Swelling behaviour of rubber vulcanizates: 2. Effects of tensile strain on swelling

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The effects of tensile strain on the swelling behaviour of acrylonitrile–butadiene copolymer rubber vulcanizates were studied by real-time pulsed nuclear magnetic resonance (n.m.r.) measurements and volume swelling measurements at equilibrium. It was shown that tensile strain causes an increase of the initial swelling rate evaluated by n.m.r. measurements and of the swelling ratio of the rubber matrix at equilibrium. This behaviour was discussed qualitatively in terms of the molecular mobility of the network chains on the basis of Treloar's theory for swelling under deformation. It was suggested that the presence of reinforcing fillers in the rubber matrix exerts two noticeable effects on swelling under deformation: (1) a transient effect through some oriented structure induced by stretching, which restricts the increase of the swelling rate; (2) a strain amplification effect, which causes the increase of the average local strain in the rubber matrix and enhances the swelling ratio more remarkably proportional to the filler concentration as compared with that of the unfilled system.

(Keywords: rubber vulcanizate; swelling; effect of strain; ^{1}H pulsed nuclear magnetic resonance; molecular mobility; carbon black; strain amplification)

INTRODUCTION

In practical use, the swelling behaviour of rubber vulcanizates immersed in organic solvents is closely related to the worsening of the physical properties of materials used for practical parts that may be in contact with solvents such as fuel, oil and so on. A high degree of swelling of a rubber matrix immersed in a given solvent indicates that the rubber vulcanizate is not suitable for use in that environment, because the presence of the solvent in the rubber matrix causes weakening of the resistance of the rubber vulcanizate to failure[1–5]. Furthermore, in practical applications of rubber parts, the active influence of external conditions, including solvents, on the materials appears more clearly under a simultaneous application of mechanical stress (e.g. tension, compression, etc.). However, in spite of its importance, there have been few studies on the swelling behaviour of rubber vulcanizates under deformation; only the macroscopic swelling behaviour of the rubber matrix at equilibrium for unfilled rubber vulcanizates has been discussed[6–9]. Usually, reinforcing fillers such as carbon black are incorporated into the rubber matrix to enhance the strength of the rubber in practical use. Hence, it is considered to be of great importance to clarify the swelling behaviour of filled rubber vulcanizates under deformation.

At a molecular level, in the swelling process of the rubber vulcanizates solvent molecules may penetrate into the rubber matrix through cooperative movement by micro-Brownian motion of the segmental polymer units[10]. Hence, in addition to rubber–solvent interactions, the rate of diffusion of the solvent into the rubber matrix, in which micro-Brownian motion of the long chains is sufficiently active, may be controlled by the molecular mobility of the rubbery chains. In the previous study[11], the temporal change of molecular mobility of network chains during the swelling process was directly observed for unfilled and filled acrylonitrile–butadiene copolymer rubber (NBR) vulcanizates by real-time pulsed nuclear magnetic resonance (n.m.r.) measurements, and was related to the diffusion behaviour of the solvent molecules. It becomes clear that the pulsed n.m.r. method complements the results obtained by macroscopic swelling measurements with more detailed information on both the rubber–solvent and rubber–filler interactions in terms of the molecular mobility of the network chains. In addition, in contrast to the macroscopic swelling measurements[12], in which the intermittent procedure of weighing the specimen before and after immersion in the solvent was done, this method seems to be very suitable for real-time observation of the swelling process of rubber vulcanizates because of the short time required for the measurement.

In this study, real-time pulsed n.m.r. measurements of the swelling process of NBR vulcanizates under deformation were carried out, and the swelling rate of the rubber matrix was evaluated by measurement of the spin–spin relaxation time T_2 in terms of the enhanced molecular mobility of the network chains through diffusion of the solvent. Furthermore, the swelling ratio of the rubber matrix at equilibrium was evaluated by the volume swelling measurement after the real-time n.m.r. measurement. From the results obtained, the effects of macroscopic strain and the incorporation of filler particles on the swelling behaviour of the rubber vulcanizates were discussed in connection with the molecular state of the rubber matrix under deformation.

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EXPERIMENTAL

Materials

The materials used are a pure (unfilled) NBR (acrylonitrile content = 41%) vulcanizate and FEF*-carbon filled NBR vulcanizates. The compounding recipes and conditions of vulcanization have already been shown in the previous paper[11]. The filler concentration for NBR systems ranges from 0 to 60 phr, as shown in *Table 1*. Ring specimens (outside diameter 22 mm, inside diameter 19 mm) for the n.m.r. measurements of NBR in the stretched state were punched out from compression-moulded sheets. The volume of the rubber specimens was ~0.2 cm^3. The swelling solvent was carbon tetrachloride (CCl_4) selected as a non-protonic solvent.

