

Viscoelastic and Thermoelastic Properties of General Purpose Commercial Vulcanized Natural Rubber

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Synopsis

Viscoelastic and thermoelastic properties of general purpose vulcanized natural rubber were investigated focusing attention on its nonideal or irreversible natures. The master curve is not composed by simple horizontal shift of stress-relaxation curves at various temperatures by the time-temperature superposition principle. In order to compose a smooth master curve, both horizontal and vertical shifts are necessary. The relative stress-time relation elucidates the fact that the stress-relaxation mechanism is caused by the chemical scission by oxidation occurring in the network system. The value of vertical shift increases with increasing temperature or strain. This phenomenon has the same meaning as the one derived from the relative stress-time relation. The activation energies are calculated using the horizontal shift factors determined empirically. The result suggests the existence of two concurrent relaxation mechanisms with different activation energies. From the stress-temperature relation at any given strain, energetic and entropic components of the stress-strain curve are obtained. The energetic component is very significant as compared with the case of ideal crosslinked natural rubber. This phenomenon is considered to be caused by the internal friction and/or chemical scission of bonds in the system associated with the deformation process of sample.

INTRODUCTION

Rubbers are complex materials. In general, they exhibit a unique combination of physical properties; at the same time vulcanized rubber compounds are possible which have a very wide range of properties. These facts provide main reasons why the physical properties of rubber are of great interest to study.

The basic feature of the phenomenon of elasticity or viscoelasticity of rubber vulcanizates has well established in the molecular theories of James and Guth¹ and Flory.² The two types of molecular mechanisms contribute to the elongation of vulcanized rubbery materials. The first one is the uncoiling and orientation of the molecular chains in the network structure, and the second one is the plastic flow mechanism. The former mechanism of extension is recoverable with time, but the extension resulting from plastic flow is irrecoverable. For vulcanized rubber the flow mechanism is mainly the result of thermal or oxidative degradation of crosslinked network structure.

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The viscoelastic data have been reported for a wide variety of vulcanized natural rubber.³⁻⁶ The mechanical behavior of this material is relatively complex. It shows elastic and/or plastic flow properties by the experimental condition.

The time-temperature superposition principle is an extremely powerful tool in the study of viscoelastic properties of polymers.⁷ On the basis of this principle, viscoelastic master curves covering many logarithmic decades of time can be obtained by simple horizontal shifting of modulus-time isotherm to that at reference temperature. The vulcanized natural rubber shows flow behavior when it is stretched to high extension ratio. The flow behavior becomes more remarkable as the temperature rises or the stretching condition extends over a long period of time. It is open to question whether the vulcanized natural rubber is recognized as the thermorheologically simple material under such condition.

To analyze the viscoelastic properties, it is presupposed that for any given strain and temperature the value of the applied force is uniquely determined. However, even vulcanized rubber suffers from some degree of irreversibility, as evidenced by the investigation of the stress-relaxation and creep, which cannot be entirely eliminated.

The kinetic theory in its simplest form attributes the elasticity of rubber to the change in the conformation of a system of long chain segments in the crosslinked network molecules in passing from the unstrained to the strained state. Such a change is associated with change in the configurational entropy of the system. It is a very important stretching mechanism in rubbery materials that the stress at constant elongation is proportional to the absolute temperature in the temperature region of rubbery behavior. It is immediately apparent that the tension in a stretched idal rubber arises from the entropy contribution, while the internal energy considered to remain unchanged. It is also open to question whether the general purpose vulcanized natural rubber show uniquely determined stress for any given strain, and the tensile force for a given state of strain is proportional to absolute temperature.

The purpose of this article is to examine to what extent the simple time-temperature superposition may still be useful for the study of relaxation modulus in the highly stretched vulcanized natural rubber over a long period of time. This paper is also intended to examine the stress-temperature relation for any state of strain to understand the contribution of entropy and/or internal energy to the total stress.

