Changes of Spin–spin Relaxation Time for EPR Composites During Mixing Process

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Synopsis

The changes of the mobility of rubber molecules for carbon black-filled EPR composites during mixing process in an internal mixer have been elucidated from T_2 measurement using pulsed nuclear magnetic resonance (NMR). The thickness of the tightly bound region which is formed by the direct interaction with carbon black was stabilized with mixing but the restriction of the molecular mobility increased with further mixing. The amount of the loosely bound region increased considerably throughout the mixing, indicating that this region is formed by entanglement and crosslinking of the molecules. T_2 of the mobile region which is a predominant part in the composites is independent of the mixing time. EPR has the thinner tightly bound shell and longer T_{2S} compared with EPDM, showing the effect of unsaturated bond in EPDM which can become a strong bond site with carbon black.

INTRODUCTION

The interaction between carbon black and rubber molecules is academically interesting and technologically important to improve the characteristics of rubber products. We reported[1] the morphological and some characteristic changes of EPR composites during mixing process, but information about the interaction between EPR and the carbon black was not provided. The direct information can be obtained by analyzing spin–spin relaxation pattern using pulsed nuclear magnetic resonance (NMR) technique, because spin–spin relaxation time (T_2) is associated with the degree of molecular mobility. Kubo et al.[2] reported the relation between molecular mobility and NMR spectra and showed that the mobile part in the molecule has a longer T_2 and the immobile part has a shorter T_2. Recently, attention has been paid to applying this method to rubber composites. For example, the composites of natural rubber,[3,4] *cis*-polybutadiene,[5,6] and EPDM[7] have been studied with pulsed NMR technique. But the details of the interaction between EPR and carbon black during the mixing process have not been reported. We now report the change of molecular mobility for EPR throughout the mixing by measuring T_2 using pulsed NMR.

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EXPERIMENTAL

Sample Preparation

The characteristics of the commercial EPR used in this study were as follows. EPDM; ML_{1+4}(100°C): 76, third monomer: 5-ethylidene-2-norbornene, iodine value: 17.6, propylene content: 44.9 wt%, EPR; ML_{1+4}(100°C): 49, iodine value: 0, propylene content: 53.1 wt%.

They were non-oil-extended rubbers. The compounding conditions were the same as the previous report,[1] as follows. The recipe is rubber 100 phr, FEF carbon black 80 phr, oil 80 phr, zinc oxide 5 phr, and stearic acid 1 phr. Commercial FEF carbon black used was Seast So, of which the average diameter is 41 Å. They were compounded in a Brabender Plasticoder at 70°C with rotor velocity of 50/33.3 rpm. The compounds were sampled at mixing times of 30 s, 2 min, 5 min, and 10 min for EPDM and at 10 min for EPR.

The amount of EPR-bound rubber was determined by a solvent extraction method. Small pieces of the composites which were sampled at each mixing time were dissolved in xylene for 48 h at room temperature. The volume of the bound rubber was measured after passing through 300 mesh wire net and dried in an oven. The correct amount of carbon black in the bound rubber was obtained from thermal balance measurements by decomposing the rubber component with heating. The dried samples were inserted into 10-mm diameter NMR tubes.

NMR Measurement

We applied solid echo sequence from which proton spin–spin relaxation time can be computed by analyzing the FID curves. A Bruker NMR spectrometer, CXP-200 type, was operated at a frequency of 200 MHz for 1 h at 30°C. The spectrometer was equipped to control the sample temperature ± 1°C. The duration of a 90° pulse and recovering time were 2 μm and 7 μm respectively. Analysis of the FID curves was done by an NEC computer, AOS-350 type, which minimized the least-square errors between the fitted function and spectra.

RESULTS AND CONCLUSION

The volume percentage of the EPDM-bound rubber to the total rubber during the mixing process is plotted in Figure 1. The fraction of the bound rubber increased rapidly until around 2 min and then increased slightly. The FID curves of the bound rubber at each mixing time are shown in Figure 2. The curves were normalized for convenience to compare with each other. The difficulty in analyzing FID curves is the low sensitivity of NMR instrument, mainly due to low magnetic field. It is noticeable in the low noise curves in Figure 2, which could allow accurate analysis of the data to obtain the details of the interaction between the rubber and the carbon black.
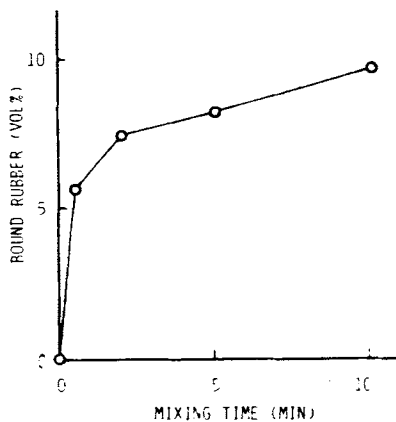
Fig. 1. Variations of the bound rubber volume percentage to the total rubber for the EPDM composite with mixing time.

