

Swelling behaviour of rubber vulcanizates:

1. Real-time pulsed nuclear magnetic resonance measurements

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Swelling behaviour of acrylonitrile-butadiene copolymer rubber vulcanizates immersed in a nonprotic solvent was studied by real-time pulsed nuclear magnetic resonance (n.m.r.) measurements. The temporal change of the proton spin-spin relaxation time, T_2 , during the swelling process was obtained. The T_2 signal for the rubber vulcanizates was resolved into two exponentially decaying components (short T_2 and long T_2). The short T_2 component is assigned to the constrained regions in the rubber matrix, which may be mainly located around the crosslinks, and the long T_2 component to the regions lying outside the constraints. It was suggested that the decreased change of the fraction of the short T_2 component by swelling is closely connected with the enhanced molecular mobility of the network chains between the adjacent crosslinks through the diffusion of the solvent. The restricted swelling behaviour of the carbon black-filled rubber vulcanizates was interpreted mainly in terms of the constrained molecular motions of the network chains through the rubber-filler interactions and spatial effects of the filler particles. It becomes clear that the real-time pulsed n.m.r. measurements complement the results of the macroscopic swelling measurements for the rubber vulcanizates with more detailed information on the molecular interactions between the rubber and solvent molecules.

(Keywords: rubber vulcanizate; swelling; ^1H pulsed n.m.r.; real-time measurement; spin-spin relaxation time; molecular mobility; carbon black)

INTRODUCTION

A basic study of the swelling behaviour of rubber vulcanizates is of great importance in practical applications. Rubber vulcanizates available for oil and fuel resistance, which are commonly in contact with solvents, have to be carefully chosen in order to meet service conditions, because the presence of the solvent molecules in the rubber vulcanizates strongly influences the physical properties of the materials including the tensile strength, tear resistance and hardness. Furthermore, the swelling behaviour of the rubber vulcanizates is closely related to the rubber-filler interactions in filled rubber vulcanizates¹⁻³. For practical use, the rubber vulcanizate is usually incorporated with highly reinforcing fillers such as carbon black to enhance the strength of the rubber matrix more than ten-fold⁴. With reinforcing fillers, the swelling of the rubber matrix is restricted relative to the unfilled system. Swelling measurements in which the resulting change in volume of a specimen exposed to the solvents is examined are most commonly used as a measure of the effects of the solvents⁵. Macroscopic volume change seems to be an appropriate measure of the general resistance of a rubber vulcanizate against a given solvent, associated with both the rubber-solvent and rubber-filler interactions. There have been many studies^{1-3,6-8} on the swelling behaviour of the rubber vulcanizates immersed in organic solvents in order to discuss those interactions by the macroscopic swelling measurements. However, the macroscopic behaviour obtained by the swelling measurements and other mechanical measurements (e.g., modulus, stress-

strain curve, etc.)^{7,9-11} cannot be directly related to the microscopic molecular state of the network chains in the rubber vulcanizates.

In the swelling process of the rubber vulcanizates through the diffusion of the molecules comparable to, or larger than, the monomer unit of a constituent polymer, including most organic solvents, the diffusive molecules may be penetrated into the rubber matrix through the cooperative movement by the micro-Brownian motion of several monomer units, i.e., polymer segment¹². Hence, the diffusion behaviour of the solvent molecules into the rubber matrix, in which the micro-Brownian motion of the long chains is sufficiently active, can be connected with the mobility of the polymer segmental unit.

For the study of the molecular mobility of the polymer chains, a pulsed nuclear magnetic resonance (n.m.r.) method provides a sensitive probe of the molecular state of a nuclear environment through the short-range nature of the magnetic dipolar interactions¹³. In particular, the spin-spin relaxation time, T_2 , is a sensitive measure of low frequency motions associated with long-range chain motions. For heterogeneous polymers, the molecular mobility and the fraction of each component can be estimated by the T_2 measurements. In the pulsed n.m.r. studies of rubbery polymers under mechanical deformation^{14,15}, it was confirmed that the change of the motional heterogeneity in the rubber matrix can be directly estimated by the T_2 measurements, related to the macroscopic mechanical properties. Hence, the pulsed n.m.r. method is considered as a suitable tool to

characterize the molecular motions in the rubbery polymers. As for the swelling process of the rubbery polymers, the results obtained by the T_2 measurements for several polymer gels have been reported, mainly concerned with n.m.r. properties at equilibrium swelling¹⁶.

There are few real-time observations of the swelling process important for the study of the dynamic character of the network chains in the rubber vulcanizates, associated with the diffusion of the solvent molecules. Recently, real-time pulsed n.m.r. measurements have been applied to the studies of the crystallization, polymerization, and gelation processes for the polymers¹⁷⁻²⁰. It becomes clear that the real-time pulsed n.m.r. measurements give the dynamic information on the molecular state of the polymer chains in nonequilibrium, contrary to other methods such as X-ray diffraction, dilatometry, and optical microscopy with the information on the static properties.

