On the separation of physical and chemical component of stress relaxation

Masayuki Ito
Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Takasaki, Gunma 370-12, *Japan*
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This paper proposes a new method to separate physical and chemical components of stress relaxation. The stress relaxation measurements of tetrafluoroethylene–propylene rubber were carried out at various temperatures ranging from 200° to 310°C. A physical stress relaxation master curve could be generated from data of early period of time by the time–temperature superposition principle. The rate of physical stress decay at given temperatures was calculated from the master curve. The rate of chemical stress relaxation was given by subtracting the rate of physical decay from experimentally obtained rate at the corresponding temperatures. The activation energy was found to be 8.4 kcal mol^{-1} for the rates of the calculated chemical stress relaxation, while it was found to be 5.7 kcal mol^{-1} for the rates which were obtained in air. The results show that the physical component of stress decay should be subtracted from the measured stress relaxation curve to obtain the rate of chemical stress decay, especially at the low temperature.

Keywords Chemorheology; stress relaxation; fluoroelastomer; master curve; activation energy; time–temperature superposition

INTRODUCTION

Data of the chemical stress relaxation rates at relatively low temperature deviate from a linear line on the Arrhenius plot. This is considered to be due to the physical decay.

The chemical stress relaxation caused by polymer chain scission is the most predominant relaxation component at high temperatures. Therefore the component of physical decay can be neglected to obtain the rate of chemical stress relaxation from the observed relaxation curve. As the contribution of the physical component to stress decay increases with decreasing temperature, it is important to separate it from the observed curve. This paper proposes a new method for separating the physical component from the measured stress relaxation curve.

EXPERIMENTAL

Material

Tetrafluoroethylene–propylene copolymer was obtained by radiation induced emulsion polymerization of tetrafluoroethylene and propylene in a 1 litre high pressure vessel. The copolymer ($\bar{M}w = 94\,000$) was mixed with 25 parts of carbon black by using a mixing roll and pressed to 0.5 mm sheets. The sheets were cured by irradiation with 2 MeV electron beam, the irradiation dose was 12 Mrad.

Stress relaxation measurement

Stress relaxation was measured under constant temperature conditions ranging from 200° to 310°C (±1°C), the extension ratio being 20%. The distance between jaws before extension was 100 mm. The apparatus which was constructed to measure in nitrogen atmosphere (200° ~ 250°C) is illustrated in *Figure 1*. The sample was pinched by the upper jaw, preheated for about 1 minute in air at the experimental temperature and was pinched by the lower jaw. The preheated sample was assembled in the thermostat and nitrogen gas (99.99% N_2) was fed in. The sample was then preheated for 15 min in nitrogen and stress was applied. The measurement in air was carried out by using usual strain gauge system[1]. The sample was also preheated for 5 min before elongation.

Non-linearity of the load cell used was less than 0.03% FS (5 kg). A weight of 100.00 g was used to calibrate the output of load cell.

