotropic than that of I. The increased mobility of II is also reflected in shorter correlation times for rotational diffusion, τ_c, of the labeled PE/MVK and PE/MIPK in solution. Unfortunately, the nitroxides II (particularly from PE/MIPK) were less stable in the bulk polymer than I and it was impracticable to make measurements in the region of the α relaxation or in the melt.

Experimental Section

ESR spectra of the labeled polymers in bulk and in *p*-xylene solution (5–7% wt/vol) were recorded as described previously[1] (Figure 1).

Spin concentrations (from comparison with a diphenylpicrylhydrazyl standard) were 1 spin per 100 000 monomer units for PE/MVK and 1 spin per 235 000 for PE/MIPK.

The isotropic nitrogen hyperfine coupling constant, a_N, was 40.3 ± 0.1 MHz for both labeled polymers.

In order to calculate τ_c from ESR spectra comprising motionally narrowed lines it is necessary to correct the observed line width for inhomogeneous broadening due to unresolved proton couplings. The correction procedure, which has been described fully elsewhere,[2] involves spectral simulations from which appropriate correction curves are constructed. With the labeled PE/MVK and PE/MIPK polymers the correction curves for the PE/CO polymer[1] were again employed to calculate values of τ_c. In these calculations the anisotropy factors b and $\Delta\gamma$ for both polymers were 320 MHz and $(2.96 \pm 0.50) \times 10^4$ rad G^{-1} s^{-1}, respectively, where $b = (4\pi/3)[A_{zz} - \frac{1}{2}(A_{xx} + A_{yy})]$ and $\Delta\gamma = -(|\beta|/\hbar)[g_{zz} - \frac{1}{2}(g_{xx} + g_{yy})]$. The comparable values for the PE/CO polymer were $b = 317$ MHz and $\Delta\gamma = 3.19 \times 10^4$ rad G^{-1} s^{-1}.

Results and Discussion

The ESR spectra of the solid spin-labeled polymers were typical of magnetically dilute, slowly tumbling nitroxides (Figure 1a). In solution the ESR spectra assumed the three-line rotationally narrowed form shown in Figure 1b.

(a) The β-Relaxation Process. The extrema separation ($2A_{zz}$) of the solid state spectrum of both polymers decreases with increasing temperature (Figure 2). There is no significant difference in behavior between the labeled PE/MVK and PE/MIPK polymers in their "amorphous" [3] state over the temperature range 220–330 K. After annealing the PE/MVK polymer, by holding it at its melting point for 10 min then cooling slowly, the extrema separation versus temperature curve is displaced as shown in Figure 2.

From changes in $2A_{zz}$ compared with the rigid limit value ($2A_{zz}^* = 64.8 \pm 0.9$ G, 182 ± 2.5 MHz) correlation times were calculated for Brownian diffusion by the method of Shimshick et al.;[4,5] these are shown in Figure 3 as an Arrhenius plot. After annealing, the correlation times and activation energy of PE/MVK diminish (Figure 3 and Table I). The labeled PE/CO polymer behaved broadly in the same manner and the relaxation in the temperature range 220–350 K was attributed to the β process (cooperative segmental motion). This mechanism presumably prevails with PE/MVK and PE/MIPK but the values of τ_c and the activation energies for these polymers are slightly lower, in both the amorphous and annealed states, than for the PE/CO polymer (Figure 3 and Table I). The greater motional freedom of the labels II over I probably accounts for this decrease. The effect of annealing was explained previously[1] on the basis that slow cooling induces ordering in the polymer forcing abnormalities, including spin-labeled segments, into more amorphous regions of the polymer matrix where movement is less restricted.

The greater motional freedom of label II compared with I is qualitatively obvious from inspection of the ESR spectra of labeled PE/MVK and PE/CO polymers. As the temperature is raised the broad line spectrum typical of a solid-state nitroxide eventually assumes the three-line rotationally narrowed form. In labeled PE/MVK this type of spectrum is clearly defined at 320 K (Figure 1c) but comparable narrow lines are not evident in labeled PE/CO until ca. 365 K (see Figure 2b of ref 1).

