

# Dynamic mechanical relaxation of lightly cross-linked natural rubber

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The isochronal mechanical relaxation spectra of lightly cross-linked natural rubbers were measured at frequency 1 Hz. The results were analysed using the empirical Havriliak–Negami (HN) equation. The HN equation fitted the relaxation spectra very well. The fitting parameters,  $\alpha$  and  $\beta$ , obtained from the data fitting were used to interpret the relation between molecular motions and structure of polymers based on the model proposed by Schönhals and Schlosser. In the high-frequency region of relaxation spectra, the values of  $\alpha\beta$  were increased with increasing sulphur content. According to the model proposed by Schönhals and Schlosser, it means that the molecular motions are related to the local intramolecular interactions and are mainly influenced by the formation of heterocyclic groups along the chain. However, in the low-frequency region of relaxation spectra, the values of  $\alpha$  were not affected by increasing sulphur content. According to the model proposed by Schönhals and Schlosser, the molecular motions in this region are related to the intermolecular interactions. They are not influenced by the level of cross-linking due to the very low level of cross-link. © 1998 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

The natural rubber is a very important material. Intensive study has been done on the properties of natural rubbers. The relationship between molecular motions and structure of the natural rubbers is one of them. Dielectric and mechanical relaxation methods are common probes for the study of molecular motions and structure. In comparison with the mechanical relaxation, considerable works have been done on the dielectric relaxation of the natural rubbers. In this study, the mechanical relaxation behaviours of natural rubbers were measured and the discussion was concentrated on the relationship between molecular motions and structure in the glass transition region.

To strengthen the natural rubber, it is vulcanized by adding the sulphur then heating it up to around 160°C. This process involves the cross-linking of the polymer chains by mono- or polysulphide bridges. An interesting side reaction along with the vulcanization is found that the heterocyclic groups are formed randomly in the main chain<sup>1–4</sup>. Schmieder and Wolf<sup>5</sup> have studied the mechanical relaxation of the sulphur-cured natural rubber using a torsion pendulum around the frequency 1 c/s. It is found that the temperature of  $\tan \delta_{\max}$  changes from  $-40^\circ\text{C}$  for 5% sulphur to  $+63^\circ\text{C}$  for 30% sulphur. Also, Mason has studied the mechanical and thermal expansion properties of the dicumyl peroxide-cured natural rubber<sup>6</sup>. It is found that there are no heterocyclic groups formed during the curing. The mechanical relaxation was carried out using a torsion pendulum around the frequency 1 c/s as in Schmieder and Wolf's method. However, the increase of the glass transition temperature with increasing the concentration of dicumyl

peroxide is not significant compared with that found for sulphur-cured natural rubber. They suggested that the effect of cross-linker on the glass transition temperature for the sulphur-cured natural rubber should be about the same as the peroxide-cured natural rubber. Therefore, the significant change of glass transition temperature for sulphur-cured natural rubber should be due to the formation of heterocyclic groups along the chains. The dielectric relaxation experiments show the same results as the mechanical relaxation experiments<sup>7,8</sup>. Although the mechanical and dielectric relaxation behaviours of natural rubbers have been studied long time ago, it is still very important to establish a theoretical model to analyse the relaxation spectra and to correlate the molecular motion of chains with the structure of chains. Thus, the well-known relationship between molecular motions and structure of sulphur-cured natural rubber is used to demonstrate it.