Real-time n.m.r. measurements of NBR in the stretched state

Pulsed n.m.r. measurements were performed on a JEOL FSE60Q spectrometer operating at 60 MHz for protons (^1H) in the phase-sensitive mode. A real-time n.m.r. measurement was carried out with a microcomputer-controlled system as previously reported[11].

Figure 1 shows the schematic illustration of the real-time n.m.r. measurement of the swelling process of NBR in the stretched state. A ring specimen was held stretched at constant strain around a Teflon rod with suitable length prepared for a given stretch ratio λ. The stretched specimen was immersed into 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 pulse sequence for the T_2 measurements was the solid echo method ($90^\circ_x \tau 90^\circ_y$), in which τ was set at 8 μs. After the T_2 measurements, volume swelling measurements by the gravimetric method were also carried out to evaluate the swelling ratio $S_{r,e}$ of the rubber matrix at equilibrium for NBR systems.

Table 1 NBR systems

Code	FEF carbon black (parts)
P-NBR	0
C20-NBR	20
C40-NBR	40
C60-NBR	60

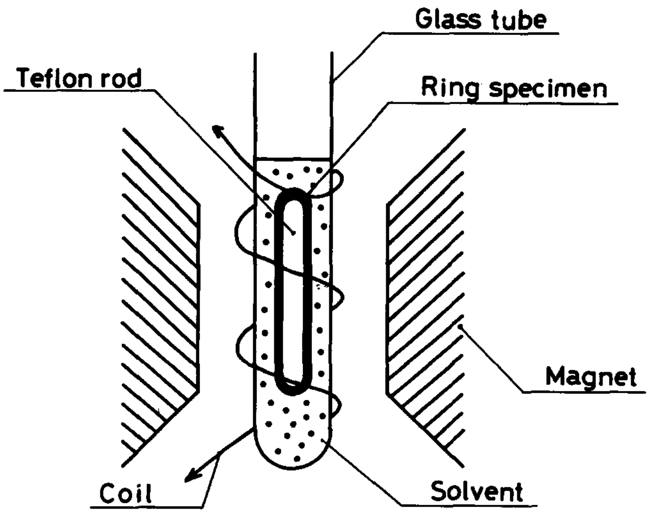

Figure 1 Schematic illustration of the real-time n.m.r. measurement of a stretched rubber specimen immersed in a solvent

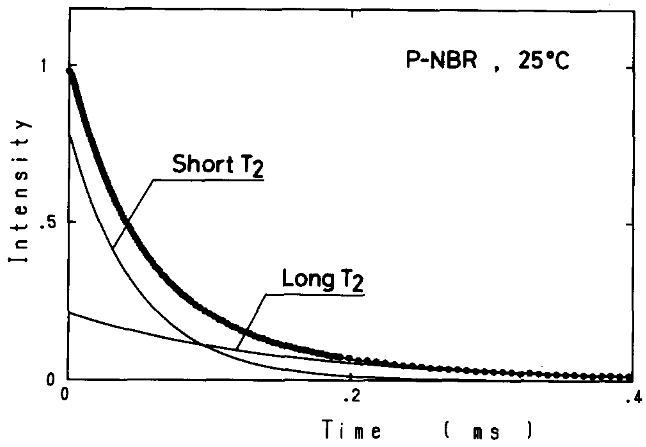

Figure 2 T_2 signal for the unfilled NBR in an unswollen state, which was resolved into two exponentially decaying components. Full curves are the calculated curves by non-linear least-squares method

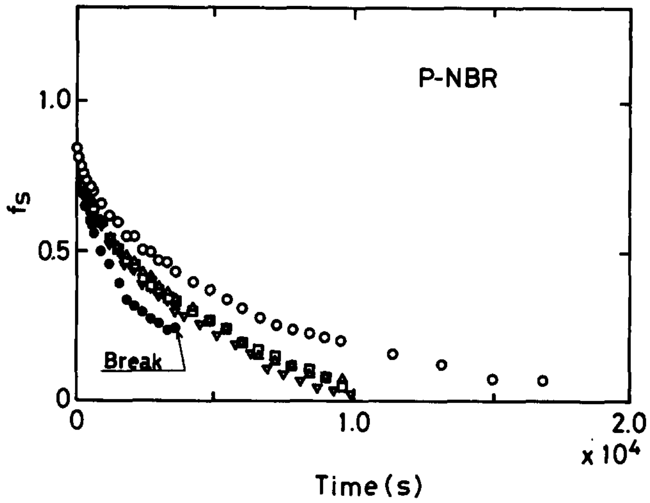

Figure 3 Temporal change of the fraction of the short T_2 component f_s for the unfilled NBR during the swelling process at various stretch ratios: (○) free swelling; (△) $\lambda = 1.43$; (□) $\lambda = 1.58$; (▽) $\lambda = 1.75$; (●) $\lambda = 2$