In an additional experiment two sample tubes containing spin-labeled PE/CO and PE/MVK were immersed in boiling

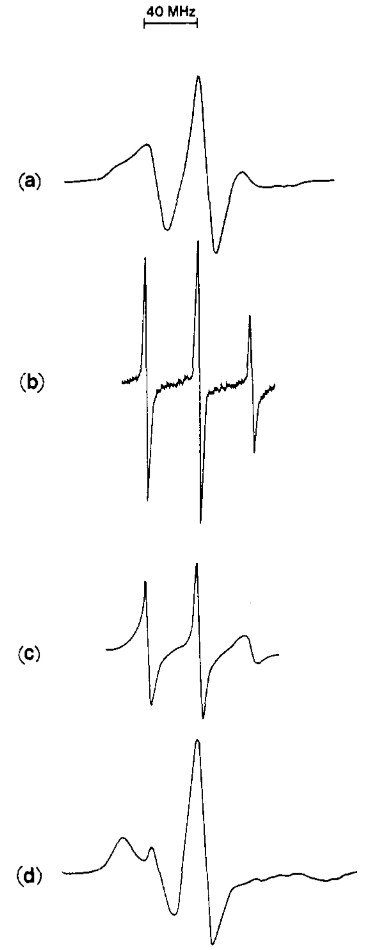


Figure 1. ESR spectra of spin-labeled polyethylenes: (a) solid PE/MVK at 299 K, (b) PE/MVK in xylene solution (5% wt/vol) at 296 K, (c) solid PE/MVK at 321 K, (d) solid PE/CO at 323 K (from ref 1).

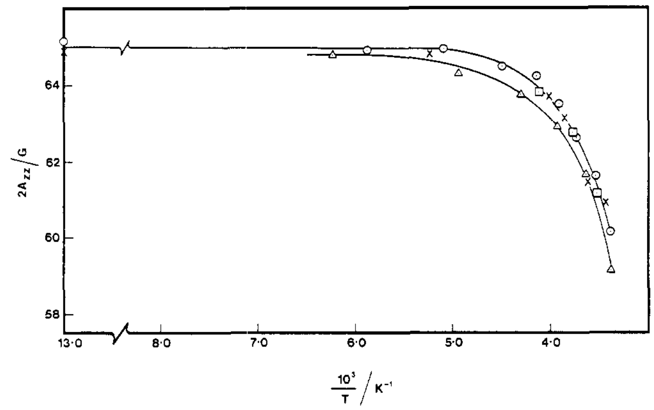


Figure 2. Change in extrema separation ($2A_{zz}$) with temperature of solid labeled polyethylenes: (⊙) amorphous[3] PE/MVK; (×) amorphous PE/MIPK, (△) annealed PE/MVK; (⊡) quenched PE/MVK.

toluene (384 K, the melting point of low-density polyethylene) for 15 min then quenched in liquid nitrogen. A series of extrema separation measurements were then made from ca. 200 K up to room temperature. For PE/MVK the values of $2A_{zz}$ lie on the curve for the amorphous polymer (Figure 2) indicating that in the quenched polymer the labeled segments are in an environment similar to the amorphous state. With the PE/CO polymer (Figure 4) the values of $2A_{zz}$ lie on the curve for the amorphous polymer only in the low-temperature range and by the time the temperature has reached room temperature the $2A_{zz}$ value lies on the curve for annealed PE/CO. On lowering the temperature again, the points for PE/CO follow the curve for the annealed polymer but those for PE/MVK remain on the curve for the amorphous polymer (compare Figures 2 and 4). It seems that the labeled PE/CO can rearrange to an extent at room temperature to eliminate some of the disorder induced by melting and quenching. However, the disorder induced by precipitation of PE/CO (following the labeling procedure) appears to be permanent because the $2A_{zz}$ value of freshly precipitated (amorphous[3]) polymer shows no tendency to diminish toward that of annealed PE/CO polymer. This odd behavior could be a consequence of strains built into the bulk polymer by the quenching treatment. Around room temperature these strains may be partially relaxed by chain movements which push the labeled segments into the less crystalline regions of the polymer. Such strains do not exist in the precipitated polymer. We must assume that similar strains are present in the quenched PE/MVK polymer, and that these can relax without significantly affecting the environment of the spin label. Again this may be a consequence of the greater mobility of the label II.