## BACKGROUND

It has been quite common to use empirical functions to analyse the shape of dielectric relaxation spectrum. Two most frequently used empirical equations are the Havriliak–Negami (HN)<sup>9</sup> and the Kohlrausch–Williams–Watts (KWW)<sup>10,11</sup> equations. The HN equations for the complex dielectric constant,  $\epsilon^*$ , can be written as

$$\epsilon^* = \epsilon_u + \frac{\epsilon_r - \epsilon_u}{[1 + (i\omega\tau_0)^\alpha]^\beta} \quad (1)$$

where  $\epsilon_u$  and  $\epsilon_r$  are the unrelaxed and relaxed values of the dielectric constants,  $\tau_0$  is the mean relaxation time and  $\omega$  is the angular frequency. In equation (1),  $\alpha$  and  $\beta$  ( $0 < \alpha \leq 1$ ,  $0 < \alpha\beta \leq 1$ ) are adjustable fitting parameters. The HN

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equation was developed from the equation of a single relaxation time model that was proposed by Debye<sup>12</sup>. In a single relaxation time model, the molecular motions would proceed with only one relaxation time. For such a single relaxation time model, the complex dielectric constant can be described by equation (1) with  $\alpha = 1$ ,  $\beta = 1$  and  $\tau_0$  as the Debye relaxation time. For many materials, the relaxation environment of each molecule is different. Therefore, molecular motions should be different and should exhibit different relaxation time. Thus, Cole and Cole<sup>13</sup> modified the single relaxation time model by adding an adjustable parameter,  $\alpha$  (i.e. in equation (1),  $0 < \alpha \leq 1$  and  $\beta = 1$ ), to fit the dielectric relaxation spectrum. The Cole–Cole equation admits symmetrical broadening about the central relaxation time  $\tau_0$  by adjusting the parameter,  $\alpha$ . Although many materials obey the Cole–Cole equation, some polymers exhibit asymmetrical distribution of relaxation time. Therefore, Davidson and Cole<sup>14</sup> modified the single relaxation time model by adding the adjustable parameter  $\beta$  (in equation (1),  $\alpha = 1$  and  $0 < \alpha\beta \leq 1$ ), to describe the asymmetrical distribution of relaxation time. In order to allow the broadening and skewing of the relaxation spectrum at same time, a more general equation, the HN equation, was proposed by Havriliak and Negami. They combined the Cole–Cole equation and the Davidson–Cole equation together. The HN equation has been successfully used to fit the dielectric relaxation spectrum for many materials<sup>15–19</sup>.

Usually, parameters ( $\epsilon_u$ ,  $\epsilon_r$ ,  $\tau_0$ ,  $\alpha$ ,  $\beta$ ) of the HN equation are determined from a single isothermal relaxation spectrum. However, the relaxation of polymer is so broad in the frequency or time domain at most temperatures that even a very wide ranging (in frequency or time) isothermal measurement covers a small part of the relaxation. It is necessary to determine parameters from several isothermal relaxation spectra to get sufficient information<sup>19</sup>. Another way to achieve the same results is to regard the parameters,  $\epsilon_u$ ,  $\epsilon_r$ ,  $\alpha$  and  $\beta$ , as linear functions of temperature:

$$\epsilon_u = \epsilon_u^0 + \epsilon_u^s(T - T_u)$$

$$\epsilon_r = \epsilon_r^0 + \epsilon_r^s(T - T_r)$$

$$\alpha = \alpha^0 + \alpha^s(T - T_\alpha)$$

$$\beta = \beta^0 + \beta^s(T - T_\beta)$$

where  $T_u$ ,  $T_r$ ,  $T_\alpha$ , and  $T_\beta$  are arbitrary chosen reference temperature, the superscript o indicates the value at an arbitrary chosen reference temperature  $T_p$ , the superscript s indicates a linear temperature coefficient. The relaxation time,  $\tau_0$  followed either an Arrhenius relation,

$$\log \tau_0 = A/T + B,$$

or the WLF relation,

$$\log \tau_0 = A/(T - T_\infty) + B.$$

These assumptions have been successfully used for many polymers<sup>16,17</sup>. Also, it is the better way to determine the parameters when the frequency region of experiment is not wide enough.