TABLE I
Curing Conditions of Vulcanized Natural Rubber Samples

Sample	Curing temperature (°C)	Curing time (min)
1	140	3
2	140	5
3	140	15

EXPERIMENTAL

Three kinds of vulcanized natural rubber samples are prepared. The curing conditions are indicated in Table I. For all samples the sulfur content is 2.2 wt %. These samples are almost the same in quality as the general purpose commercial ones.

Measurement of the tensile force is made with the nonbonded type Transducer 120T-2000C and Amplifier SD-500A of Kyowa Electronic Instruments Co., Ltd. The temperature of the test piece is controlled in the air oven capable of maintaining the desired temperature from 20°C to 130°C to better than $\pm 0.5^\circ\text{C}$ for an extended period of time.

For the study of the viscoelastic property the test piece is stretched to the desired length at constant temperature, and allowed to relax until the lapse of 12 h or more. The values of strain α [$= (L - L_0)/L_0$, L_0 the length of the unstretched test piece and L that of the stretched state] range between 0.36 and 2.00. All tests were carried out on freshly cut test pieces, care being taken to avoid prior deformation of the sample which has been expected to affect the subsequent relaxation behavior. These procedures were performed at 20 temperatures from 20°C up to 120°C with approximately 5°C intervals.

For the study of stress-temperature relation at any given state of strain, the test piece is stretched to the desired length at 23°C (room temperature) and allowed to relax until the tensile force reaches to a steady value; then the temperature of the piece is elevated to 60°C at a rate of 5°C/h. The temperature is kept at 60°C for about 1 h; after that it is decreased almost at the same rate as the increasing process to room temperature. The rate of change in temperature is so gradual that the test piece is assumed that it is almost in its thermally equilibrium state and the value of the stress is recognized as the one developed at every temperature.

RESULTS AND DISCUSSION

Viscoelastic Properties

It might be expected that for chemically crosslinked rubber the stress-relaxation curve should recover in as much as thermoplastic flow is suppressed by the crosslinks. It is certain that the simple time-temperature superposition is valid for such rubber.

The stress relaxation curves for the sample listed in Table I obtained at various temperatures are shifted to reference temperature, 40°C, by the time-temperature superposition principle, but they are not superposed exactly as predicted by this principle. The inapplicability of the superposition principle in the treatment of our data is not surprising since the sample showed irreversible behavior when it is stretched to relatively high extension or it is kept at high temperature for a period of experimental time. At high temperature the tension decreased continuously and never attained to a steady value in the period of experimental time, and the length of the test piece does not recover to the initial length L_0 after the load is removed. The sample tested in this work is not the thermorheologically simple material.

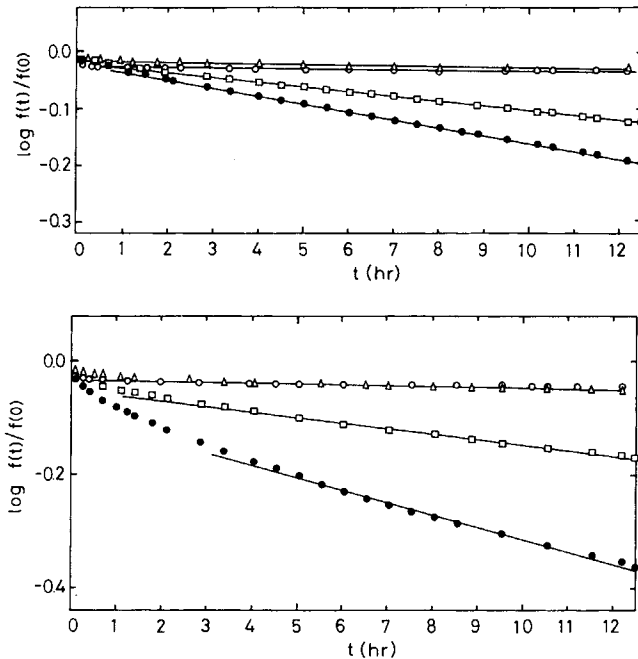


Fig. 1. The relative stress relaxation of sample 3 measured at strains of (a) $\alpha = 0.36$ and (b) 1.07 and temperatures of 40°C (○), 80°C (△), 100°C (□), and 110°C (●).