The FID curves were best fitted by the sum of 2 exponentials as follows within the limits of experimental errors, indicating that the bound rubber has two rubber components.

$$A_{exp}(-t/T_{2L}) + B_{exp}(-t/T_{2S})$$

where t is the time, $A + B = 1$, and longer T_2 is expressed as T_{2L}, shorter one is T_{2S}.

Nishi et al.[3] examined the nature of the bound rubber of natural rubber to which a swelling agent was introduced using pulsed NMR technique. The molecular motion in the tightly bound region remained unaltered and
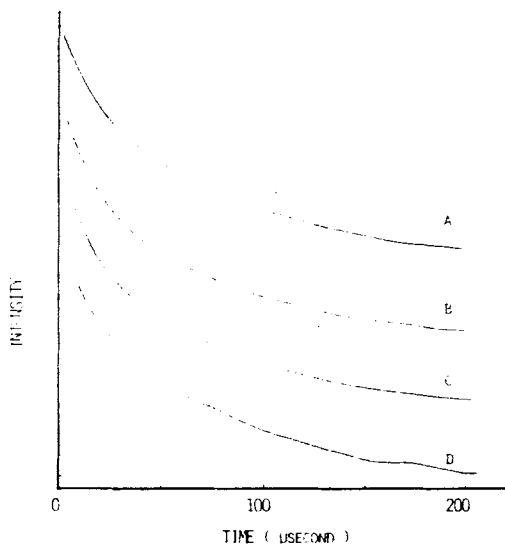

Fig. 2. Spin–spin relaxation decays for the EPDM-bound rubber at each mixing time: A: 30 s mixing, B: 2 min mixing, C: 5 min mixing, D: 10 min mixing.

molecular motion in the loosely bound region increased rapidly with increasing solvent concentration, showing the characteristics of each region. O'Brien et al.[5] demonstrated the three distinct region model for carbon filled *cis*-polybutadiene composites from T_2 measurement. The three regions are: a tightly bound rubber lying adjacent to the carbon black, a loosely bound region, and a mobile rubber region. The thickness of the tightly bound shell was estimated. These results indicate the existence of the three regions which have different T_2 values, that is different degrees of molecular mobility, in the rubber composites.

It is reasonable to think that the T_{2S} component in this study corresponds to the tightly bound region existing in the vicinity of the carbon black and T_{2L} corresponds to the loosely bound region which is less restrained compared with T_{2S} component. The changes of T_{2S} and T_{2L} during the mixing process for the EPDM are shown in Figure 3. T_{2S} decreased rapidly with mixing time, which indicates that the tightly bound rubber became more restrained with the increased direct interaction between the tightly bound rubber and the carbon black throughout the mixing. On the other hand, T_{2L} decreased slightly with the mixing, showing increased restriction of the loosely bound rubber but its change with mixing time is not as rapid as T_{2S} region. The influence of the mixing is more pronounced for the change in T_{2S}. In the case of EPDM composites at each mixing time, the FID curves were fitted well by one exponential component, of which T_2 was 3.3×10^{-4} s and did not change throughout the mixing. This T_2 component corresponds to the mobile region which is a predominent part of the composite and is almost independent of the mixing. On the premise that the tightly bound rubber surrounds the carbon black surface immediately, the thickness of the tightly bound layer was calculated mathematically. The fraction of the tightly bound component was obtained with pulsed NMR technique and the carbon black surface area was calculated from its diameter. The thickness
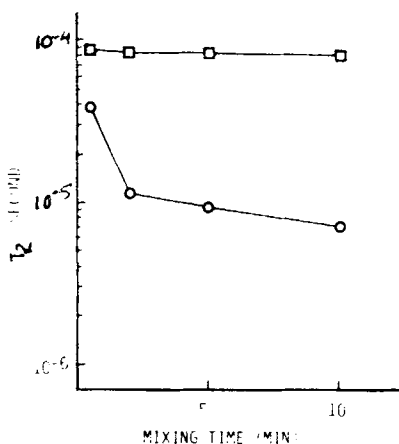