RESULTS

Results of real-time n.m.r. measurements

Figure 2 shows the T_2 signal for the unfilled system (original) at 25°C. The T_2 signal $M(t)$ was resolved into two exponentially decaying components (short T_2 and long T_2) on the basis of the following equation[11]:

$$M(t) = \sum_i M_i \exp(-t/T_{2i}) \quad (1)$$

where M_i is proportional to the total number of protons and T_{2i} is the spin–spin relaxation time T_2 for the ith component. The proton fraction of ith component f_i can be evaluated by $M_i/\sum_i M_i$.

Figure 3 shows the temporal change of the fraction of the short T_2 component during the swelling process for the unfilled system in both unstretched and stretched

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* FEF, see ASTM code N550

states ($1<\lambda\leqslant 2$). The unfilled specimen breaks at $\lambda=2$ before reaching equilibrium swelling and thus the swelling ratio could not be evaluated at equilibrium. The decreasing behaviour of the fraction of the short T_2 component depends strongly on λ. With the increase of λ, the fraction of the short T_2 component decreases more quickly.

Figures 4, 5 and *6* show the temporal change of the short T_2 component for the filled systems C20-NBR, C40-NBR and C60-NBR, respectively. With the increase of λ, the fraction of the short T_2 component decreases in a similar manner to that for the unfilled system.

Results of volume swelling measurements

The swelling ratio $S_{r,e}$ of the rubber matrix at equilibrium is given by:

$$S_{r,e}=1/v_{r,e} \qquad (2)$$

where $v_{r,e}$ is the volume fraction of the rubber matrix in non-filler portion of the swollen system, i.e. equal to (rubber matrix)/(rubber matrix + solvent), at equilibrium.

Figure 7 shows the plot of $S_{r,e}$ against λ for NBR systems, in which λ equals $S_{s,e}^{1/3}$ in the case of free swelling. The $S_{r,e}$ value increases with the increase of λ. In the unstretched state, $S_{r,e}$ decreases with increasing filler concentration, consistent with the results for the swelling rate at the early and intermediate stages of the swelling process[11]. However, $S_{r,e}$ for the filled systems is higher in the stretched state ($\lambda\geqslant 1.75$) than that for the unfilled system. In particular, $S_{r,e}$ for C60-NBR increases remarkably with stretching and becomes higher than that for any other systems. It should be noted that $S_{r,e}$ at $\lambda=2$ becomes larger with increasing filler concentration, in contrast with the case of free swelling.

DISCUSSION

Temporal change of the molecular mobility of the network chains

In the previous study[11], the short T_2 component for NBR systems was assigned to regions of the network chains in more constrained conformations around the crosslinks or transient points fixed through the dipole–dipole interactions between the polar side-groups, in

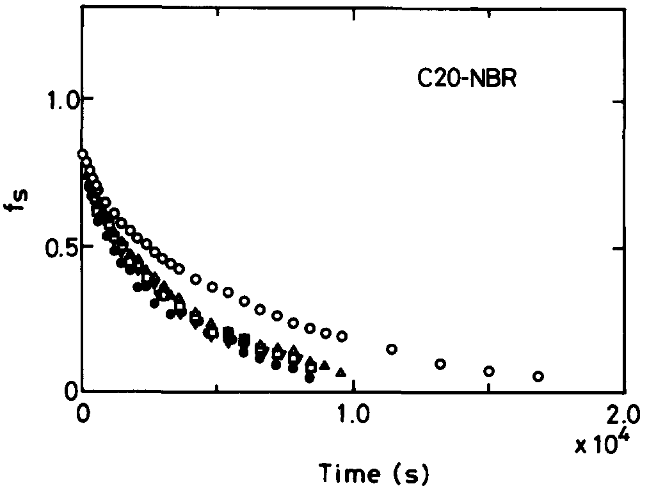

Figure 4 Temporal change of the fraction of the short T_2 component f_s for C20-NBR during the swelling process at various stretch ratios: (○) free swelling; (△) $\lambda=1.43$; (□) $\lambda=1.58$; (▽) $\lambda=1.75$; (●) $\lambda=2$

