

Effect of Oxidized Carbon Black on the Mechanical Properties and Molecular Motions of Natural Rubber Studied by Pulse NMR

SHIGEO ASAI, HIROMUNE KANEKI, MASAO SUMITA, and KEIZO MIYASAKA

Department of Organic and Polymeric Materials, Faculty of Engineering, Tokyo Institute of Technology, Ookayama 2-12-1, Meguro-ku, Tokyo 152, Japan

SYNOPSIS

The mechanical properties such as elastic modulus and stress-relaxation and spin-spin relaxation time T_2 from pulse NMR were measured for surface-oxidized carbon-black-filled natural rubber. The extent of reinforcement increased with CB volume percent in the range of 0–30%. At a given CB percent, this quantity increased by surface oxidation of fillers and decreasing filler size. From pulse NMR experiment, it was found that there were three components in rubber molecules which have different values for T_2 . Stress-relaxation time and elastic moduli fitted one master curve against effective volume, fraction which is the sum of filler and bound rubber fraction. It was found that the distance between particle surfaces is the most important factor influencing reinforcing properties of filled polymers.

INTRODUCTION

The effect of a dispersed phase on the mechanical properties of various polymeric composite materials has been treated both theoretically^{1–3} and experimentally^{4–6} by a number of authors. There is, however, little agreement among investigators, and the specific effects caused by interactions between the matrix and dispersed phase are not clearly defined as yet. Major fillers have been surface-modified to improve adhesive properties to matrices which facilitate interaction between particles and polymers. Oxidation of carbon black produces acid groups on its surface. It is well known that incorporation of surface-oxidized CB into rubber molecules produces a significant increase in bound rubber due to strong interactions between its active carbon black and rubber molecules.^{7,8} It is important to characterize and control the level of dispersion or agglomeration of small particles in polymeric composites. Many procedures have been used through the years to characterize dispersion and the extent of interaction between fillers and matrices. These include optical microscopy,^{9–13} electron microscopy,^{14,15} small angle

light¹⁶ and X-ray scattering,^{17,18} mechanical energy dissipation,¹⁹ direct measurement of immobilized phase,²⁰ and pulse NMR.^{7,8,21} Pulse NMR studies have produced important information on the structure of bound rubber phases produced by mechanical mixing.^{8,21} In this paper, we investigate the effect of surface oxidized carbon black on the mechanical properties and molecular motion of natural rubber using pulse NMR.

EXPERIMENTAL

Composite Sample Preparation

Natural rubber (RSS No. 1, molecular weight $M_n = 100\,000$, from Nihon Zeon Co.) and two kinds of carbon black (Seast 300, 27 nm in diameter and Seast V, 56 nm in diameter from Tokai Carbon Co.) were used in this study. In order to investigate the effect of the surface activity of fillers, Seast 300 was oxidized in boiled nitric acid for 2 h. By this treatment, polar groups such as carboxyl and hydroxyl groups are incorporated in the surface of CB. Natural rubber was mixed with a given amount of carbon black in a two roll mill for 10 min at the temperature of 55°C. Prior to mixing, the carbon black was dried at 80°C for 24 h under vacuum. Films about 0.5 mm

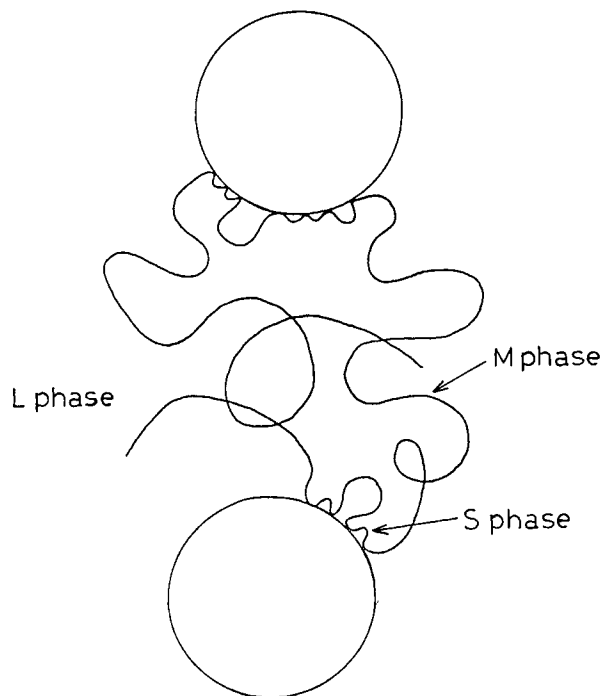


Figure 1 Schematic representation of the bound rubber molecules.