In this study, the swelling process of acrylonitrile-butadiene copolymer rubber (NBR) vulcanizates (unfilled and filled systems) immersed in carbon tetrachloride (CCl_4) was studied by a real-time pulsed n.m.r. measurement. By using the proton (^1H) T_2 measurements, the temporal change of the molecular mobility of the network chains in the rubber vulcanizates during the swelling process was directly observed without the contribution to the n.m.r. signal from the solvent. From the results obtained by T_2 measurements, the diffusion behaviour of the solvent molecules at molecular level was discussed, and was related to the effects of carbon black fillers on the swelling behaviour of the rubber matrix. Furthermore, the temporal change of the motional heterogeneity in the rubber matrix was compared with the change of the macroscopic volume swelling ratio of the rubber matrix, and the correlation between both properties was estimated on the basis of the diffusion equation.

EXPERIMENTAL

Materials

The materials used are a pure (unfilled) NBR (Nippon Zeon Co. Ltd; Nipol 1041B, acrylonitrile content = 41%) vulcanizate and carbon-filled NBR vulcanizates with the filler concentration ranging from 20 to 60 phr (i.e. parts per hundred parts of rubber by weight). The compounding recipes and cure condition for the materials are shown in Table 1. The volume of the rubber specimens for all the experiments was approximately 0.2 cm^3 . A swelling solvent, CCl_4 , was selected as a nonprotonic solvent.

Real-time pulsed n.m.r. measurements

Pulsed n.m.r. measurements were performed with Jeol-FSE60Q spectrometer operating at 60 MHz for ^1H in the phase-sensitive detection mode. The recovery time of the spectrometer following a sequence of pulses was $10 \mu\text{s}$ and 90° pulse was $2 \mu\text{s}$ duration. The n.m.r. signal was fed into a transient recorder with a signal averager (Kawasaki Electronica Co. Ltd, Model KR3160) and was stored in memory, which was controlled by a microcomputer (NEC Ltd, Model PC9801F). Instantaneously, the digitized data (4000 words) on the n.m.r. signal were transferred to the memory of the microcomputer. Then, all the n.m.r. signals obtained during

the swelling process of the rubber vulcanizates were analysed by the nonlinear least squares method after the real-time measurements.

In a real-time measurement of the swelling process of NBR, a rubber specimen was immersed in a 10 mm diameter n.m.r. glass tube with the solvent at 25°C , and the real-time T_2 measurement was started immediately after the immersion of the specimen. The temperature of the system was controlled by means of cold air flowing through liquid N_2 and an electrical heater. The pulse sequence for the T_2 measurements was solid echo pulse sequence ($90_x \tau 90_y$) (ref. 21), in which τ was set at $8 \mu\text{s}$.

Swelling measurements

In all the swelling measurements, a rubber specimen was immersed in the n.m.r. tube with the solvent at 25°C , consistent with the conditions for the n.m.r. measurements. The volume swelling ratio of the rubber matrix was evaluated by the gravimetric method, which consists of weighing the specimen in air before and after the immersion and calculating the volume change of the specimen for a chosen time⁵.

RESULTS

Change of molecular mobility of network chains

Generally, the transverse magnetization decay signal (T_2 signal), $M(t)$, for a random motion of nuclear spins is given by the following^{22,23} under the assumption that the correlation function of the dipolar local field $\omega(t)$, $\langle \omega(t)\omega(t+\tau) \rangle$, is expressed as $\exp(-\tau/\tau_c)$.

$$M(t) = M_0 \exp[-\sigma_0^2 \tau_c^2 \{\exp(-t/\tau_c) + t/\tau_c - 1\}] \quad (1)$$

where t is the time, τ_c is the correlation time for the thermal motion of nuclei, M_0 is the constant proportional to the total number of nuclei with magnetic moment and σ_0^2 is the second moment for the rigid lattice which is connected with the interactions among the nuclear spins. In this study, on the basis of equation (1) for $\sigma_0 \tau_c \ll 1$, the T_2 signal for the rubber vulcanizates was analysed. Hence, $M(t)$ is approximated by

$$M(t) = M_0 \exp(-t/T_2) \quad (2)$$

and

$$T_2 \approx (\sigma_0^2 \tau_c)^{-1} \quad (3)$$

Figure 1 shows the temporal change of T_2 signal for the unfilled system (P-NBR) during the swelling process. With the increase of the immersion time, the T_2 signal decays more slowly, which reflects the enhancement of the average molecular mobility of the network chains in the rubber matrix through the diffusion of the solvent

Table 1 Compounding recipes of NBR (parts). Cure condition: 20 min at 160°C

	P-NBR	C20-NBR	C40-NBR	C60-NBR
NBR	100	100	100	100
FEF black	-	20	40	60
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
Sulphur	0.5	0.5	0.5	0.5
Acc. CZ ^a	1	1	1	1
Acc. TT ^b	2	2	2	2