Fig. 3. Variations of T_2 for the EPDM-bound rubber as a function of mixing time: ($\square$): T_{2L} for the loosely bound region, ($\bigcirc$): T_{2S} for the tightly bound region.

of the total bound rubber on the carbon surface was calculated in the same way in order to determine the contribution of the loosely bound region at each mixing time. The relationship between the thickness of the tightly bound layer, total bound rubber on the carbon black, and the mixing time are shown in Figure 4. The thickness of the tightly bound layer is extremely thin at 30 s mixing and increased pronouncedly until 2 min mixing, and is stabilized after 2 min. Whereas, the thickness of the bound rubber increased almost linearly throughout the mixing, indicating that the loosely bound region increased in volume after the stabilized shell of the tightly bound layer was formed.

In the previous paper,[1] the morphological changes of the composites during the mixing were observed as follows. The pellets of the carbon black broke into smaller pieces at early mixing stage (around 30 s mixing) and then the agglomerates of the carbon became thinner and are incorporated into the rubber phase within 2 min of mixing. After mixing, rapid morphological changes were not observed. The thinner layer and longer T_{2S} of the tightly bound rubber until 2 min mixing in this study is parallel to this morphological figure. A large amount of the carbon agglomerates did not form the thick tightly bound layer and the interaction with the carbon black was weaker at this stage, which brought about longer T_{2S}. The completion of the tightly bound layer around 2 min mixing is parallel to the completion of the homogeneous dispersion of the carbon agglomerates into the rubber phase. It is interesting that the thickness of the tightly bound layer was stabilized after 2 min mixing, but T_{2S} diminished with further mixing. The mixing led to an increase in the restriction of the tightly bound rubbers in the vicinity of the carbon black surface.
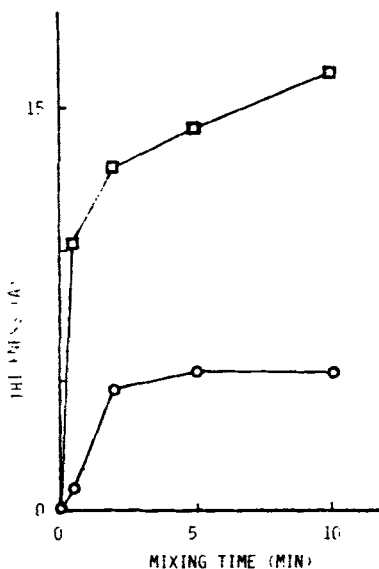

Fig. 4. Variation of the thickness for the total bound rubber (□) and the tightly bound rubber (○) as a function of mixing time.

Sample	Vol% of bound rubber	T_{2S} (s)	T_{2L} (s)	Thickness of tightly bound region (Å)	Thickness of bound region (Å)
EPR	5.1	$1.1 \ 10^{-5}$	$7.1 \ 10^{-5}$	3.1	9.1
EPDM	9.6	$7.0 \ 10^{-6}$	$7.7 \ 10^{-5}$	5.3	16.7

Increase in the volume of the bound rubber after 2 min of mixing is attributable to an increase in the volume of the loosely bound region which does not interact with the carbon black directly.

Kaufman et al.[7] measured the T_2 of EPDM composite which was compounded with 50 phr SAF carbon using a hot two-roll laboratory mill. T_2 of the tightly bound region, the loosely bound region, and the mobile region were 12×10^{-5} s, 1×10^{-4} s, and $3 \ 4 \times 10^{-4}$ s, respectively, at around room temperature. T_{2S} and T_{2L} after 10 min mixing in our study have one order shorter values. The difference in mixing conditions is a factor which causes different T_2 values and we must consider the degree of mixing when investigating rubber composites. The T_2 measurement of EPR was done in the same way as above. The results of the study for EPR-bound rubber at 10 min mixing are listed in Table I with the data of the EPDM. The volume of the bound rubber of EPR is one half of the EPDM and the tightly bound layer has thinner thickness, half of the EPDM. It is interesting that there is a small difference in T_{2L} between the EPDM and the EPR, but T_{2S} of the EPDM is much shorter than that of the EPR. It is generally accepted that the interaction between carbon black and rubber is both chemical and physical.[8] Therefore, it is reasonable to think that the difference of the bound layer thickness and T_{2S} between the EPDM and the EPR is due to the unsaturated chemical bond of the third monomer in EPDM which contributes to the bond sites which interact with carbon black. On the contrary, there is little difference in T_{2L} between them. It is considerable that T_{2L} is determined by chain entanglement or crosslinking of rubber molecules, so that the contribution of the third monomer is negligible.

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