thick were compression-molded from the rubber-carbon mixtures at the temperature of 55°C for 1 min under a pressure of 180 kg/cm², followed by quenching into ice water.

NMR Measurements

The NMR measurements were performed on a Nihon Bruker PC-20 Spectrometer operated at 20 MHz in the diode mode. The spin-spin relaxation time (T_2) was measured by the solid echo method at 40°C. For each measurement 1024 points were collected and averaged with a cumulative number of 100 and an attenuation of 30, and analyzed by an NEC PC-9801 computer.

Tensile Test and Stress Relaxation Measurements

Tensile tests were conducted on a Toyo Baldwin Tensilon UTM-III at a crosshead speed of 20 mm/min at 23°C.

The stress-relaxation time τ_m was measured by adding 75% strain to the composite films at the temperature of 23°C. Although this strain is larger than that of a conventional stress relaxation test, this time may be one of the measures for the extent of reinforcing effect. The τ_m is the time required for the stress to be reduced 1/e of its initial value.

RESULTS AND DISCUSSION

The spin-spin relaxation time T_2 was estimated from the free induction decay (FID) of the echo signal. The FID can be generally expressed as an exponential function by the equation

$$M(t) = M(0) \cdot \exp(-t/T_2) \quad (1)$$

The logarithmic form (2) usually yields a linear relationship between the amplitude of magnetization M and the decay time t :

$$\ln[M(t)] = \ln[M(0)] - t/T_2 \quad (2)$$

where $M(0)$ is the initial FID amplitude.

In the case of polymers, the FID is usually a combination of several components. Assink and Wilkes found two components in linear and crosslinked polyurethanes²² corresponding to the relaxation of protons in the hard and soft segment domains, respectively. In this study, three components, having

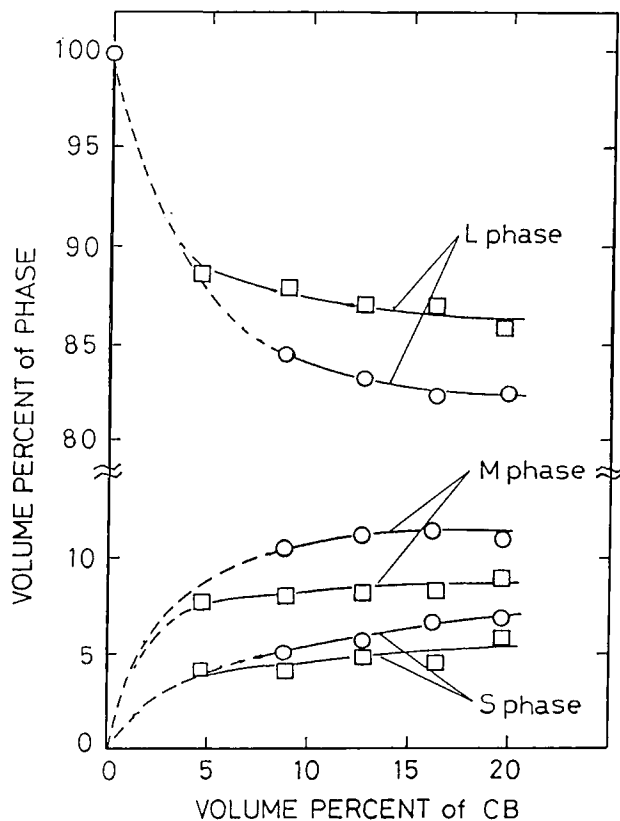


Figure 2 Volume fraction of S, M, and L phases as a function of volume fraction of CB: (□) unoxidized CB; (○) oxidized CB.