This behavior can be attributed to the chemical reaction such as chain scission by the oxidative cleavage or reorganization of the network structure by ionic interchange,⁸ and the stress bearing mechanism changes with temperature. If the change in structure is due to bond cleavage, it has a certain effect on the stress. The relative stress $f(t)/f(0)$ is plotted against time t as shown in Figures 1(a) and (b), where $f(t)$ is the stress at time t in a test piece maintained at fixed strain and $f(0)$ is the initial stress. If the rate of bond scission is constant, the decay curve due to chemical stress—relaxation obeys the decay law,

$$f(t)/f(0) = \exp(-ct) \quad (1)$$

where c is constant which has the same meaning with the rate of bond cleavage.⁹ As seen in these figures, at the long time region, $\log f(t)/f(0)$ vs. t plots show linear relation, i. e., the characteristic of chemical stress—relaxation, and indicate that some portion of the stress—relaxation would be due to the bond cleavage.^{8,9} Such linear relation is not observed at the short time region in which the stress decay is mainly attributed to a slow redistribution of stress on the molecular scale. Viewed in this way, there are clearly some differences in relaxation mechanism between the two time regions.

To investigate the relation between the rate of bond cleavage and temperature, the plot of slope c vs. temperature is shown in Figure 2. The value

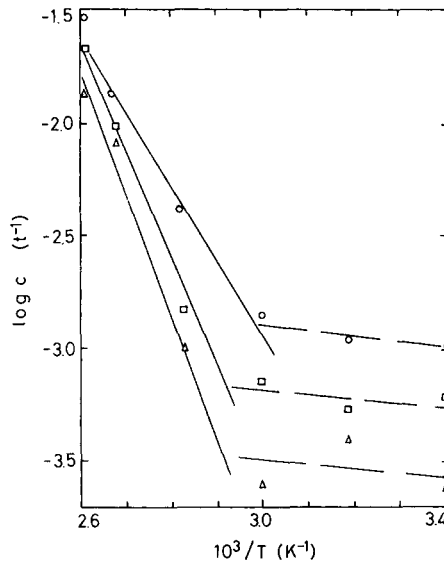


Fig. 2. Logarithm of the slope c plotted against temperature for sample 3 measured at $\alpha = 0.36$ (Δ), 1.07 (\square), and 2.00 (\circ).

of slope c of the linear portion increases with temperature and strain. This indicates the chemical scission occur more easily at high temperature or at highly stretched state. At low temperature region the slope c is almost constant value.

The scission of network chain will reduce the number of effective chain maintaining the stress.⁹ In such a case, the following consideration should be reasonable for composing a master curve. There are required not only a horizontal shift along the log-time axis due to the changing of the rate of molecular motions with temperature, but also a vertical shift along the modulus axis due to the changing structure and other factors.¹⁰⁻¹² According

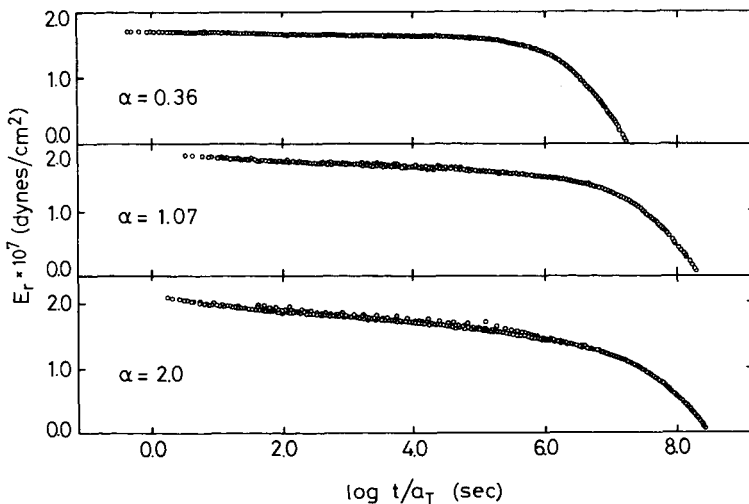


Fig. 3. Composite master curves of sample 3 for indicated strains reduced to 40°C .