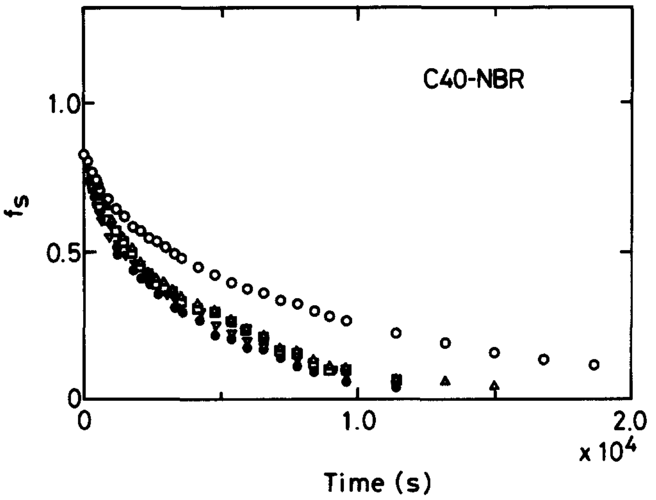

Figure 5 Temporal change of the fraction of the short T_2 component f_s for C40-NBR during the swelling process at various stretch ratios: (○) free swelling; (△) $\lambda=1.43$; (□) $\lambda=1.58$; (▽) $\lambda=1.75$; (●) $\lambda=2$

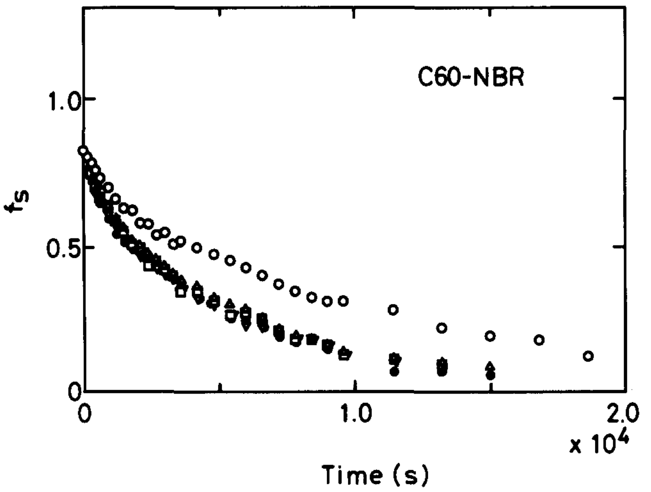

Figure 6 Temporal change of the fraction of the short T_2 component f_s for C60-NBR during the swelling process at various stretch ratios: (○) free swelling; (△) $\lambda=1.43$; (□) $\lambda=1.58$; (▽) $\lambda=1.75$; (●) $\lambda=2$

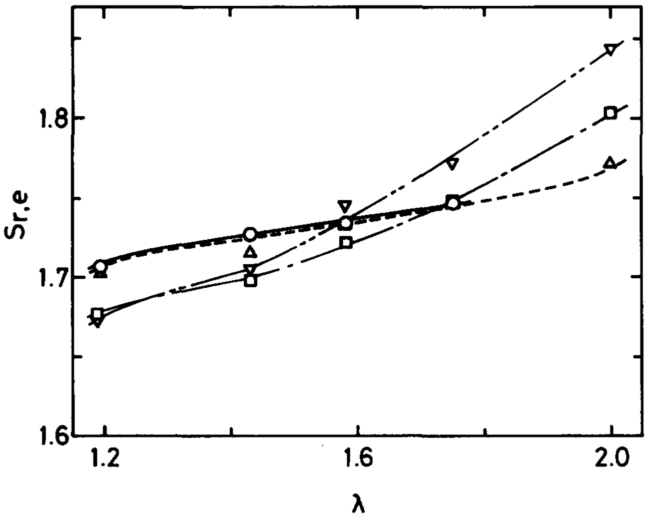

Figure 7 $S_{r,e}$ plotted against λ for the unfilled and filled NBR: (——○——) P-NBR; (– – –△– – –) C20-NBR; (—·—□—·—) C40-NBR; (—··—▽—··—) C60-NBR

comparison with the long T_2 component assigned to those remote from the constraints[13,14]. Furthermore, the decrease of the fraction of the short T_2 component by swelling was directly connected with the enhanced molecular mobility of the network chains through the diffusion of the solvent molecules with high mobility.