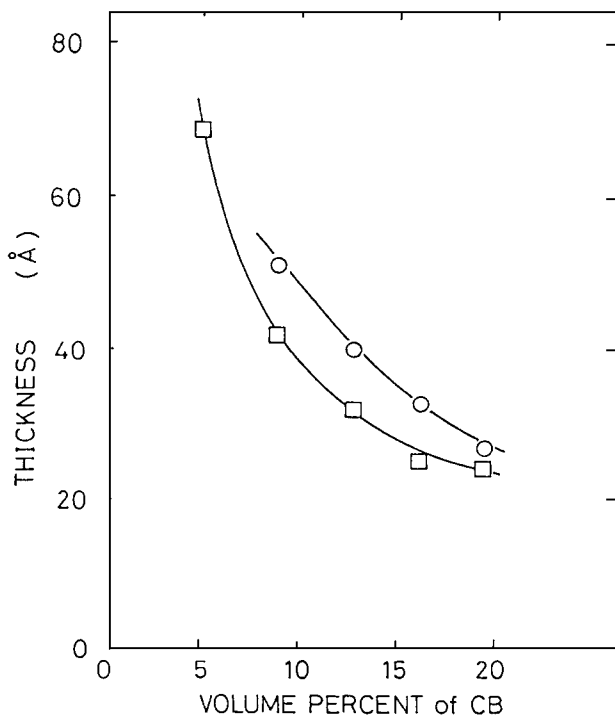


Figure 3 Bound rubber thickness as a function of volume fraction of CB: (□) unoxidized CB; (○) oxidized CB.

an FID which can be shown by the following equations, were clearly observed:

$$\begin{aligned}
 M(t) = & M(s) \cdot \exp\{-[t/T_2(s)]^{\mu(s)}\} \\
 & + M(m) \cdot \exp\{-[t/T_2(m)]^{\mu(m)}\} \\
 & + M(l) \cdot \exp\{-[t/T_2(l)]^{\mu(l)}\} \quad (3)
 \end{aligned}$$

where s , m , and l express the short T_2 , medium T_2 , and long T_2 component, respectively, and μ represents the Weibull coefficient, which was found to be about 2.0 for $\mu(s)$, $\mu(m)$, and $\mu(l)$. The $M(s)$, $M(m)$, and $M(l)$ are obtained from each intersection in the semilog plot of FIDs, and the fraction of each phase can be calculated according to the following equations:

$$\begin{aligned}
 F(s) &= M(s)/[M(s) + M(m) + M(l)] \\
 F(m) &= M(m)/[M(s) + M(m) + M(l)] \\
 F(l) &= M(l)/[M(s) + M(m) + M(l)] \quad (4)
 \end{aligned}$$

The short T_2 component corresponds to the NMR signal from the tightly bound rubber molecules (S phase); the medium T_2 component corresponds to the NMR signal from the loosely bound rubber molecules (M phase); and the long T_2 component cor-

responds to the NMR signal from the rubber molecules which are not under the influence of CB (L phase). Figure 1 shows the schematic representation of the bound rubber molecules. For our samples, the values of $T_2(s)$, $T_2(m)$, and $T_2(l)$ were about 20, 200, and 500 μ s, respectively. The value of $T_2(l)$ was equal to that of natural rubber. These two type of bound rubber for CB-filled rubbers have been reported by others.^{7,8,21}

Figure 2 shows plots of the fraction (%) of S, M, and L phases with different T_2 values, calculated from eq. (4), against the volume percent of CB. The volume percent of S and M phases is increased for samples containing oxidized CB. For the natural rubber containing oxidized CB, the fraction of S phase increases with the increase of the CB content, but the fraction of M phase changes little with the increase of the CB content. The main reason is considered to be the overlap of the CB particles in the M phase when the CB content is large.