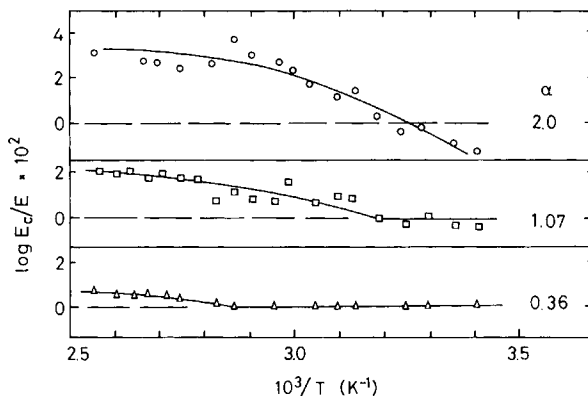


Fig. 4. The value of E_c/E plotted against temperature for sample 3, where E represents a stress at temperature T and time $t = 0$ and E_c is the stress on the master curve corresponding to E .

to this consideration, the stress-relaxation curves at various temperatures were shifted along both the log-time axis and the modulus one successfully until they are superimposed to form a continuous composite curve. The composite curves obtained are shown in Figure 3. Similar curves are obtained for all the samples studied. These curves generally consist of two regions, the rubbery plateau and terminal regions. The plateau region is fairly wide and gradually decreases with time. The slopes at the terminal region are almost the same for each strain. The modulus in the plateau region is of the order of magnitude of 10^7 dyn/cm² and changes rapidly with time at the terminal region from this value to the value of almost zero.

The value of E_c/E (E = stress at temperature T and $t = 0$, E_c = stress on master curve corresponding to E) are plotted against temperature as shown in Figure 4. As is seen in this figure, the $\log E_c/E$ increases with temperature or with the strain; when the strain is small, the value is zero until the temperature is increased to a certain degree. These results also show that the vertical shift is related to change in structure in the system. Accurately, when α is small (e.g., 0.36) and temperatures are not so high,

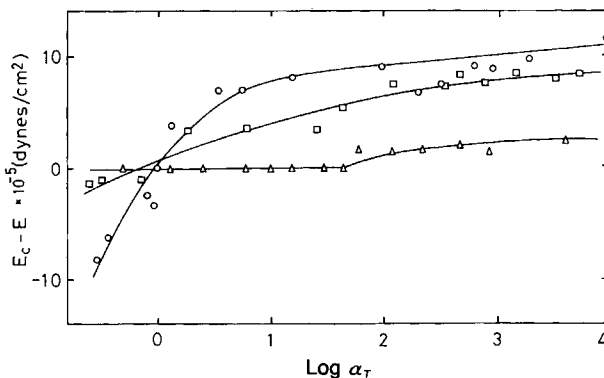


Fig. 5. Vertical shift $E_c - E$ plotted against $\text{Log } a_T$ for sample 3. α : (○) 2.0; (□) 1.07; (△) 0.36.

the composite curve is obtained by simple horizontal shifting of the modulus–time isothermal segments to a reference temperature. But though α is small, vertical shift is needed for the high temperature isothermal segments. In Figure 5, the values of vertical shift $E_c - E$ are plotted against $\log a_T$. This plot illustrates the extent of change in $E_c - E$ value with time. The shift value increases as the time proceeds, and this result also means that the chemical scission increases with the lapse of time. This phenomenon has in quality the same meaning as the result derived from the relative stress–time relations mentioned above.

From these results of stress–relaxation measurements for general purpose vulcanized natural rubber, the vertical shift, needed in the analysis, is attributed to the changing structure by bond cleavage or other factors, which corresponds to the reduction of the number of effective chains maintaining the stress. The number N/cm^3 of effective chains is calculated using the equation⁵

$$f = NkT(L/L_0 - L_0^2/L^2) \quad (2)$$

where f is the force per unit area, k is the Boltzmann constant, and T is the absolute temperature. At constant extension, $L/L_0 = 3$, the force f is measured at several temperature, and N is calculated using eq. (2). From this experimental result it is affirmed that the number of effective chains decreases with increasing temperature.