It is quite common in dielectric studies to fit the relaxation spectrum with the HN equation. Although it is not so common for mechanical studies, it has been shown that the HN equation fits the mechanical relaxation spectrum as well as the dielectric, including isochronal scans<sup>16,20,21</sup>. For mechanical relaxation, the HN equation is

modified as

$$E^* = E_u - \frac{E_r - E_u}{[1 + (i\omega\tau_0)^\alpha]^\beta} \quad (2)$$

where  $E_u$  and  $E_r$  are the unrelaxed and relaxed modulus of polymer, respectively. Again,  $0 < \alpha \leq 1$  and  $0 < \alpha\beta \leq 1$ . Parameters still have the same relation with temperature as dielectric case.

$$E_u = E_u^0 + E_u^s(T - T_u) \quad (2a)$$

$$E_r = E_r^0 + E_r^s(T - T_r) \quad (2b)$$

$$\alpha = \alpha^0 + \alpha^s(T - T_\alpha) \quad (2c)$$

$$\beta = \beta^0 + \beta^s(T - T_\beta) \quad (2d)$$

$$\log \tau_0 = A/T + B, \quad (2e)$$

or

$$\log \tau_0 = A/(T - T_\infty) + B \quad (2f)$$

Although the HN equation has been successfully used to fit the dielectric and mechanical relation data, it is still limited to correlating the parameters of the HN equation with the molecular motions and structure of polymer chains. Recently, a model<sup>18</sup> has been proposed to explain the shape of the dielectric relaxation spectrum near the glass transition temperature. It suggested that the molecular motions of polymer in the glass transition are controlled by both intra- and intermolecular interactions. Considering the scale of molecular motion, the model suggested that in the high-frequency region (i.e.,  $\omega\tau \gg 1$ ), the relaxation was controlled by the local chain dynamics, and in the low-frequency region (i.e.,  $\omega\tau \ll 1$ ), the relaxation was controlled by the intermolecular interaction. From equation (1) or equation (2), it can be found that on the plot of  $\log(\text{loss peak})$  versus  $\log(\omega\tau)$ , the slope of relaxation loss peak on the high-frequency side is proportional to the product  $-\alpha\beta$  and on the low-frequency side, the slope is proportional to  $\alpha$ . Therefore, parameter  $\alpha$  can be correlated to the intermolecular dynamics and the product  $\alpha\beta$  can be correlated to very local intramolecular dynamics of the polymer<sup>19</sup>.

## EXPERIMENTAL SECTION

The natural rubber, 2-mercapto benzothiazoles, 2-benzothiazole disulfide, ZnO, stearic acid and sulphur were mixed using a tow roll mill. Three different samples, NR04, NR06 and NR10 were prepared under the same conditions. The only difference among these samples is the amount of sulphur in the sample. The amount of sulphur, based on natural rubber, is 0.4, 0.6, and 1 phr for NR04, NR06 and NR10, respectively. The recipes for the samples are listed in Table 1. The vulcanization was done by heating the samples up to 165°C for 10 min. Then the sample was cut into strips (typically 30 × 10 × 3 mm) for the measurement of mechanical relaxation behaviour. The dynamic mechanical

**Table 1** The recipes for the samples

Sample	Natural rubber	Sulphr	DM <sup>a</sup>	M <sup>b</sup>	ZnO	Steric aid
NR04	100	0.4	0.2	0.1	1.0	0.5
NR06	100	0.6	0.2	0.1	1.0	0.5
NR10	100	1.0	0.2	0.1	1.0	0.5

relaxation measurement was done in tension using a DMA (TA instrument Co.) with fixed mode (1 Hz) and at 5°C/min.

PHENOMENOLOGICAL DATA FITTING

In order to correlate the parameters of the HN equation with the molecular motions and structure of polymer chains, the curve fitting of relaxation spectrum was done by non-linear least-squares optimization of the fit of the HN equation to both the experimental storage and loss moduli isochronal curves. In this study, the discussion is concentrated on the glass relaxation. In the glass transition region, the drop of storage moduli is dramatic. Thus, the object function for minimization is written as

$$f = \sum (\log E_{cal}'(i) - \log E_{exp}'(i))^2 + \sum (\log E_{cal}''(i) - \log E_{exp}''(i))^2$$

where  $E'$  and  $E''$  are the storage and loss moduli, the subscripts 'cal' and 'exp' indicate the calculate value from equation (2) and the experimental value of storage and loss moduli, respectively. The object function ignores the connection between  $E'$  and  $E''$  occasioned by a Kramers-Kronig-like relation. The minimization of object function was done by using Marquardt's Method.