^a *N*-cyclohexyl-2-benzothiazyl sulphenamide

^b Tetramethylthiuram disulphide

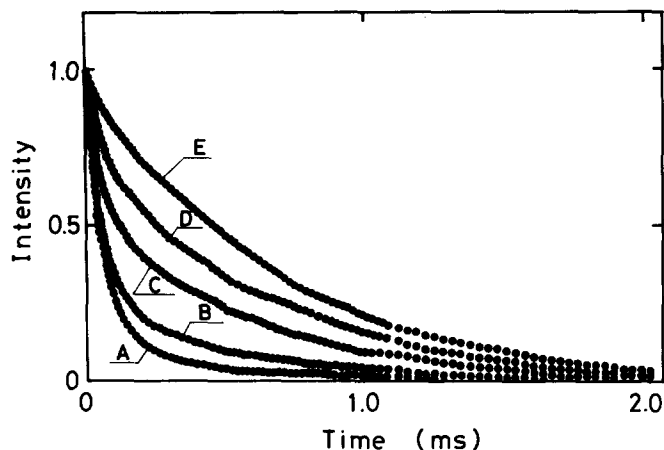


Figure 1 Temporal change of the T_2 signal for the unfilled NBR during the swelling process: curve A, 15 s; curve B, 616 s; curve C, 3616 s; curve D, 9616 s; curve E, 18617 s

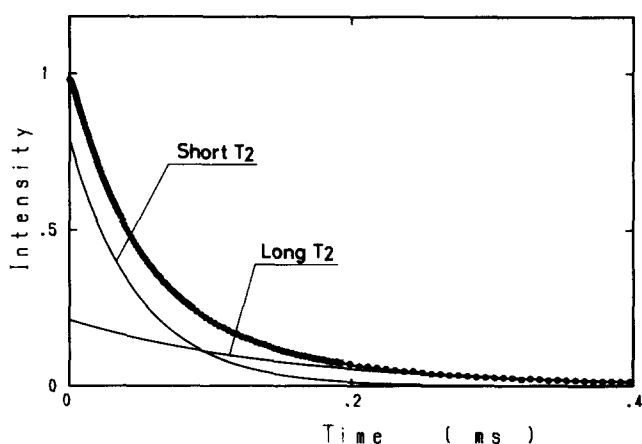


Figure 2 T_2 signal for the unfilled NBR in an unswollen state, which is resolved into two exponentially decaying components. Solid lines are the calculated curves by nonlinear least squares method

molecules, corresponding to the decrease of τ_c . Figure 2 shows the analysed T_2 signal for P-NBR in an unswollen state, which was resolved into two exponentially decaying components (short T_2 and long T_2), owing to some motional heterogeneity in the rubber matrix.

In a previous pulsed n.m.r. study of NBR under deformation¹⁴, it was found that short T_2 becomes shorter and its fraction increases with stretching, and thus the short T_2 component was assigned to the regions of the network chains in more constrained conformations under the influence of the crosslinks in comparison with those remote from the constraints^{24–28}. These results will be interpreted later in terms of a distribution of correlation times along the molecular chain between the adjacent crosslinks. This assignment is supported by the fact that the fraction of the short T_2 component for NBR increases with the increase of the crosslink density during the curing process and attains a limited value at the end of the reaction²⁹.

It is also probable for high nitrile NBR systems with polar side groups that the network chains and crosslink regions interact through the dipole–dipole interaction between the polar groups and perturb the segmental motion of each other, in which transient constrained regions may be formed comparable to those in the vicinity of the crosslinks or entanglements. The enlargement of

the constrained regions in the rubber matrix may cause the increase of the fraction of the short T_2 component (ca. 80% at 25°C; ref. 14). All the results of the T_2 measurements for the unswollen NBR systems are shown in Table 2. With the increase of the filler concentration, both short T_2 and long T_2 become shorter through the rubber–filler interactions involved in the decrease of the molecular mobility of the overall network chains. However, the fraction of the short T_2 component for C60–NBR is lower than that for other systems. This may reflect some spatial inhomogeneity generated in the rubber matrix owing to the inhomogeneous distribution of the carbon black fillers or inhomogeneity in the crosslink density at the high filler concentration, which may lead to the increase in the fraction of the less constrained regions of the network chains¹⁴.

Figure 3 shows the temporal change of the T_2 values of the components for NBR systems during the swelling process. With the increase of the immersion time, long T_2 becomes longer and short T_2 becomes shorter gradually. Figure 4 shows the temporal change of the fraction of each component for the unfilled system. The fraction of the long T_2 component increases, which comes from the decrease of that of the short T_2 component, and at the late stage of the swelling process the short T_2 component disappears. Figure 5 shows the temporal change of the fraction of the short T_2 component for NBR systems. With the increase in the filler concentration, the fraction of the short T_2 component decreases more slowly, that is, the time required for the disappearance of the short T_2 component becomes longer. The molecular mobility of the network chains in the rubber matrix may then come to be apparently averaged through the diffusion of the solvent molecules.