Figure 3 shows the bound rubber thickness as a function of the volume percent of CB. The bound rubber thickness was calculated using the volume of the S and M phases and the surface area of CB. It can be seen that the bound rubber thickness decreases with the increase of the CB content. It is

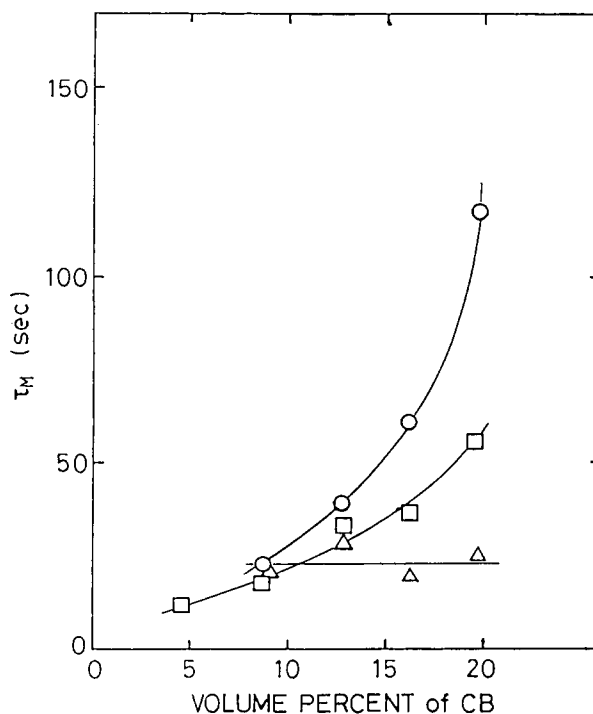


Figure 4 Stress-relaxation time as a function of volume fraction of CB: (□) unoxidized CB (27 nm); (○) oxidized CB (27 nm); (△) unoxidized CB (56 nm).

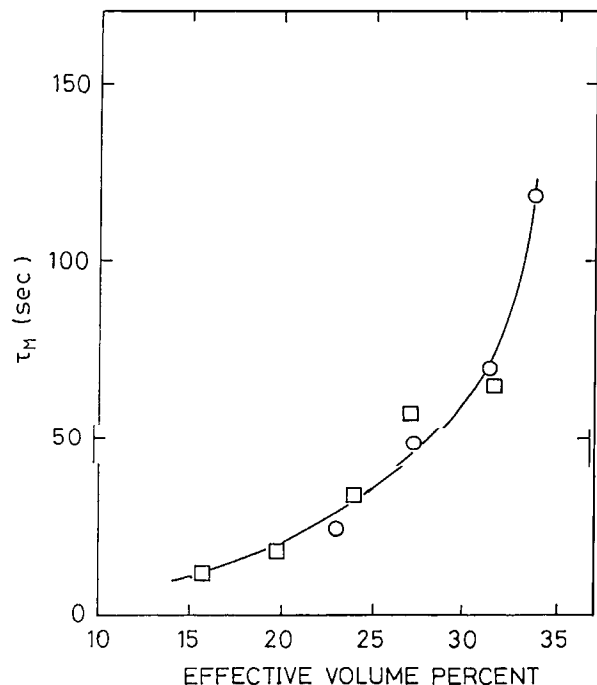


Figure 5 Stress-relaxation time as a function of effective volume percent: (□) unoxidized CB; (○) oxidized CB.

clear that the oxidative treatment of CB increases the bound rubber thickness.

Figure 4 shows the stress relaxation time τ_m as a function of the volume percent of CB. The stress relaxation time τ_m is the time required for stress to decrease to $1/e$ of its initial value. The values of τ_m of the samples which contain CB of 56 nm in diameter hardly vary until the volume percent of CB is 20%. On the other hand, for the samples which contain CB of 27 nm in diameter, the τ_m increases with the increase of CB content, and the oxidative treatment of CB enhances that tendency. In other words, the oxidative treatment of CB enhances the reinforcement effect of CB. The bound rubber formed by the oxidative treatment of CB is considered to be the principal cause of the reinforcement effect. So, we regarded the bound rubber as a part of the CB particles, and we calculated the effective volume percent which was defined as the sum of the volume percent of CB and the bound rubber (S and M phase).