Since the fitting process is an iterative one, an initial guess for the parameters must be prepared. There are 10 parameters,  $E_u^0, E_v^0, E_r^0, E_r^s, \alpha^0, \alpha^s, \beta^0, \beta^s, A, B$ , for the glass transition to be determined. Since, it is around  $200 \times 2$  experimental data points for an isochronal relaxation curve. The determination of parameters usually proceeds satisfactorily. There is no constraint on the parameters.

RESULTS AND DISCUSSION

Figures 1 and 2 are the isochronal storage and loss moduli of samples along with the best fit of equation (2) (only the glass transition of the relaxation is shown). They show the typical relaxation spectrum of lightly cross-linked materials. The storage moduli drops from  $\sim 10^9$  to  $\sim 10^6$  Pa in the glass transition region. The glass transition temperatures are

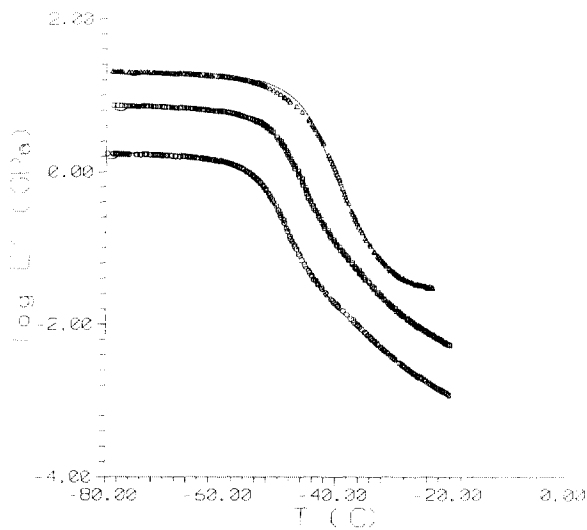


Figure 1 Isochronal plot of the storage moduli measured for (a) NR04 (O), (b) NR06 (□), (c) NR10 (Δ). The solid curve is the best fit of equation (2). For clarity of plotting, the log  $E'$  curves for NR06 and NR10 were displaced upward by 0.5 and 1.0, respectively

-52.72, -50.00 and -47.03°C for NR04, NR06 and NR10, respectively. Although the increase of glass transition temperature is not as great as mentioned by McCrum *et al.*<sup>3</sup>, it does increase with increasing concentration of sulphur in the samples. However, the increase of the glass relaxation temperature is larger than the dicumyl peroxide-cured natural rubber<sup>3</sup>. Obviously, the reasons for the increase in glass transition temperature are the formation of heterocyclic groups along the polymer chains and the cross-link of polymer chains. According to McCrum *et al.*<sup>3</sup>, the major factor of the increase of glass transition temperature is the formation of heterocyclic groups. The formation of heterocyclic groups more effectively increases the energy barrier of glass transition. In Figure 3, a normalized loss modulus ( $E''/E_{max}''$ ) versus  $\log(\tau_{max}/\tau)$  of samples is shown. The relaxation time,  $\tau$ , was back-calculated from phenomenological data fitting. The subscript, max, indicates the value of peak of loss modulus curve. As shown in Figure 3, the normalized loss modulus