For the analysis of the temporal change of the fraction of short T_2 component, the parameter F_n is defined as:

$$F_n \equiv [f_s(0) - f_s(t)]/f_s(0) \qquad (3)$$

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. The degree of the change of the short T_2 component into the long T_2 component can be estimated in terms of F_n. For the unfilled and filled systems in the unstretched state, the time dependence of F_n was shown to be expressed as[11]:

$$F_n = k_n t^{1/2} \qquad (4)$$

where k_n corresponds to the swelling rate evaluated by the real-time T_2 measurements. Experimentally or empirically[10,12], on the basis of Fick's second law for the diffusion equation, the swelling ratio S_r at time t is approximately given by:

$$S_r = 1 + k_s t^{1/2} \qquad (5)$$

where k_s corresponds to the swelling rate evaluated by the volume swelling measurements. It was also shown that k_n can be directly related to the macroscopic swelling rate k_s in equation (5) as follows:

$$k_n = k_s/A \qquad (6)$$

where A is a constant equal to 0.43 for NBR systems. These relations expressed by equations (5) and (6) seem to be qualitatively reasonable considering the diffusion behaviour of the solvent molecules controlled by the molecular mobility of the rubber matrix[10].

Figure 8 shows the plot of F_n against $t^{1/2}$ for the unfilled system at each stretch ratio. The swelling rate k_n can be evaluated from the slope of the linear portion of the plots. All the plots for the filled systems in the unstretched and stretched states also give nearly straight lines in accordance with equation (4), and the evaluated values of k_n are plotted against λ as shown in *Figure 9*. The swelling rate increases with the increase of the stretch ratio, although the increase of the swelling rate for the filled systems becomes suppressed at $\lambda > 1.5$. This behaviour reflects that the swelling is enhanced in the presence of the corresponding tensile stress at a given stretch ratio as compared with that for the stress-free (unstretched) rubber.

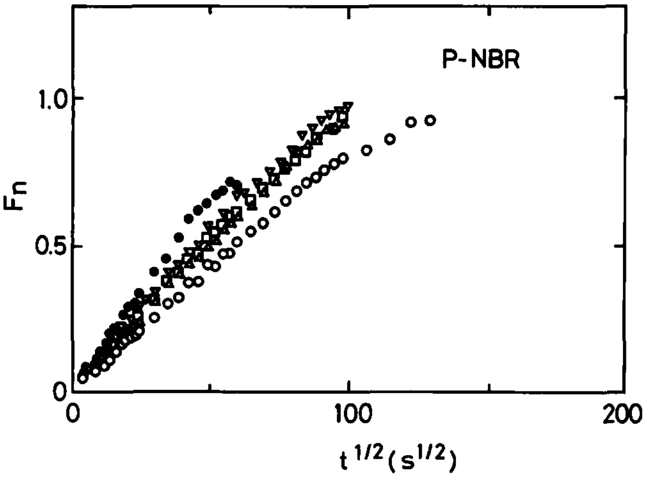

Figure 8 F_n plotted against $t^{1/2}$ for the unfilled NBR at various stretch ratios. Symbols are identified as in *Figure 3*

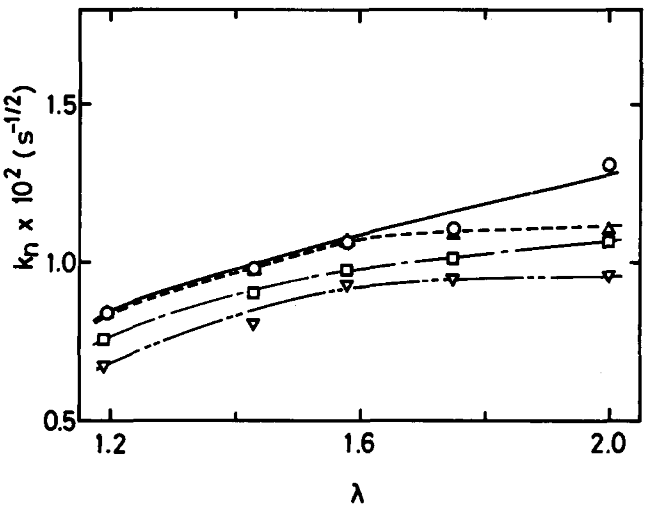

Figure 9 Plot of k_n against λ for the unfilled and filled NBR: (——○——) P-NBR; (---△---) C20-NBR; (—·—□—·—) C40-NBR; (—··—▽—··—) C60-NBR

Origin of dependence of swelling on strain

Flory[6] and Gee[7] showed that the effect of tensile stress increases the amount of swelling of a solvent in a rubber matrix. Furthermore, Treloar solved a more complicated problem of determining the equilibrium swelling ratio in the presence of any type of strain such as simple (uniaxial) elongation or compression, equi-biaxial elongation and hydrostatic pressure[8,9]. Generally, it can be understood that the reduction or increase in the swelling is mainly determined by the hydrostatic component of the applied stress. Hence, a tensile stress, for which the hydrostatic component is negative, leads to an increase in the swelling of the rubber matrix.