Figure 5 shows the stress relaxation times τ_m as a function of the effective volume percent. It can be seen that the plots of τ_m for the samples which contain oxidized CB and nonoxidized CB lie on one master curve. Similarly, we can obtain one master curve for the elastic modulus. Figure 6 shows the elastic modulus E as a function of the effective volume percent. When we regard the bound rubber as

a part of the CB particles, we can thus obtain one master curve for the mechanical properties such as the stress-relaxation time τ_m and the elastic modulus E .

Figure 7 shows the stress relaxation times τ_m as a function of the interparticle distance. It can be seen that the value of τ_m increases significantly when the interparticle distance is less than 200 Å. The interparticle distance of the samples which contain CB of 56 nm in diameter is longer than 200 Å, and this is the main cause of the small values of τ_m for those samples in Figure 4. Thus the interparticle distance is an important factor to the reinforcement effect of CB. This distance corresponds to the diameter of the Gaussian chain in this natural rubber. Wu reported that the ligament thickness, i.e., the surface to surface interparticle distance, is the single parameter determining whether rubber-particle-filled polymers will be tough or brittle.^{23,24} In our cases, when the average ligament thickness, i.e., surface to surface interparticle distance is smaller than the diameter of the Gaussian chain in this rubber molecules, fillers have significant reinforcing effect.

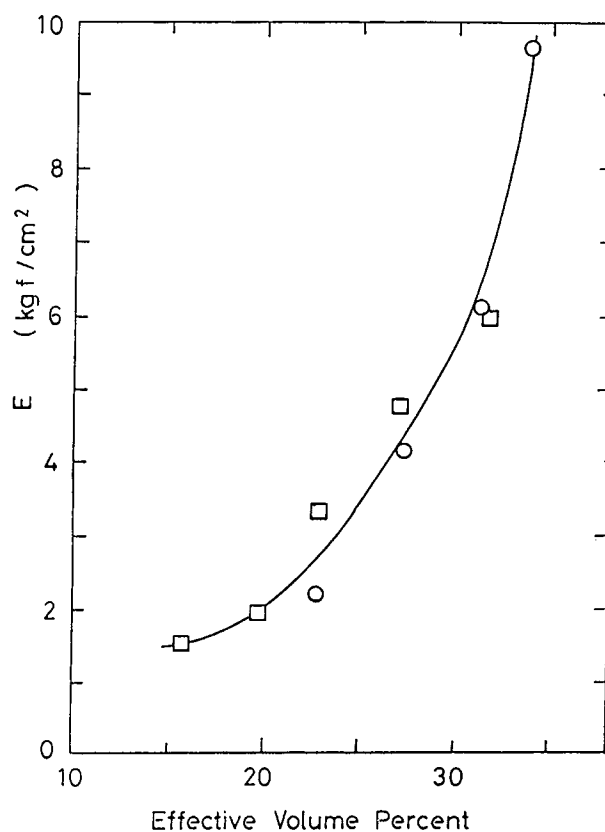


Figure 6 Elastic modulus as a function of effective volume percent: (□) unoxidized CB; (○) oxidized CB.

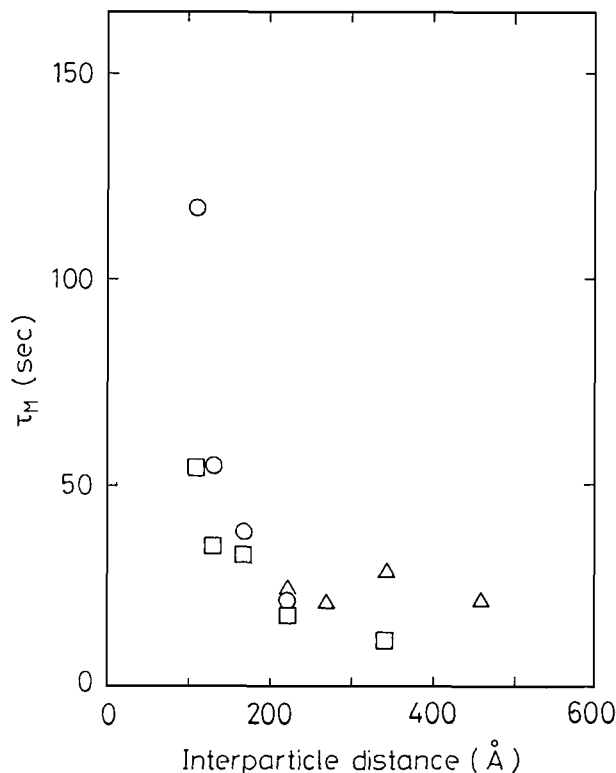


Figure 7 Stress-relaxation time as a function of interparticle distance: (\square) unoxidized CB (27 nm); (\circ) oxidized CB (27 nm); (\triangle) unoxidized CB (56 nm).