As is well known, the horizontal shift factor a_T represents the temperature dependence of the relaxation mechanism caused by the thermal motion of the chain molecules. In Figure 6 is shown the temperature dependence of horizontal shift factor a_T . The shift factor was determined empirically so as to obtain the best superposition among the modulus curves of different temperature. As seen in Figure 6, a_T follows an equation of the simple Arrhenius form,

$$\log a_T = (\Delta H_a/R)(T^{-1} - T_0^{-1}) \quad (3)$$

where ΔH_a is an activation energy and the Arrhenius plot is divided into two segments with different slope. It appears two different mechanisms are involved. The activation energies obtained from Arrhenius plots are listed in Table II.

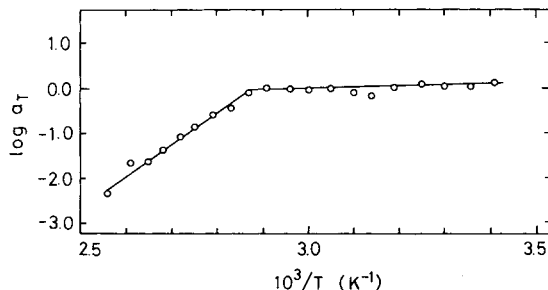


Fig. 6. Temperature dependence of the horizontal shift factor a_T of sample 3 measured at $\alpha = 0.36$.

TABLE II
 Activation Energies Obtained from the Arrhenius Plot of the Shift Factor a_T

α	Sample 1		Sample 2		Sample 3	
	Temp range (°C)		Temp range (°C)		Temp range (°C)	
	Low (kcal/mol)	High (kcal/mol)	Low (kcal/mol)	High (kcal/mol)	Low (kcal/mol)	High (kcal/mol)
0.83	12.0	31.2	15.5	27.0	8.20	30.0
2.00	5.95	35.7	10.0	28.0	11.1	44.9
			10.7	32.7	7.46	37.2

The activation energies associated with the deformation mechanisms in the low temperature region (corresponding to the plateau region in the master curve) are less than that of in the high temperature one (corresponding to the terminal region of the master curve). Stress-relaxation mechanisms in the plateau region are supposed to be attributed to the reorientational motion of rather short segments of network chain between the crosslinking points, but in the terminal region the motion of very long segments show the plastic flow, and this mechanism may have an advantage over other mechanisms.

Thermoelastic Properties

For the examination of the thermoelastic phenomena it is necessary to develop the relations between force, length, and temperature on the one hand and thermodynamic quantities, internal energy, and entropy on the other. The fundamental equation in rubber elasticity is given by

$$f = (\partial U / \partial L)_{v,T} + T(\partial f / \partial T)_{p,L} \quad (4)$$

where U is the internal energy and p is the pressure. From this equation the equilibrium tensile force which maintain an elastic substance at a length L is composed of two contributions, a kinetic (or entropic) tensile force $T(\partial f / \partial T)_{p,L}$ and an internal tensile force $(\partial U / \partial L)_{v,T}$. In applying this equation to study the kinetic and internal tensile forces, difficulty may arise on account of the imperfect elasticity or irreversibility of the vulcanized rubber such as tested in this study. The thermodynamic equilibrium is the necessary condition for the measurement of stress-temperature relation for study of the kinetic tensile force. In this work the stress is measured while the temperature is increased or decreased, but the rate of change in temperature is 5°C/h; this rate is so slow that the thermal equilibrium condition in the test piece is satisfied. This satisfaction is affirmed by consulting the data about the thermal conductivity (3.8×10^{-4} cal/cm · s · deg) and specific heat (1.6 J/g · deg) of vulcanized natural rubber at 300 K published by Schallamach.^{13,14}

The test piece is held at a room temperature for each value of strain for a sufficient time to allow the stress to relax to an essentially constant value, after which the temperature is elevated gradually. But when the temperature is elevated, the stress begins to relax at every temperature, this tendency become more notable in high temperature region or high value of strain. The experimental result for the stress-temperature relation for given value of strain are shown in Figure 7. For small value of strain the stress increases linearly with temperature, and this characterizes the property of entropic tensile force. The linear relation between stress and temperature is not observed for a large value of strain. The reason is considered that the contribution of the stress-relaxation advantage over the entropic tensile force. The temperature is kept at 60°C for about 1 h; in this step the stress relaxes to some extent. After that temperature is decreased; in this process, the stress-relaxation is expected to be very much less. As shown in the figure, the stress-temperature relation is linear for all states of strain when the measurement is practiced while the temperature is decreased.