Table 2 Results of T_2 measurements for the unfilled and filled NBR in the unswollen state

	Short T_2 , μs (proton%)	Long T_2 , μs (proton%)
P-NBR	49 (79%)	160 (21%)
C20-NBR	47 (78%)	153 (22%)
C40-NBR	46 (78%)	142 (22%)
C60-NBR	44 (73%)	138 (27%)

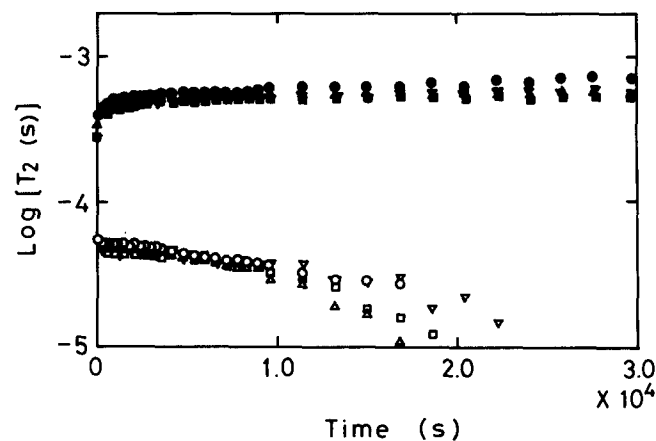


Figure 3 Temporal change of the T_2 values of the components for the unfilled and filled NBR: (O, ●), P-NBR; (Δ, ▲), C20-NBR; (□, ■), C40-NBR; (▽, ▼), C60-NBR

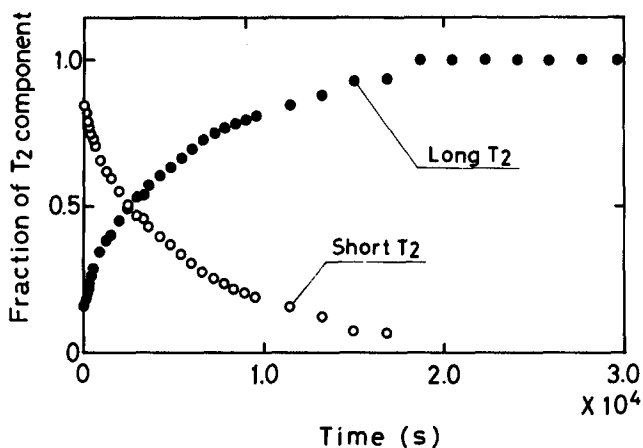


Figure 4 Temporal change of the fractions of the T_2 components for the unfilled NBR

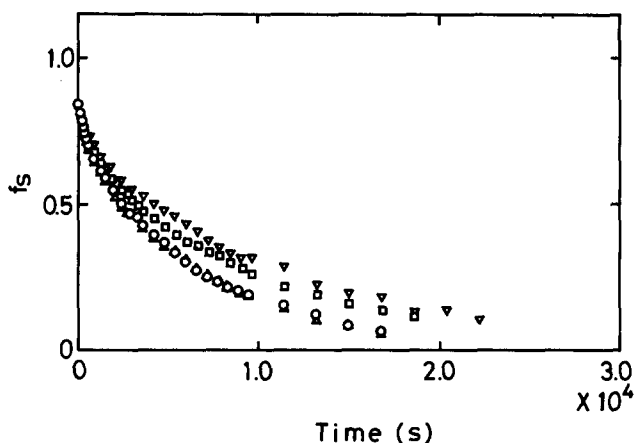


Figure 5 Temporal change of the fraction of the short T_2 component, f_s , for the unfilled and filled NBR: (O), P-NBR; (Δ), C20-NBR; (\square), C40-NBR; (∇), C60-NBR

Change of swelling ratio of rubber matrix

Experimentally or empirically^{6-8,12,30}, it is confirmed that the kinetics of the diffusion of the solvent molecules for the rubbery polymers is approximately Fickian, for which the boundary condition is the condition of constant surface concentration. Hence, on the basis of Fick's second law for diffusion, the swelling ratio of the rubber matrix, S_r , at a time t is approximately expressed as

$$S_r = 1/v_r = 1 + k_s t^{1/2} \quad (4)$$

where v_r is the volume fraction of the rubber matrix in nonfiller portion of the swollen system, i.e., equal to (rubber matrix)/(rubber matrix + solvent), and k_s corresponds to the swelling rate evaluated by the swelling measurement. Figure 6 shows the plots of S_r against $t^{1/2}$ for NBR systems. Dependence of S_r on time is almost consistent with equation (4), except for that at longer time near the equilibrium swelling. The swelling behaviour of the unfilled system is qualitatively similar to that of the filled system, but the swelling rate evaluated from the linear portion becomes lower with the increase of the filler concentration, although the value for P-NBR is almost identical with that for C20-NBR.