The total change in the Gibbs free energy of the swollen rubber (rubber matrix + solvent) on passing from the unstretched unswollen state to the stretched swollen state is expressed as the sum of the free energies of mixing of polymer and solvent molecules and of network deformation. According to Treloar[8,9], for the case of simple tensile stress (i.e. uniaxial elongation), the equilibrium condition on the basis of the Flory–Huggins theory becomes:

$$(RT/V_s)[\ln(1-v_r) + v_r + \chi v_r^2 + (\rho V_s/M_c\lambda)] = 0 \qquad (7)$$

where R is the molar gas constant, T the absolute temperature, V_s the molar volume of the solvent, v_r the volume fraction of the polymer, χ a parameter associated with the polymer–solvent interactions, ρ the density of the rubber, M_c the number-average chain molecular weight and λ the stretch ratio in the direction of the applied force. Hence, from equation (7), the value of v_r can be determined for a given value of λ. By measurements for rubber vulcanizates of simple elongation in a variety of swelling solvents, the validity of the theoretical relation between the strain and the degree of swelling was elucidated, except in the case of poor solvents for the polymers[8,9].

Dependence of swelling on strain

The form of $\ln(1-v_r)$ in equation (7) can be expanded into a series:

$$\ln(1-v_r)=-(v_r+v_r^2/2+v_r^3/3+\cdots) \qquad v_r<1 \tag{8}$$

Hence, on substitution of the first two terms in equation (8) into equation (7), the final result is approximately given by:

$$1/v_r \sim B\lambda^{1/2} \tag{9}$$

where B is a constant equal to $[M_c(1/2-\chi)/\rho V_s]^{1/2}$. Namely, the swelling ratio $S_{r,e}$ $(=1/v_r)$ of the rubber matrix at equilibrium becomes proportional to $\lambda^{1/2}$ in the stretched state.

Figure 10 shows schematically the typical change of the swelling ratio S_r of the rubber matrix during the swelling process of NBR systems in CCl_4 (plot of S_r against $t^{1/2}$ according to equation (5))[11]. At shorter time S_r is approximately proportional to $t^{1/2}$. At the late stage of swelling, the slope of the plot begins to decrease, showing a delayed approach to equilibrium swelling. The initial swelling rate can be evaluated from the linear portion of the plot. Hence, in order to estimate qualitatively the effects of strain on the swelling rate for NBR systems, the characteristic time t_c near the equilibrium for free swelling is selected, as shown schematically in *Figure 10*, although the duration of the linear portion at each strain is not necessarily identical. Namely, for free swelling:

$$t_c=[(S_{r,e}-1)/k_s]^{1/2} \tag{10}$$

and $S_{r,e}$ in stretched states is substituted by the swelling ratio S_r at t_c as follows:

$$S_{r,e} \sim S_r(t=t_c)=1+k_s t_c^{1/2} \tag{11}$$

Hence, from equations (6) and (9), the relation between k_n and λ is assumed to be expressed in the final form:

$$k_n \sim (1/At_c^{1/2})(B\lambda^{1/2}-1) \tag{12}$$

Figure 11 shows the plot of k_n against $\lambda^{1/2}$ for NBR systems. The full lines in the figure give the calculated results with regard to the relation between k_n and $\lambda^{1/2}$ on the basis of equations (9)–(12), where $t_c^{1/2}$ and B were obtained from the k_n and $S_{r,e}$ for free swelling. The calculated results may not give a good fit to the experimental results, but the plot for the unfilled system shows a linear relation (broken line in the figure), qualitatively consistent with equation (12). Furthermore, the plots for the filled systems deviate from the linear relation, associated with the restriction of the increased swelling, especially at $\lambda>1.5$. The decreasing tendency in the slope of the plot for the filled systems becomes noticeable with the increase of λ. Probably, the restriction of the increased swelling (initial swelling rate) for the filled systems in the stretched states may be caused by both the constrained molecular motions[13] and some local molecular orientation of the network chains induced by stretching (analogous to the spatial effects of filler particles on the swelling)[15].

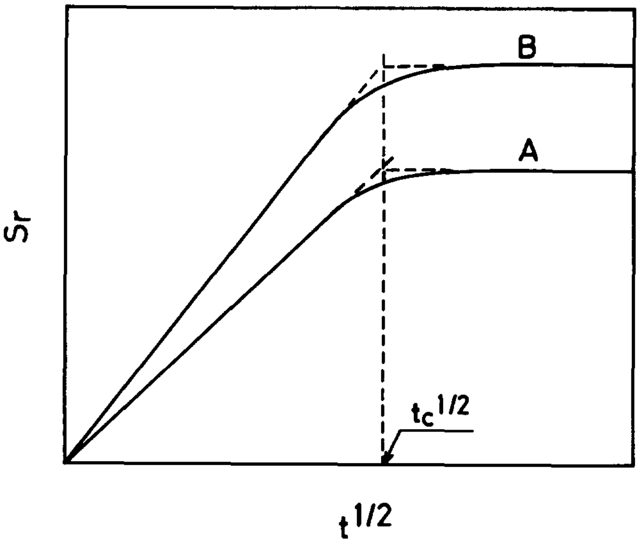

Figure 10 Schematic illustration of the swelling behaviour of NBR (plot of S_r against $t^{1/2}$). Characteristic time t_c near the equilibrium for free swelling (curve A) is selected. Swelling ratio $S_{r,e}$ at equilibrium for A and B curves are substituted by S_r at t_c on the basis of equation (11)