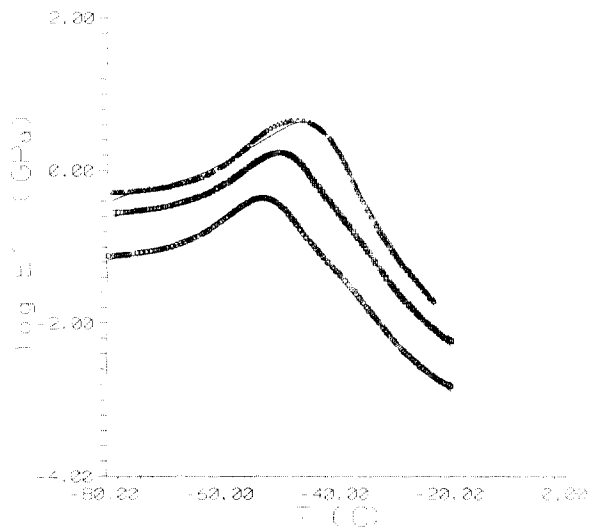


Figure 2 Isochronal plot of the loss moduli measured for (a) NR04 (O), (b) NR06 (□), (c) NR10 (Δ). The solid curve is the best fit of equation (2). For clarity of plotting, the log  $E''$  curves for NR06 and NR10 were displaced upward by 0.5 and 1.0, respectively

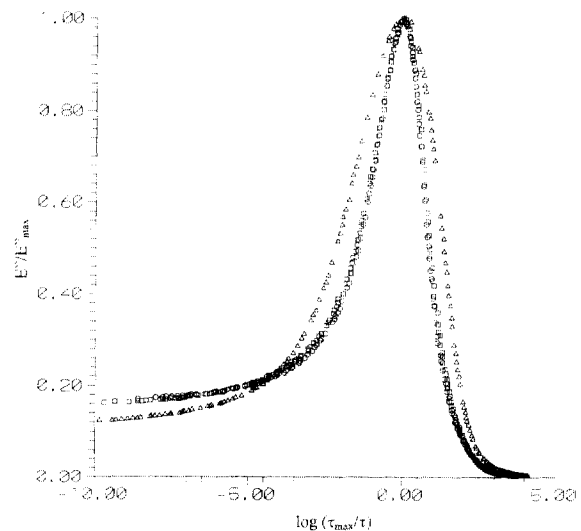


Figure 3 Normalized loss moduli ( $E''/E_{max}''$ ) versus  $\log(\tau/\tau_{max})$  of: (a) NR04 (O); (b) NR06 (□); (c) NR10 (Δ)

**Table 2** The fitting parameters

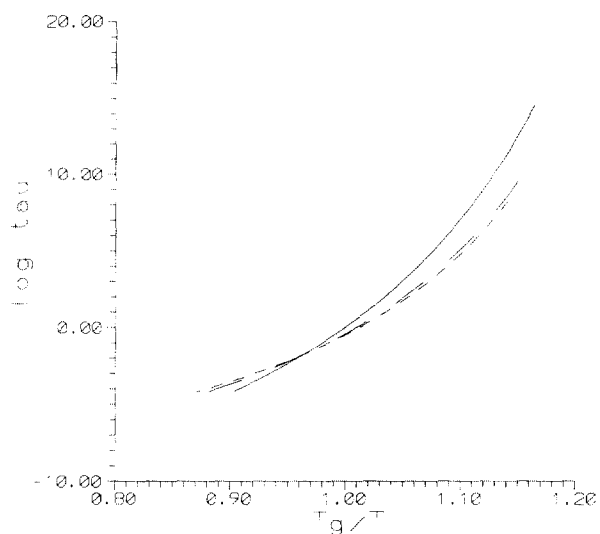
Sample	$E_u^0$	$E_u^0$ ( $\times 10^2$ )	$T_u$	$E_r^0$	$E_r^0$ ( $\times 10^5$ )	$T_r$	$A$	$B$	$T_x$	$\alpha^0$	$\alpha^s$ ( $\times 10^3$ )	$T_\alpha$	$\beta^0$	$\beta^s$ ( $\times 10^2$ )	$T_\beta$
NR04	2.42	-3.03	193.0	$-8.11 \times 10^{-5}$	-9.79	260.0	641.62	-11.08	160.0	0.759	-2.14	260.0	1.093	1.58	260.0
NR06	3.29	-4.04	193.0	$2.54 \times 10^{-4}$	-11.30	260.0	736.45	-12.06	160.0	0.776	-1.72	260.0	0.933	1.37	260.0
NR10	2.71	-1.31	193.0	$3.12 \times 10^{-3}$	6.52	260.0	1031.11	-15.56	160.0	0.887	0.00	260.0	0.530	0.78	260.0