The results of the T_2 measurements and swelling measurements for NBR systems at equilibrium swelling are summarized in Table 3. As seen in Table 3, at

equilibrium T_2 for C60-NBR is slightly longer than that for C40-NBR, although the swelling ratio at equilibrium for the former is a little lower than that for the latter. The enhanced molecular mobility of the network chains for C60-NBR relative to that for C40-NBR may be associated with some motional heterogeneity in the rubber matrix induced by the inhomogeneous distribution of the filler particles or inhomogeneity in the crosslink density at the high filler concentration, which causes the increase of the fraction of the less constrained regions of the network chains in comparison with other NBR systems, as shown in Table 2.

DISCUSSION

Effects of the diffusion of the solvent on the molecular mobility of the network chains

As already described, it is believed that the rate of the diffusion of the solvent molecules having sizes comparable to, or larger than, the monomer unit of a constituent polymer in a rubber vulcanizate may be mainly controlled by the molecular mobility of the polymer segmental unit. The diffusion of the solvent in the rubber matrix expands the system, and thus weakens the molecular interaction between neighbouring polymer chains. This implies that the polymer chains between the crosslinks move more freely and thus the molecular mobility of the network chains is enhanced through the diffusion of the solvent molecules. On the other hand, it was shown by neutron scattering experiments for perdeuterated elementary chains of a polymer gel³¹ that the average elementary chain dimension observed on the slightly swollen gel ($1 < S_r < 3$) is equal to that observed on the dry gel, and

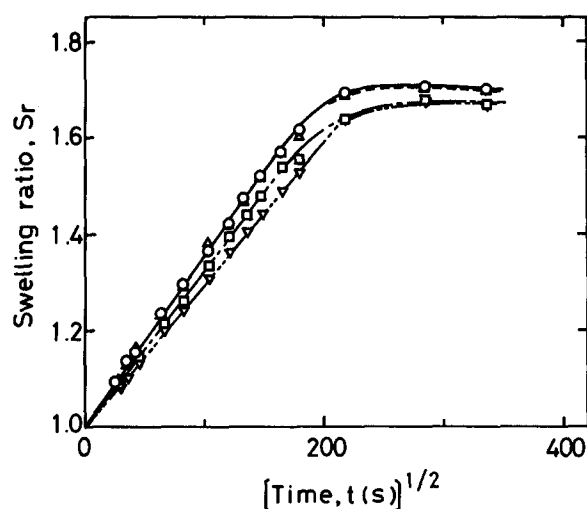


Figure 6 Swelling ratio of the rubber matrix, S_r , plotted against $t^{1/2}$ for the unfilled and filled NBR: (—○—), P-NBR; (---△---), C20-NBR; (- - - □ - - -), C40-NBR; (- · · · · · ▽ · · · · ·), C60-NBR

Table 3 Results of T_2 measurements and swelling measurements for the unfilled and filled NBR at equilibrium swelling

	T_2 (μ s)	S_r
P-NBR	720	1.71
C20-NBR	646	1.71
C40-NBR	616	1.68
C60-NBR	620	1.67

that at S_r higher than 3 the radius of gyration exhibits a dependence of $(S_r)^{1/3}$.

This result leads implicitly to the conclusion that the network chains can swell from the unswollen state to the swollen reference state at small swelling degree without any deformation of the elementary chains. Thus, it is suggested for NBR systems immersed in CCl_4 ($S_r < 2$) that the average chain dimension of the network chains in NBR may hardly vary through the diffusion of the solvent, so that effects of exerted strain on the molecular mobility of the network chains, which were examined by the pulsed n.m.r. measurements of the rubber vulcanizates under deformation^{14,29}, may be negligible in the present study of the swelling behaviour of NBR.

In the swelling process of NBR systems, it is noticeable that with the increase of the immersion time in the solvent, the fraction of the short T_2 component decreases and eventually disappears as a result of the averaged molecular mobility of the overall network chains. At the early stage of the swelling process, which involves the rapid increase of the T_2 value of the long T_2 component, the solvent molecules may come to be more easily located on the network chains remote from the crosslinks than those on the network chains in the vicinity of the constraints with low mobility. This is because the diffusion of the solvent molecules occurs mainly through the cooperative movement by the micro-Brownian motion of the polymer segment. At the intermediate stage, together with the swelling of the rubber matrix, the fraction of the constrained regions of the network chains may decrease through the interaction between the network chains and solvent molecules. This causes the decrease of the fraction of the short T_2 component. At the late stage, in which a single T_2 component is apparently observed, the relaxation time may be expressed as^{32,33}

$$T_2^{-1} = f_s T_{2s} + f_l / T_{2l} \quad (5)$$

where f_s and f_l are the fractions of the short and long T_2 components ($f_s \ll f_l$), and T_{2s} and T_{2l} are short T_2 and long T_2 , respectively. Then, the increased swelling of the overall network chains in the rubber matrix may proceed to reach the equilibrium swelling, followed by the increase of T_2 .