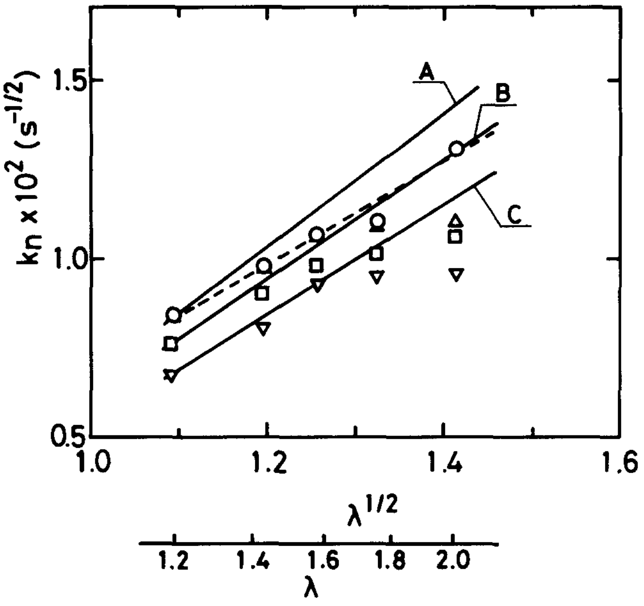

Figure 11 Plot of k_n against $\lambda^{1/2}$: (○) P-NBR; (△) C20-NBR; (□) C40-NBR; (▽) C60-NBR. Full lines show the calculated relations for the unfilled and filled NBR on the basis of equation (12): A, P-NBR and C20-NBR; B, C40-NBR; C, C60-NBR. The broken line is fitted to the experimental results for P-NBR

On the other hand, the swelling ratio $S_{r,e}$ at equilibrium increases with stretching more remarkably in the filled systems than in the unfilled system, especially at $\lambda>1.5$ as shown in *Figure 7*. Namely, in contrast to the dependence of the swelling rate on the strain, $S_{r,e}$ increases remarkably at $\lambda\sim2$ with increasing filler concentration. Therefore, it is considered that the dominant effects of the incorporated filler particles on the swelling at a late stage of the swelling process may be different from those at the early and intermediate stages of the swelling process.

Strain amplification effect on swelling

In filled rubber vulcanizates, strain amplification is considered to be a useful concept for understanding the reinforcement of the rubber matrix through the incorporation of reinforcing filler particles[13,16]. For filled systems, the rigid filler does not share in deformation, and thus the inclusion of the filler attached to the network chains causes the average local strain in the rubber matrix to exceed the macroscopic strain. The strain amplification

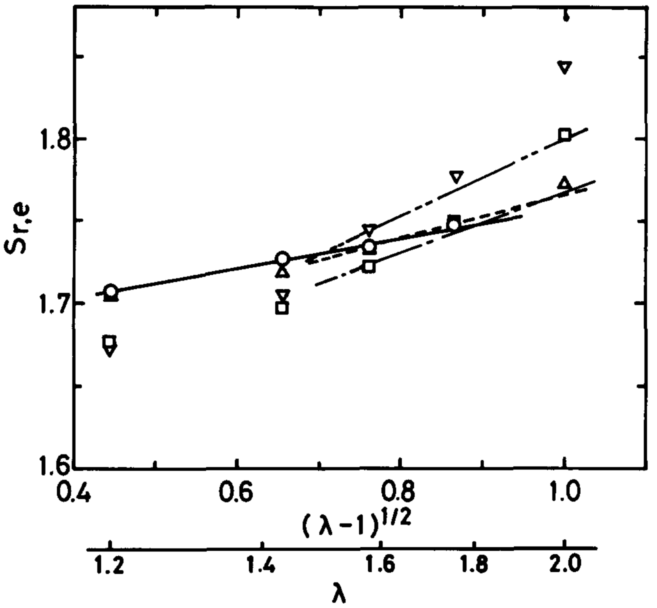

Figure 12 $S_{r,e}$ plotted atainst $(\lambda-1)^{1/2}$ for the unfilled and filled NBR: (——○——) P-NBR; (– – –△– – –) C20-NBR; (—·—□—·—) C40-NBR; (—··—▽—··—) C60-NBR. The full line is fitted to the experimental results for P-NBR. Lines for the filled NBR at $\lambda > 1.5$ show the calculated relations on the basis of equations (14) and (15)