CONCLUSION

The spin-spin relaxation time T_2 was measured by pulse NMR for oxidized CB filled natural rubber (NR) as a function of CB concentration and particle size. Three components (S, M, and L phase), having a different value of T_2 , were observed. The proportion of the S phase increased as CB concentration increased. The proportion of the S phase was higher at a given CB concentration if the CB was oxidized. At the same concentration of CB, the mechanical properties (elastic modulus and stress-relaxation time) depended on the surface activity of CB and the particle size, but, considering the volume of the bound rubber (carbon gel) calculated from the proportion of the S and M phase, they fitted one master-curve. The distance between particle surfaces was

one of the most important factors in NR reinforcement.

REFERENCES

1. V. Zorll, *J. Appl. Polym. Sci.*, **10**, 1315 (1966).
2. E. H. Kerner, *Proc. Phys. Soc. (London)*, **B69**, 808 (1956).
3. S. Uemura and M. Takayanagi, *J. Appl. Polym. Sci.*, **10**, 113 (1963).
4. R. F. Randel and T. L. Smith, *Am. Rocket Soc. J.*, **31**, 599 (1961).
5. I. Galperin and T. K. Kwei, *J. Appl. Polym. Sci.*, **10**, 673 (1966).
6. R. F. Randel, *Trans. Soc. Rheol.*, **2**, 53 (1958).
7. H. Serizawa, T. Nakamura, M. Ito, K. Tanaka, and A. Nomura, *Polym. J.*, **15**(3), 201 (1983).
8. H. Serizawa, M. Ito, T. Kanamoto, K. Tanaka, and A. Nomura, *Polym. J.*, **14**(2), 149 (1982).
9. C. H. Leigh-Dugmore, *Rubber Chem. Technol.*, **29**, 1303 (1956).
10. N. A. Stamp and H. E. Railsback, *Rubber World*, **151**, 41 (1964).
11. A. I. Medalia, *Rubber Age*, **97**, 82 (1965).
12. Y. Suetsugu, J. L. White, and T. Kyu, *Adv. Polym. Technol.*, **7**, 427 (1987).
13. E. M. Dannenberg, *Ind. Eng. Chem.*, **44**, 813 (1952).
14. K. Min and J. L. White, *Rubber Chem. Technol.*, **60**, 361 (1987).
15. B. B. Boonstra and A. I. Medalia, *Rubber Chem. Technol.*, **36**, 15 (1963).
16. Y. Suetsugu, T. Kikutani, T. Kyu, and J. L. White, *Colloid. Polym. Sci.*, **268**, 118 (1990).
17. R. J. Young and D. H. A. Al-Khudhairy, *J. Mater. Sci.*, **21**, 1211 (1986).
18. G. D. Wignall, N. R. Farrar, and S. Morris, *J. Mater. Sci.*, **25**, 69 (1990).
19. K. D. Ziegel, *J. Colloid Int. Sci.*, **29**, 1, 72 (1969).
20. I. Pliskin and N. Tokita, *J. Appl. Polym. Sci.*, **16**, 473 (1972).
21. K. Fujimoto and T. Nishi, *Nippon Gomu Kyokaishi*, **43**, 465 (1970).
22. K. A. Assink and G. L. Wilkes, *J. Appl. Polym. Sci.*, **26**, 3689 (1981).
23. S. Wu, *J. Appl. Polym. Sci.*, **35**, 549 (1988).
24. A. Margolia and S. Wu, *Polymer*, **29**, 2170 (1988).

Received October 5, 1990

Accepted January 3, 1991