In the rubber vulcanizates, the long chains between the crosslinks have the freedom to take up the variety of the statistical conformations, and the secondary forces between the molecules (i.e., intermolecular interactions) must be weak to achieve the inherent elasticity, apart from the fact that all the molecules are linked together chemically through the crosslinks³⁴. Hence, it can be assumed that the intramolecular contributions (i.e., interaction between nuclei located on an individual polymer chain between the adjacent crosslinks) to n.m.r. dipolar relaxation are more sensitive than the intermolecular contributions (i.e., interaction between nuclei located on different polymer chains) on account of the short-range nature of magnetic dipolar interactions.

Any constraints such as permanent chemical crosslinks and molecular entanglements have a major effect on the long-range conformational motions and provide the dominant contribution to the spin-spin relaxation time, T_2 . For the rubber vulcanizates, the resolution of the T_2 signal into two components may be attributable to the spatial distribution of T_2 (i.e., correlation times) along

the polymer chain between the crosslinks. The value of T_2 for each element of the polymer chain depends on the contour length from the point of the constraint. In qualitative discussion of the constrained motion for the bound part of fold and cilia in semicrystalline polymers by Douglass *et al.*³⁵, T_2 for each element of the polymer chain takes the form

$$T_2^2 = \exp(3N\alpha^2) T_{2RL}^2 \quad (6)$$

where N is the number of the element, α is the typical bend angle which corresponds to the angle between successive polar axes and denotes the magnitude of the bend between the respective chain segments, and T_{2RL} is the rigid lattice T_2 . In the above expression, the flexibility of the segments may decrease remarkably as α or N decreases. The value of T_2 increases progressively as the contour distance from the point of the constraint increases.

Figure 7 schematically shows the spatial distributions of the correlation times along the network chain between the crosslinks (or other constraints) both in unswollen and swollen states. The motional correlation time, τ_c , ($\approx (\sigma_0^2 T_2)^{-1}$ in equation (3)) decreases as the contour distance from the crosslink, r , increases. This behaviour can be qualitatively understood on the basis of equation (6). Within the constrained region in the vicinity of the crosslink, no correlation time shorter than that of the network chain lying outside the constrained region will exist, because the segmental motion in the crosslink region is strongly hindered. Hence, the constrained region protons assigned to the short T_2 component are separately treated from the relatively free region protons assigned to the long T_2 component. In the swelling process of the rubber matrix, the change of the spatial distribution of the correlation times may occur as shown in Figure 7.

According to Ferry³⁶, the monomeric friction coefficient, ζ_0 , is interpreted as an inverse measure of local molecular mobility and is the most important factor in determining the time required for complete conformational rearrangement of a polymer chain between two crosslinks or two entanglements. ζ_0 is the frictional force per unit velocity (calculated per monomeric unit) encountered by a short segment of the polymer chain as it pushes its way through its

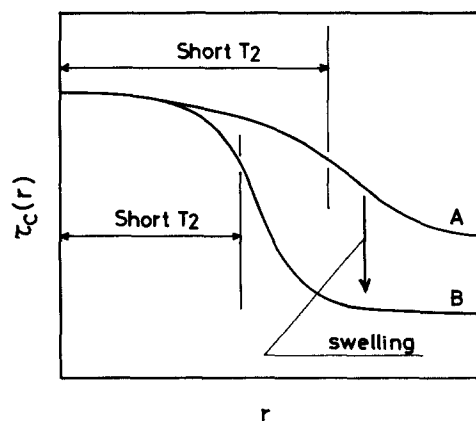


Figure 7 Schematic illustration of the temporal change of the spatial distribution of τ_c along the network chain between the adjacent crosslinks during the swelling process. r corresponds to the contour length along the molecular chain from the constraint

surroundings with thermal energy, randomly undergoing conformational rearrangements. Therefore, the increase of ζ_0 may correspond to the increase of τ_c for the monomeric unit. ζ_0 depends on the chemical structure of the rubber, and changes sensitively with environmental effects such as temperature, pressure, and plasticization with diluent. The dependence of the local friction coefficient on temperature is similar to that on the solvent content in the rubber matrix.

Through the diffusion of the solvent, the local friction coefficient for the network chains in the region on which the solvent molecules come to be located diminishes rapidly, and thus the decrease of the correlation times for those network chains occurs. Hence, the decreased fraction of the short T_2 component assigned to the constrained regions can be interpreted as the change of the spatial distribution of the correlation times along the polymer chain to the crosslink with the swelling of the rubber matrix. This is schematically shown in *Figure 7* (from line A to line B). Furthermore, as shown in *Figure 3*, short T_2 becomes shorter and its fraction decreases with the increase of the immersion time. With the decrease of the fraction of the constrained regions corresponding to the short T_2 component, the value of short T_2 gradually approaches that of T_2 in a limited constraint on the motions ultimately achieved ($\approx 10 \mu\text{s}$). This behaviour is qualitatively understood in terms of the change of the spatial distribution of T_2 along the polymer chain between the crosslinks, as shown in *Figure 7*.