effect leads to a higher stress as compared with that in the unfilled system. Hence, in the swelling process of the filled systems, the increased average local strain in the rubber matrix proportional to the filler concentration should cause the increase of $S_{r,e}$ on the basis of equation (7). However, as for the swelling behaviour of NBR systems immersed in CCl_4, the detailed discussion for the dependence of the equilibrium swelling on the strain using equation (9) may not be valid, because of the low degree of swelling ($S_{r,e} < 2$) as reported by Treloar[8,9].

In this study, in order to examine qualitatively the dependence of $S_{r,e}$ on λ by using the strain amplification concept, the $S_{r,e}$ value was plotted against $(\lambda-1)^{1/2}$ as shown in *Figure 12*, instead of against $\lambda^{1/2}$. The plot for the unfilled system gives a nearly straight line, and the experimental relation is approximately given by:

$$S_{r,e} = C_0(\lambda-1)^{1/2} + C_1 \qquad (13)$$

where C_0 and C_1 are constants. For $1.2 < \lambda < 1.5$, the slopes of the plot for the filled systems are almost identical with that for the unfilled system as shown in *Figure 12*.

In the T_2 measurements of NBR systems under deformation[13], the dependence of T_2 on λ could be reasonably understood by using the strain amplification concept on the molecular mobility of the network chains in the stretched state at $\lambda > 1.5$. Hence, for $\lambda > 1.5$, on the assumption that the average local strain in the filled rubber matrix is amplified proportional to the filler concentration as compared with that in the unfilled rubber matrix, the experimental relation between $S_{r,e}$ and λ in equation (13) for the filled systems can be expressed as:

$$S_{r,e}(\lambda, c) = C_0[X(\lambda-1)]^{1/2} + C_1(c) \qquad \lambda > 1.5 \quad (14)$$

where X is the strain amplification factor, c the volume fraction of the filler and C_1 a constant depending on c. The strain amplification factor in equation (14) is assumed to be expressed by:

$$X(c) = 1 + 0.67fc + 1.62f^2c^2 \qquad (15)$$

where f ($=6.5$) is the shape parameter of the filler[16,17]. The lines for the filled systems at $\lambda > 1.5$ in *Figure 12* show the calculated relation between $S_{r,e}$ and $(\lambda-1)^{1/2}$ for the filled systems on the basis of equations (14) and (15). It is found that the strain amplification concept may be qualitatively applicable to the dependence of the equilibrium swelling on the strain for the filled systems to some degree, although the deviation of the experimental results from the calculated relations becomes noticeable at $\lambda \sim 2$.

Thus, from the results of the dependence of k_n and $S_{r,e}$ on the strain for NBR systems, it is suggested that the presence of filler particles in the rubber matrix can be interpreted as at least two types of effects on the swelling behaviour of the rubber matrix in the stretched states, especially at $\lambda > 1.5$. The first is a transient restraint, which reduces the initial swelling rate through some oriented structure induced by stretching, associated with the constrained molecular mobility of the overall network chains. The second is a permanent strain amplification effect depending on the filler concentration, which enhances the swelling ratio at equilibrium relative to that of the unfilled system.

CONCLUSIONS

The effects of tensile strain on the swelling behaviour of NBR systems (unfilled and filled) immersed in CCl_4 were studied by real-time n.m.r. measurements and measurements of the swelling ratio at equilibrium. By the T_2 measurements, it was directly observed that the increase of the molecular mobility of the rubber matrix through diffusion of the solvent is enhanced with increase of the strain. On the basis of the theory proposed by Treloar, the effects of the tensile strain on the swelling rate and the swelling ratio at equilibrium could be qualitatively discussed. It is suggested that the presence of reinforcing fillers such as carbon black exerts two noticeable effects on the swelling of the rubber matrix under deformation: (1) a transient spatial effect caused by some oriented structure, induced by stretching, restricts the initial swelling rate; (2) a strain amplification effect proportional to the filler concentration increases the average local strain in the rubber matrix and causes the increase of the swelling ratio at equilibrium under tensile strain more remarkably in comparison with that for the unfilled system. Therefore, for practical use of rubber parts that are commonly in contact with solvents such as fuels and oils, the reinforcing fillers as well as the polymers have to be carefully chosen to meet service conditions. A more precise study of the swelling behaviour of rubber vulcanizates under various conditions will be made in the near future.

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