The units for  $E_u^0$ ,  $E_r^0$  are GPa, the units for  $E_u^s$  and  $E_r^s$  are GPa/K, the units for  $A$  and  $T_u$ ,  $T_r$ ,  $T_x$ ,  $T_\alpha$ ,  $T_\beta$  are K and the units for  $\alpha^s$  and  $\beta^s$  are  $K^{-1}$

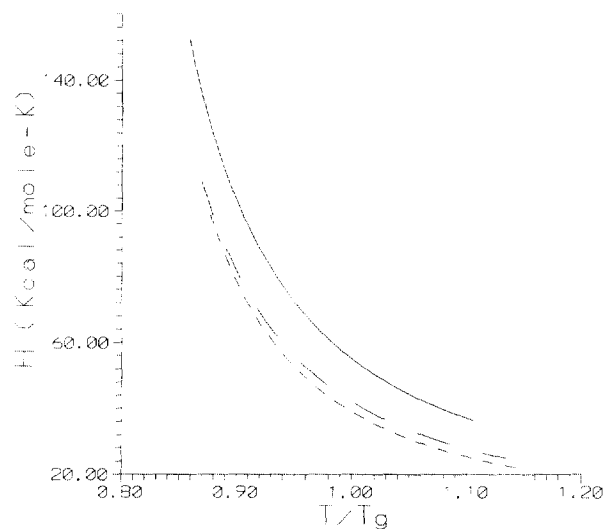
curves of samples become broader with increase of the concentration of sulphur in the region  $\log(\tau_{max}/\tau) > -4.0$ . However, the high frequency 'tail' of the loss modulus curves decrease with increasing the concentration of sulphur. Furthermore, there is no significant difference of normalized loss modulus in the low frequency region. The results are the same as those reported by Stratton and Ferry<sup>22</sup>.

In order to quantify the relaxation characteristics, the parameters in equation (2) were determined by fitting to the experimental data. The results are shown in Table 2. As shown in Figures 1 and 2, the fitting is very well as expected.

As mentioned in the previous section, the molecular motions of polymer in the glass transition are controlled by both intra- and intermolecular interactions. Such effects can be examined by observing the relation between the relaxation time and temperature. Over the glass transition-temperature region, temperature dependencies are non-Arrhenius. For different polymers, the glass transition occurs in different temperature regions. The relaxation time is not only affected by intra- and intermolecular interaction but also by the temperature. Therefore, some normalization scheme must be invoked to allow comparisons among different polymers of the effect of temperature on the relaxation time. Recently, Angel<sup>23</sup> suggested a normalization scheme to study this effect. The relaxation time,  $\tau$ , is plotted as a function of temperature normalized by the glass transition temperature. Such normalization scheme has recently been successfully utilized in polymers<sup>24</sup>. The relaxation time of the sample was back-calculated by equation (2f) from the relaxation spectrum fitting. Then, the relaxation time was plotted as the function of temperature normalized by the glass transition temperature, measured by the dynamic relaxation experiment. The results are shown in Figure 4. As shown in Figure 4, in the low-temperature region (that is high-frequency region), the relaxation time is increased with increasing concentration of sulphur. However, the difference of relaxation time among samples is not significant in the high-temperature region (that is, low-frequency region). This can be explained by the difference in structure among samples. In a relative scale, in the high-temperature region the molecular motions would be expected to be large scale and inter-molecularly cooperative in nature. On the other hand, in the low-temperature region, the molecular motions would be expected to be small scale and very local in nature. According to Glatz-Reichenbach *et al.*<sup>19</sup>, in the styrene-butyl acrylate system, the cross-link points would not result in much change of molecular motions when the concentration of cross-link agent is less than 1 wt.%. Up to 1 wt.% of cross-link agent it would interfere the long-range relaxation, but it would not inhibited the local molecular motion. In this study, the concentration of sulphur is so low (less than 1 phr) that the average length of the segments between cross-link points is higher than the average length of the