On the other hand, the continuous distribution of the swelling ratio in the rubber matrix from the outer (swelling) regions to the inner (less swelling) regions also has to be considered with regard to the change of the motional heterogeneity in the network chains during the swelling process, although internal stresses generated for both regions caused by the differences in the swollen states may be relieved immediately through the conformational rearrangement of the rubbery chains. However, the change of the motional heterogeneity observed during the swelling process cannot be simply understood as the coexistence of the swollen outer part having a single T_2 component and unswollen inner part having two T_2 components in a specimen. Probably, in a real system, the change of the motional heterogeneity in the rubber matrix observed through the diffusion of the solvent may be caused by following two complicated effects: in any given volume element the solvent molecules are preferably located on the regions remote from the constraints with low mobility; and the coexistence of outer more swelling part and inner less swelling part in a specimen.

As for the effects of carbon black filler on the swelling behaviour of the rubber matrix, as shown in *Figure 5*, the time required for the disappearance of the short T_2 component in the swelling process becomes longer with the increase of the filler concentration. There appear to be two main effects on the restriction of swelling as follows: constrained anisotropic motions of the network chains in the vicinity of the carbon black fillers through the rubber–filler interactions; and spatial effects of the filler particles on the diffusive path length for the solvent molecules. According to Kraus¹, as long as the adhesive bond between the rubber and filler is not disrupted with the diffusion of the solvent, swelling in the direction tangential to the filler surface will be zero at the surface,

while perpendicular to the surface the local swelling deformation will be larger than that in unfilled networks. The net effect will cause a decrease in swelling. If it is assumed that swelling varies continuously with the distance from the filler surface, the swelling of the filled system becomes isotropic and equal to the swelling of the unfilled system at the point far from the filler surface.

In the swelling measurements for the filled rubber vulcanizates with various types of carbon blacks, it was confirmed that at the equilibrium swelling the restriction of swelling of the rubber matrix can be correlated with the number of reactive sites on the carbon black surface. This behaviour can be connected with the constrained molecular mobility of the network chains through the rubber–filler interactions. Therefore, it is reasonable that the diffusion of the solvent molecules in the rubber matrix may become more restricted with the increase of the filler concentration. However, for the filled systems with equal surface loadings of SRF, HAF, and MT carbon blacks, which show very similar equilibrium swelling, Stickney *et al.*³ reported that the initial swelling rates of SRF-filled system (59 phr) and MT-filled system (195 phr) are almost identical and much lower than that of HAF-filled system (20 phr). Hence, the spatial effects of the filler particles on the swelling behaviour of the rubber matrix might not be negligible, especially at the early and intermediate stages of the swelling process observed by the real-time n.m.r. measurements. More detailed real-time n.m.r. study of the effects of the carbon black fillers on the swelling behaviour of the rubber matrix (closely related to the molecular mobility of the network chains) will be carried out for the filled systems with various types of fillers in the near future.

Correlation between the molecular mobility and swelling ratio of the rubber matrix

In the real-time T_2 measurements for NBR system, it is found that the swelling behaviour of the rubber matrix can be mainly connected with the characteristic change of the fraction of the short T_2 component during the swelling process, as shown in *Figure 5*. Thus, for the analysis of the temporal change of the fraction of the short T_2 component, the parameter F_n is defined as

$$F_n \equiv [f_s(0) - f_s(t)]/f_s(0) \quad (7)$$

where t is the immersion time, and $f_s(0)$ and $f_s(t)$ are the fractions of the short T_2 component at $t=0$ and t , respectively. From the value of F_n , the degree of the change of the fraction of the short T_2 component into that of the long T_2 component can be estimated. *Figure 8* shows the plots of the swelling ratio of the rubber matrix, S_r , against F_n evaluated at a given time for the unfilled and filled NBR systems. The plots give a universal straight line, described as

$$S_r = AF_n + 1.0 \quad (8)$$

Here, A is estimated to be 0.43 for NBR systems. This relation may be qualitatively reasonable in consideration of the diffusion of the solvent molecules controlled by the molecular mobility of the network chains. Hence, on the basis of equation (4), F_n should be expressed as

$$F_n(t) = k_n t^{1/2} \quad (9)$$

where k_n is k_s/A .

