Polymer Journal, Vol. 10, No. 5, pp 557—558 (1978)

The Effects of Magnetic Susceptibility Inhomogeneities on T_2 Data from Carbon Black Filled *cis*-Polybutadiene

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(Received January 25, 1978)

ABSTRACT: This communication examines the contribution of local magnetic field gradients in carbon black-filled elastomers to the NMR linewidth. It is concluded that the extremely short T_2 observed in the filled material is not due to these field gradients but derives from severe motional constraints placed upon the rubber molecules in the immediate vicinity of the filler particles.

KEY WORD Elastomer / NMR / Carbon Black / Susceptibility /

Magnetic resonance methods have provided useful and detailed information on carbon black-rubber systems.[1–6] NMR linewidth data have been particularly fruitful in indicating the presence of three distinct regions in filled rubbers, as characterized by the molecular mobility of the constituent rubber chains: a region of unbound rubber, bound rubber in an outer shell around the carbon black which is rather less mobile, and an inner shell of tightly bound rubber which experiences very limited motions on the T_2 time scale of $\sim 10^{-4}$ s.[2,5,6]

In establishing this model, no account was taken of susceptibility (χ) variations in the filled material. Earlier work on polyisoprene,[3,4] using high-resolution NMR methods, has showed that inhomogeneities in χ produced no observable line broadening. However, these experiments were sensitive only to the highly mobile fraction and in all probability provided no information on the effects, if any, on the rubber which resides close to the carbon black surface.

The purpose of this note is to demonstrate that even in the interfacial region between the carbon black and the rubber phase, χ is unlikely to offer a significant contribution to the line shape and that the extremely short T_2's observed in these systems are, in fact, due to severe restrictions imposed on the motion of the interfacial rubber.

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Estimates of magnetic field gradients introduced by the carbon black particles in an applied magnetic field B_0 are based upon a model of carbon black spheres, of susceptibility χ, embedded in a polymer matrix of susceptibility zero. Because of the smallness of χ this calculation will assume that the field disturbance introduced by the carbon particles is a superposition of the disturbances caused by single particles. This problem is the magnetic analog of the dielectric sphere in an electric field. The local magnetic field (or, more correctly, the local magnetic induction) $\Delta B(r, \theta)$ arising from the magnetization of the carbon black spheres may be written[7]

$$\Delta B(r, \theta) = k \times \frac{3\cos^2\theta - 1}{r^3} \tag{1}$$

where $k \simeq B_0 \chi a^3$ and (r, θ) are polar coordinates in a frame of reference which has B_0 along the z-axis. a is the radius of the carbon black sphere.

The distribution in the local field $\Delta B(r, \theta)$ which characterizes the inhomogeneous dipolar broadening of the line shape in the vicinity of the carbon black particle is denoted $P(r, \theta)$. Thus, the free induction decay of the magnetization vector M may be written as the Fourier transform of $P(r, \theta)$.[8]

$$M(t) = \iint \cos[\gamma t \Delta B(r, \theta)] P(r, \theta) \mathrm{d}r \mathrm{d}\theta \tag{2}$$

where

$$P(r, \theta)\mathrm{d}r\mathrm{d}\theta = N \sin\theta\, r^2\, \mathrm{d}r\mathrm{d}\theta \tag{3}$$

and γ is the gyromagnetic ratio for protons. Writing $r^3 = a^3 u$ and $\xi = \cos\theta$, eq 3 may be written

$$M(t) \propto \int_1^{(R/a)^3} \int_0^1 \cos\left\{\frac{\gamma k t(3\xi^2-1)}{a^3 u}\right\} \mathrm{d}\xi \mathrm{d}u \tag{4}$$

$(R-a)$ is the thickness of the bound rubber layer.[6] Considering a further change of variables

$$\omega = \frac{6\gamma k t}{\pi a^3 u} \quad \text{and} \quad s = \sqrt{\omega}\, \xi \tag{5}$$

eq 4 becomes

$$M(t) \propto \int_1^{(R/a)^3} \left\{ \frac{\cos \pi\omega/6}{\sqrt{\omega}} \int_0^{\sqrt{\omega}} \cos\left(\frac{\pi}{2} s^2\right) \mathrm{d}s + \frac{\sin \pi\omega/6}{\sqrt{\omega}} \int_0^{\sqrt{\omega}} \sin\left(\frac{\pi}{2} s^2\right) \mathrm{d}s \right\} \mathrm{d}u \tag{6}$$

The integrals inside the curly brackets are the familiar Fresnel integrals which are tabulated.[9] The expression inside the brackets, denoted $Q(\omega)$, is the contribution to the total magnetization from an infinitesimal shell of radius r. A plot of $Q(\omega)$ *vs.* ω is shown in Figure 1, for which the time for $Q(\omega)$ to decay to half the initial magnitude is $\omega_{1/2} = 2.33$. Substituting $\omega_{1/2}$ into the expression for ω in eq 5 provides a reasonable approximation to T_2.[10]

$$T_2 \cong \frac{2.33\pi r^3}{6\gamma k} \tag{7}$$

Data relevant to several carbon black materials studied earlier[6,11] are listed in Table I. Also included are the T_2's calculated for the shell of rubber on the surface of the carbon black particle, T_2^a, and for the outermost shell of bound rubber, T_2^R.

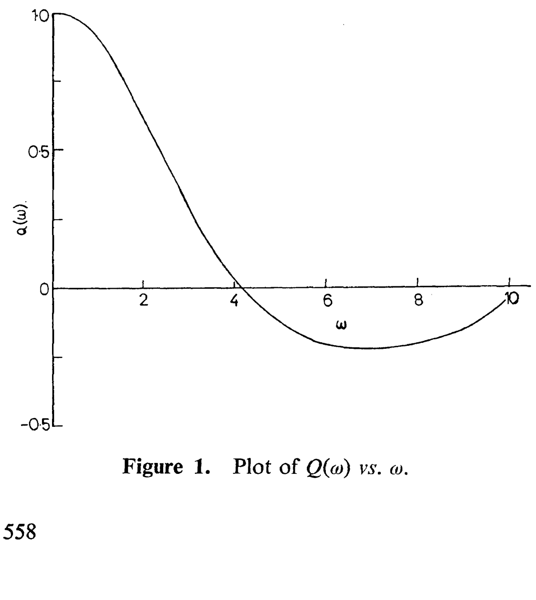

Figure 1. Plot of $Q(\omega)$ *vs.* ω.

Table I. Data pertaining to various carbon blacks along with calculated T_2's ($B_0 = 9395$ G)

Carbon black[a]	X, 10^6	a, nm	R, nm	T_2^a, s	T_2^R, s
GPF	0.42	27.5	28.7	0.0116	0.0132
SRF	−1.48	35.5	37.4	0.0033	0.0038
FEF	−1.38	19.0	20.3	0.0035	0.0043
HAF	−1.59	12.0	12.7	0.0031	0.0036
ISAF	−1.51	11.3	11.8	0.0032	0.0037

[a] GPF, general purpose furnace; SRF, semi-reinforcing furnance; FEF, fast extrusion furnace; HAF, high abrasion furnace; ISAF, intermediate super abrasion furnace.

The results in Table I show that T_2's of the order of milliseconds are predicted from magnetic field inhomogeneities due to the magnetism of the carbon black particles. Thus, our earlier interpretation of the observed T_2's of the order of 10^{-5} s in terms of a tightly bound layer of rubber in the immediate vicinity of the carbon black particles[6] would appear to be an entirely reasonable one.

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