**Figure 4** The relaxation time versus  $T_g$ -normalized temperature. The dashed curve with shorter segments represents the NR04. The dashed curve with longer segments represents the NR06. The solid curve represents the NR10



**Figure 5** The activation energy of relaxation versus  $T_g$ -normalized temperature. The dashed curve with shorter segments represents the NR04. The dashed curve with longer segments represents the NR06. The solid curve represents the NR10

segment involved in the glass transition process<sup>4</sup>. Therefore, it is expected that there is no effect of cross-linker on the molecular motions with short relaxation time (high-temperature region). Although it is expected that there is no effect of cross-linker on the local molecular motions, the formation of heterocyclic groups along the polymer chain does increase the energy barrier of intra-chain molecular

motions resulting in the increase of relaxation time. As shown in Figure 4, this will have much effect on local molecular motions than inter-molecular motions. Another interesting result of Figure 4 is the slope of the curves. The slope of curves indicates the activation energy of relaxation. The activation energy was calculated by  $H = 2.303RT^2 / (T - T_\infty)^2$ . In Figure 5, the activation energy is plotted as the function of normalized temperature,  $T/T_g$ . As shown in Figure 5, the activation energy is increased with increasing the sulphur concentration. Again, it is due to the increase of formation of heterocyclic groups along the polymer chain, perhaps, and cross-linking.

The parameters,  $\alpha$  and  $\beta$ , are back-calculated by equation (2c) and equation (2d) from data fitting. The parameters,  $\alpha$  and  $\beta$ , are not only affected by the structure of polymer but also by the temperature. Therefore, some normalization scheme must be invoked to allow comparisons among different polymers of the effect on temperature on the  $\alpha$  and  $\beta$ . The normalized temperature will be defined as  $T - T_g$  and

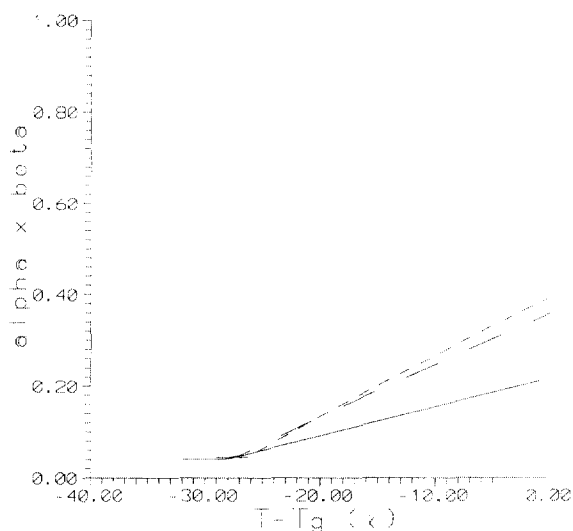


Figure 6 The fitting parameters  $\alpha\beta$  versus temperature. The dashed curve with shorter segments represents the NR04. The dashed curve with longer segments represents the NR06. The solid curve represents the NR10