Figure 9 shows the plots of F_n against $t^{1/2}$ for NBR systems. All the plots for the unfilled and filled systems

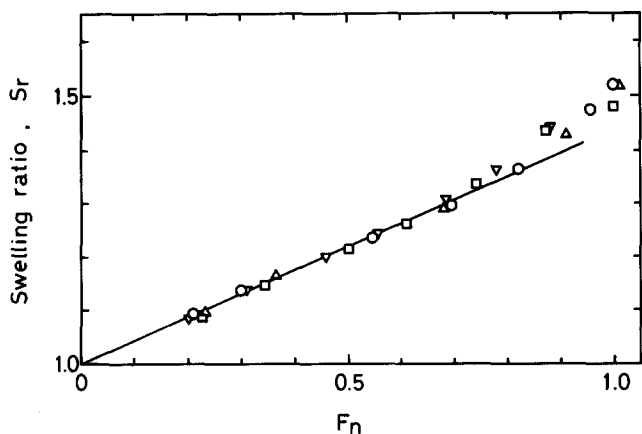


Figure 8 S_r plotted against F_n at a given time for the unfilled and filled NBR: (O), P-NBR; (Δ), C20-NBR; (\square), C40-NBR; (∇), C60-NBR

give nearly linear relations in accordance with equation (9). The slope of the linear portion of the plot, k_n , corresponds to the relative swelling rate evaluated by the real-time n.m.r. measurements. Thus, it becomes clear that the temporal change of the swelling ratio of the rubber matrix can be directly related to that of the molecular mobility of the network chains by the real-time n.m.r. measurements, while the swelling measurements only give the information on the macroscopic volume swelling ratio of the rubber matrix with the intermittent procedure, which consists of weighing a specimen (in air and usually in water) after the immersion at a given time.

CONCLUSIONS

Real-time ^1H pulsed n.m.r. techniques were applied to the studies on the swelling process of the rubber vulcanizates immersed in a nonprotonic solvent. It is believed that the solvent molecules may be penetrated into the rubber matrix through the cooperative movement by the micro-Brownian motions of the polymer chains, and thus that the diffusion of the solvent may be mainly controlled by the molecular mobility of the network chains. The T_2 signal for the rubber vulcanizates was resolved into two exponentially decaying components (short T_2 and long T_2). The short T_2 component is assigned to the constrained regions of the network chains around crosslinks (or entanglements) and the long T_2 component to the relatively less constrained regions of the network chains remote from the constraints. This assignment may be mainly interpreted as the spatial distribution of the correlation times along the individual polymer chain between the adjacent crosslinks owing to the short-range nature of the magnetic dipolar interactions (mainly, intra-contributions to n.m.r. relaxation). Furthermore, for NBR systems with polar side groups, the appearance of the transient constrained regions through the dipole-dipole interaction between the polar side groups in the different polymer chains may contribute to the increase of the fraction of the short T_2 component. It is confirmed that the decreased change of the fraction of the short T_2 component through the interaction between the polymer chains and solvent molecules is connected with the enhanced molecular mobility of the rubber matrix through the diffusion of the solvent.

From the results by the real-time n.m.r. measurements,

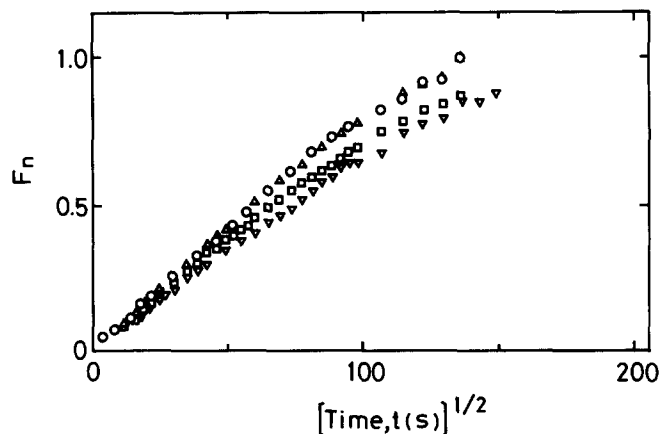


Figure 9 F_n plotted against $t^{1/2}$ for the unfilled and filled NBR on the basis of equation (9): (O), P-NBR; (Δ), C20-NBR; (\square), C40-NBR; (∇), C60-NBR

the swelling behaviour of the rubber vulcanizates immersed in the solvent are suggested to be as follows. Initially, the solvent molecules come to be easily located on the network chains remote from the constraints such as the crosslinks in any volume element from the outer to the inner. At the early and intermediate stages of swelling, the observed motional heterogeneity in the rubber matrix is due to both the inhomogeneous distribution of the solvent molecules in the network chains along the molecular chain and coexistence of the outer more swelling part and inner less swelling part in a specimen. At the late stage of swelling, the motional heterogeneity in the rubber matrix is apparently averaged, and the swelling of the overall network chains proceeds to reach the equilibrium swelling. The constrained molecular motions of the network chains in the vicinity of the filler particles are associated with the restricted swelling of the rubber matrix as compared with the unfilled system.

It becomes clear that the pulsed n.m.r. method complements the results of the macroscopic swelling measurements with more detailed information on the rubber-solvent interactions at the molecular level. Moreover, it can be expected that the real-time n.m.r. measurements are applicable to the studies on the swelling behaviour of the filled systems with various types of the filler particles and that of the rubber vulcanizates in stretched states important for the practical use, directly connected with the molecular mobility of the network chains.

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