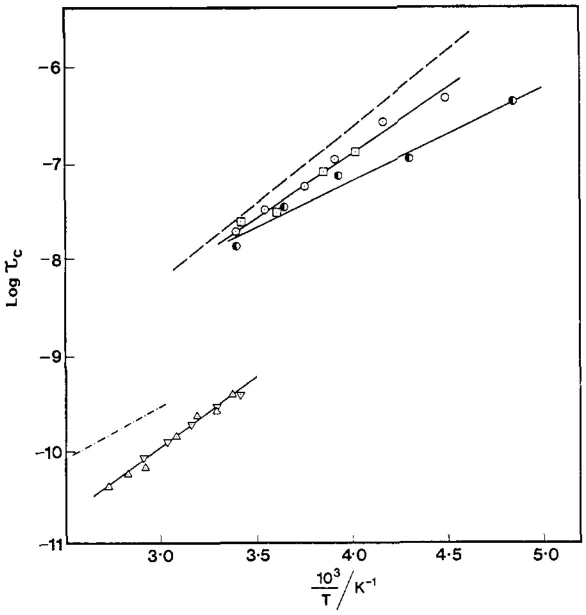


Figure 3. Correlation map for labeled polyethylenes (τ_c in s): (⊙) amorphous PE/MVK; (⊡) amorphous PE/MIPK; (◐) annealed PE/MVK; (△) PE/MVK in xylene solution (5% wt/vol); (▽) PE/MIPK in xylene solution. (- - -) Amorphous PE/CO and (- · -) PE/CO in xylene solution (from ref 1).

Table I
Activation Energies for Relaxation in Labeled Polyethylenes

Region	Polymer	Temp range, K	Activation energies, kJ mol^{-1} Amorphous	Annealed
β transition	PE/MVK PE/MIPK	220–330	25.1 ± 1.2	18.3 ± 1.8
	PE/CO[a]	220–350	28.6 ± 2.0	23.9 ± 1.5
Solution (in xylene)	PE/MVK PE/MIPK	293–367	27.6 ± 1.1	
	PE/CO[a]	330–390	22.9 ± 1.9	

[a] From ref 1.

(b) Anisotropic Motion. In ref 1 it was noted that in the temperature range 320–340 K the spectrum of solid labeled

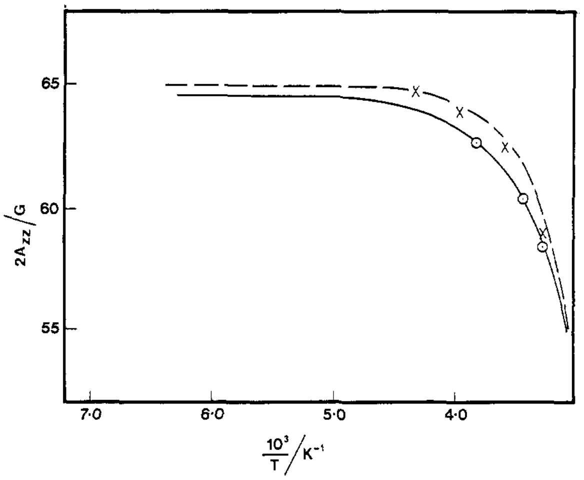


Figure 4. Change in extrema separation ($2A_{zz}$) with temperature of labeled PE/CO: (×) increasing T; (⊙) decreasing T. Broken and solid lines for amorphous and annealed PE/CO, respectively (from ref 1).

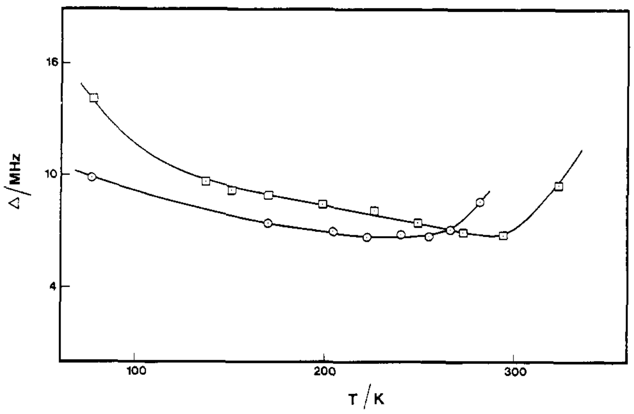


Figure 5. Change with temperature in half-width at half-height (Δ) for low-field lines of solid-state spectra: (⊙) amorphous PE/MVK; (⊡) amorphous PE/CO (from ref 1).

PE/CO showed a marked subsplitting of the low-field peak (Figure 1d, also Figure 2 of ref 1). This was interpreted as arising from anisotropic motion of the spin label. The alternative explanation, that the low-field "fork" arises from a motionally narrowed spectrum superimposed on the powder spectrum, seemed improbable as it would require a significant proportion of the chain segments to rotate with a correlation time $<10^{-9}$ s, i.e., a very rapid relaxation. The concept of anisotropic motion of the label in PE/CO is also consistent with its structure. The oxazolidine-*N*-oxyl radical (I) is rigidly held with its z axis aligned in the direction of the main chain so that the onset of crankshaftlike motion involves only rotation in the x–y plane and tends to average out the anisotropy between the x- and y-tensor elements. The resulting motional narrowing of the lines due to these elements could give rise to the sharp subsplitting of the low-field line. Until large scale reorientations occur at higher temperatures the direction of the z axis would remain effectively fixed.