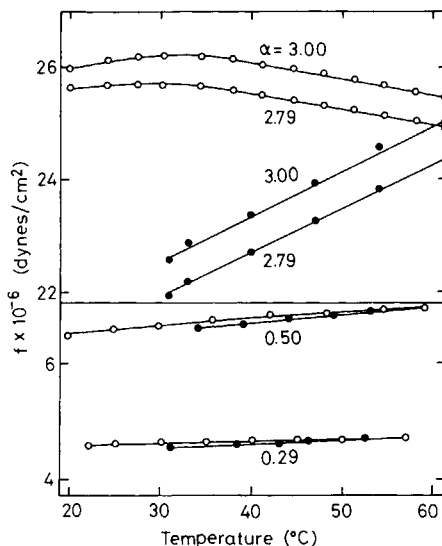


Fig. 7. The stress-temperature relation of sample 3 at indicated strains, the increasing (○) and decreasing (●) temperature measurements.

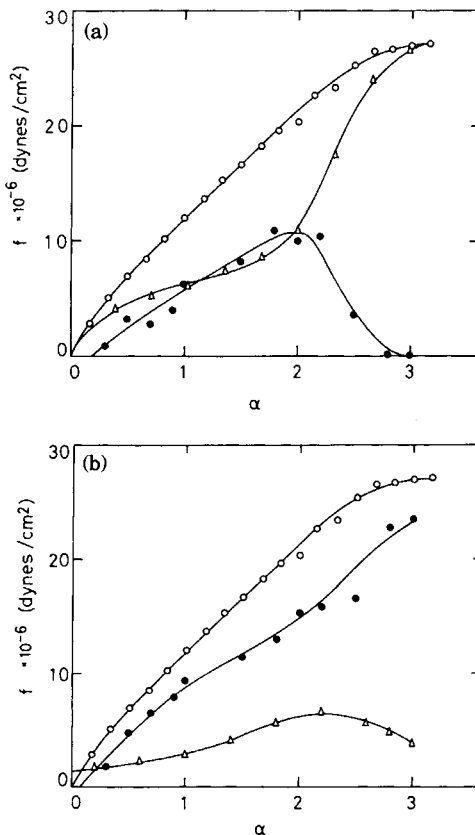


Fig. 8. The stress-strain relation of sample 3 calculated at 25°C from (a) increasing temperature and (b) decreasing temperature measurements: (○) total stress; (△) stress contributed from internal energy; (●) stress contributed from entropy.

From these data we are able to obtain kinetic tensile force and internal one if stress-strain relation is provided. The stress-strain relation at 25°C is shown in Figure 8(a) and (b), and both the kinetic and internal tensile forces are plotted against strain. In Figure 8(a), it is seen that when the stress is measured while the temperature is increased, the entropic component of total stress increases with strain, passes a maximum at about the value of strain 2, and then decreases rapidly to a very small value at high strain. The contribution of internal energy component dominates the entropic one all over the range of strain tested. The internal energy changes are due to change in the inter- and intrachain interaction in the network, and bond cleavage also contributes to the internal energy change. Such an energy change is associated with these mechanisms all related to the relaxation mechanisms. This is the main reason why contribution of internal tensile force is significant in Figure 8(a). Figure 8(b) shows the result when the stress is measured while the temperature is decreased. In this process, stress-relaxation is suppressed. In this case kinetic tensile component increases almost monotonously, and the dominant component of the stress is the kinetic tensile one. But there is added a significant internal tensile component. This result may be associated with the fact that the general purpose commercial vulcanized natural rubber such as tested in this work is not an ideal crosslinked rubber.

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