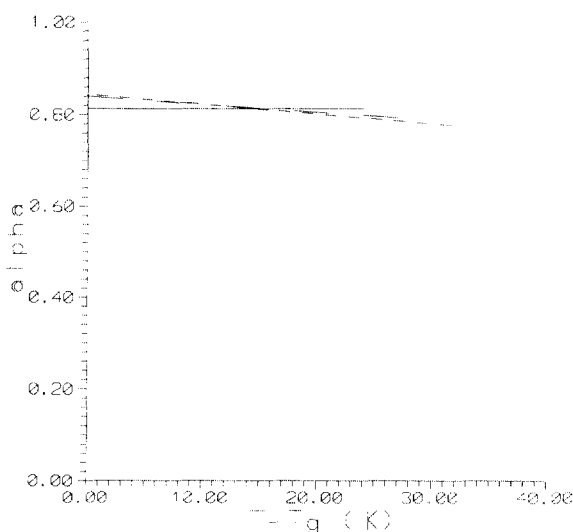


Figure 7 The fitting parameters  $\alpha$  versus temperature. The dashed curve with shorter segments represents the NR04. The dashed curve with longer segments represents the NR06. The solid curve represents the NR10

the parameters are plotted versus normalized temperature. In Figure 6, the values of  $\alpha\beta$  are plotted as a function of  $T - T_g$ . According to the dynamic model proposed by Schönhals and Schlosser<sup>18</sup>, in the high-frequency region, the loss dielectric constants,  $\epsilon''(\omega)$  can be scaled as

$$\epsilon''(\omega) \propto (\omega\tau)^{-n}$$

where  $n = \alpha\beta$ , in this study. In the high-frequency region (low-temperature region), the molecular motions would be expected to be intra-chain and very local in nature. As shown in Figure 6, in the low-temperature region (near the glass transition temperature), the values of product of  $\alpha\beta$  are decreased with increasing sulphur concentration. Thus, the local molecular motions are correlated with the concentration of sulphur. However, the detailed physical interpretation of the model is not yet clear. One may argue that there may be multiple environments that the segments of motion experience. Those segments close to the cross-link points and the heterocyclic groups are constrained, while those far away from the cross-link points and heterocyclic groups are relaxed in a manner more like uncross-linked polymer. In the styrene-butyl acrylate system<sup>19</sup>, the values of the product of  $\alpha\beta$  were not affected by the concentration of cross-link agent at all. Therefore, the significant change of product of  $\alpha\beta$ , in this study, would be expected to be due to the formation of heterocyclic groups along the chain. In the temperature region far away from the glass transition temperature, the difference of values of  $\alpha\beta$  is getting less, even no difference. It seems to suggest that there is no effect on the extremely local motion by the formation of heterocyclic groups. The scale of molecular motions interfered with by the formation of heterocyclic groups might depend on the density of the heterocyclic groups. In Figure 7, the values of  $\alpha$  were plotted as a function of  $T - T_g$ . According to the dynamic model proposed by Schönhals and Schlosser<sup>18</sup>, in the low-frequency region, the loss dielectric constants, can be scaled as

$$\epsilon''(\omega) \propto (\omega\tau)^m$$

where  $m = \alpha$ , in this study. In the low-frequency region (high-temperature region), the molecular motions would be expected to be inter-chain and large-scale motions in nature. As shown in Figure 7, in the high-temperature region, the difference of  $\alpha$  is not significant as  $\alpha\beta$  (the magnitude of  $\alpha$  is not same as  $\alpha\beta$ ) Thus, the molecular motions are not much interfered by the level of sulphur concentration. The result is same as the styrene-butyl acrylate system reported by Glatz-Reichenbach. The level of sulphur is too low to have significant effect on the large scale motions.

### CONCLUSIONS

We have investigated the influence of concentration of sulphur on the molecular dynamics of natural rubbers polymers. The glass transition temperature of natural rubbers was increased with increasing the concentration of sulphur. The major factor of this effect is the formation of heterocyclic groups along the chains.

The results showed that the HN equation could describe the relaxation spectra very well. The relaxation time increased with increasing the concentration of sulphur in the low-temperature region and no significant difference in the high-temperature region. On the basis of the model proposed by Schönhals and Schlosser, the results suggest

that the local motions were interfered by the formation of heterocyclic groups along the polymer chains. However, the large-scale motions were not interfered with by the cross-link points and the formation of heterocyclic groups. Also, the same conclusions are obtained from the analysis of parameters,  $\alpha$  and  $\alpha\beta$ .

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