Support for the above interpretation came from measurements of the half-width at half-height (Δ) of the low- and high-field peaks. For slow, isotropic motion Δ should increase from the rigid limit value with increasing temperature,[6] but the labeled PE/CO polymer showed a marked decrease in Δ as the temperature was increased from 77 K (the rigid limit temperature), and this behavior was also attributed to anisotropic motion.[1]

The motion of label II in the PE/MVK and PE/MIPK polymers should have more isotropic character through rotations about the C(1)–C(2) axis in cooperation with crankshaft motion. The absence of any subsplitting in the spectra of these labeled polymers (Figures 1a and 1c) is therefore not surprising. By the same token, however, the change in Δ with temperature for these polymers should also reflect this greater motional freedom and an increase in Δ as the temperature rises above the rigid limit would be expected. Contrary to this, however, Figure 5 shows that *Δ for the low-field line* of PE/MVK decreases with increasing temperature, though rather less acutely than for PE/CO. This may indicate a lower degree of anisotropy in the motion of label II but it also casts some doubt on the validity of employing the Δ-temperature plot as a diagnosis of anisotropic motion. It has been pointed out that factors, such as electron-nuclear hyperfine interactions, which contribute to the rigid-limit width may be quickly averaged out with the onset of molecular motion, resulting in a decrease in Δ.[6] This decrease can occur when rotation of the spin label is isotropic and could account for our observations, particularly on the labeled PE/MVK polymer. Satisfactory resolution of this point may require spectral simulation experiments which we hope to conduct in the future.

(c) Relaxations in Solution. The correlation map in Figure 3 also includes data for the labeled PE/MVK and PE/MIPK polymers in p-xylene solution. The line for the corresponding measurements on PE/CO is included for comparison purposes. There is no measurable difference between the PE/MVK and PE/MIPK polymers but at any given temperature the value of τ_c for these polymers is about half that of the labeled PE/CO polymer. Therefore the difference in mobility between labels I and II is more obvious in solution than in the bulk polymer.

If the temperature of the xylene drops below 333 K the polyethylene comes out of solution as a cloudy, gelatinous precipitate. When this occurs the lines in the ESR spectrum of labeled PE/CO broaden abruptly signifying a marked increase in τ_c. The ESR spectra of the labeled PE/MVK and PE/MIPK polymers in contrast show no marked change on precipitation and the values of τ_c lie on the same Arrhenius plot as those from solution spectra. Clearly the labels II have as much mobility in the precipitated swollen state as in solution while the movement of the label I is greatly hindered on precipitation. This somewhat surprising effect must again have its origin in the greater motional freedom of label II compared with I.

The activation energy for the relaxation of labeled PE/MVK and PE/MIPK polymers in solution from Figure 3 is 27.6 ± 1.1 kJ mol^{-1}. Following previous practice[2] of deducting the activation energy for viscous flow of the solvent (9.0 kJ mol^{-1}) yields 18.6 kJ mol^{-1} as the energy barrier to internal rotations of the spin-label II, compared with 13.9 kJ mol^{-1} for the internal barriers in labeled PE/CO. The latter figure was ascribed to the barrier to segmental rotation in the "isolated" polymer chain. This assignment is reasonable because the barrier is quite close to that found for internal rotation in the ethane molecule (12 kJ mol^{-1} in the gas phase) and because relaxation of the label I requires rotation of one or more segments. In the case of label II less significance can be attached to the internal barrier since rotational motion of II is more complex than that of I.

Although rotation of label II is significantly faster than that of label I the energy of activation for II is the greater. It follows that label II must owe its greater mobility to a higher preexponential factor than that of I. This is simply a consequence of the greater conformational freedom of II.

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References and Notes

(1) A. T. Bullock, G. G. Cameron, and P. M. Smith, *Eur. Polym. J.*, **11,** 617 (1975).
(2) A. T. Bullock, G. G. Cameron, and P. M. Smith, *J. Phys. Chem.*, **77,** 1635 (1973).
(3) The term "amorphous" is used loosely here and in ref 1 to indicate that the polymer was not treated to induce crystallization.
(4) R. C. McCalley, E. J. Shimshick, and H. M. McConnell, *Chem. Phys. Lett.*, **13,** 115 (1972).
(5) A. T. Bullock, G. G. Cameron, and P. M. Smith, *J. Polym. Sci., Part A-2*, **9,** 499 (1971).
(6) R. P. Mason and J. H. Freed, *J. Phys. Chem.*, **78,** 1321 (1974).

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:

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

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