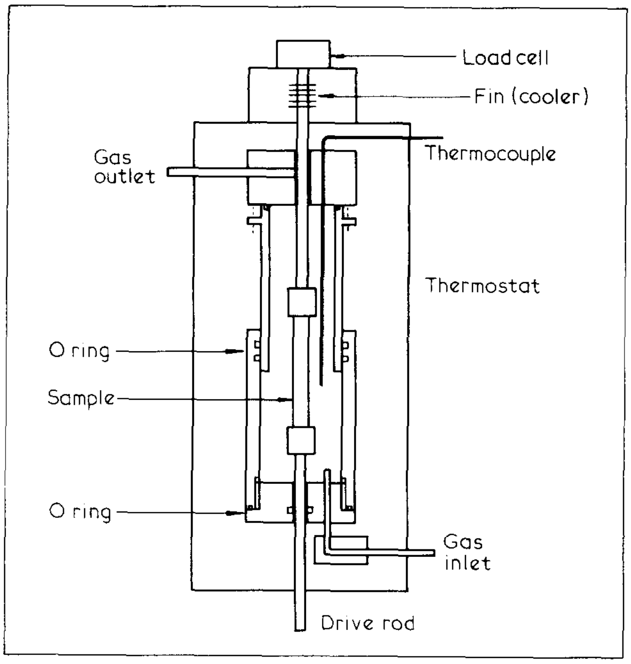

Figure 1 Apparatus for stress relaxation in nitrogen atmosphere

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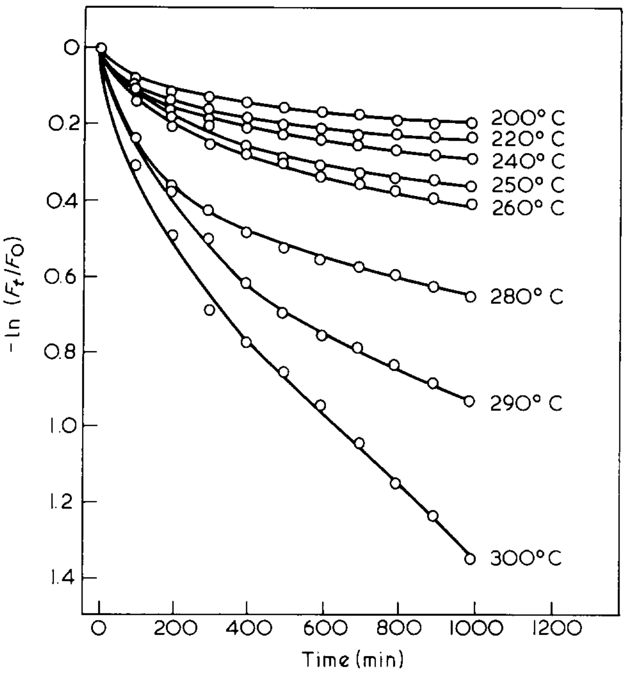

Figure 2 Stress relaxation curves for tetrafluoroethylene–propylene rubber at various temperatures in air

RESULTS

Stress relaxation in air

Figure 2 shows the stress decay curves at various temperatures ranging from 200° to 300°C. Each of the decay curves is found to be Maxwellian after a certain period of time and is expressed by equation (1):

$$F_t/F_0 = \exp(-Kt) \qquad (1)$$

where F_t is the stress at time t, F_0 is the initially measured stress and K is the rate of stress relaxation.

The activation energy calculated from the rate of stress decay in air (K_{air}) was found to be 5.7 kcal mol^{-1} from 200° to 250°C and 14.9 kcal mol^{-1} from 250° to 300°C. (Arrhenius plot of K_{air} is shown in *Figure 9* with other data.) The observation of two different activation energies dependent on the temperature range is due to the following reason: K_{air} has two components, one is the rate of physical relaxation (K_{phys}) and the other is the rate of chemical stress relaxation (K_{chem}) which is caused by polymer chain scission by heat. The relation among K_{air}, K_{phys} and K_{chem} is expressed in equation (2):

$$K_{air} = K_{phys} + K_{chem} \qquad (2)$$

At high temperature the component of chemical stress decay is considered to be predominant and K_{air} can be regarded as K_{chem}. But the contribution of K_{phys} cannot be neglected at relatively low temperare, as the rate of polymer chain scission decreases exponentially with decreasing temperature.

Calculation of physical decay

Figure 3 shows the relaxation modulus, $Er(t)$ at early period of time after extension. The temperature range is from 200° to 310°C. The disentanglement of the polymer chain occurs rapidly after extension and its rate decreases with passing time. However, the rate of chemical reaction (polymer chain scission) is almost constant during the measurement. Therefore the physical decay is predominant in the early period of time after extension of the sample.

From this point of view, a physical relaxation master curve was made according to the time–temperature superposition principle[2,3]. The curves of log $Er(t)$ vs. log t at different temperatures could be superposed by means of a horizontal shift along the log t axis. The master curve is shown in *Figure 4*. *Figure 5* shows the shift factors. The reference temperature is 200°C. From the master curve, the physical stress decay curves at 200°C, 220°C, 240°C and 250°C are calculated and are shown in *Figure 6*.

Separation of physical and chemical components

The rates of chemical stress relaxation are calculated by subtracting the physical components from observed rates in air (K_{air}), as shown in *Table 1*, K_{mc} is referred to as the rates of physical decay calculated from the master curve. In air, 34% of observed value is found to be the physical

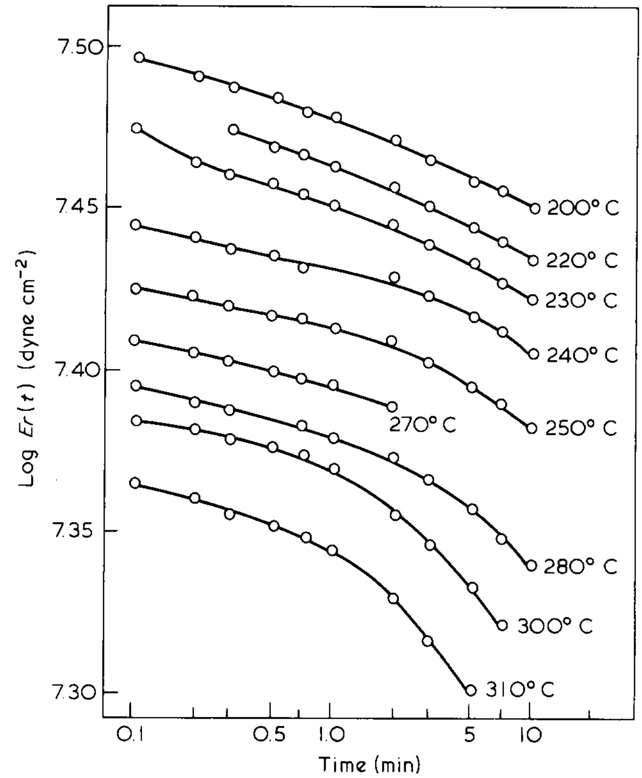

Figure 3 Stress relaxation modulus at various temperatures

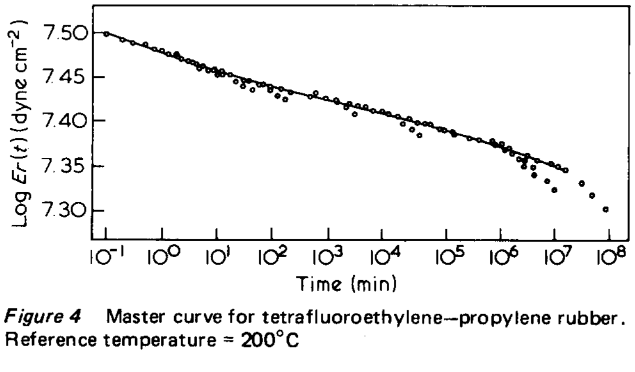

Figure 4 Master curve for tetrafluoroethylene–propylene rubber. Reference temperature = 200°C

decay at 200°C. The component of the physical decay is found to decrease with increasing temperature.

Another method of separation

Separation assigning relaxation in nitrogen as physical decay. As the chemical stress relaxation is caused by oxidative chain scission, the stress decay in nitrogen atmosphere is thought to be the physical decay. The difference between the rates of decay in air and in nitrogen may correspond to the rate of chemical stress relaxation.

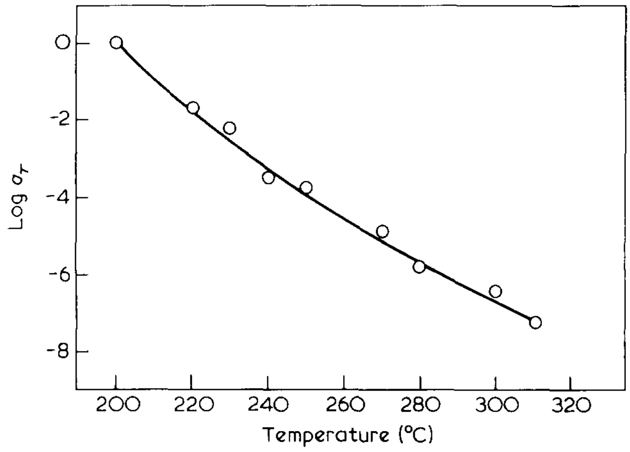

Figure 5 The relationship between temperature and shift factor. Reference temperature = 200°C

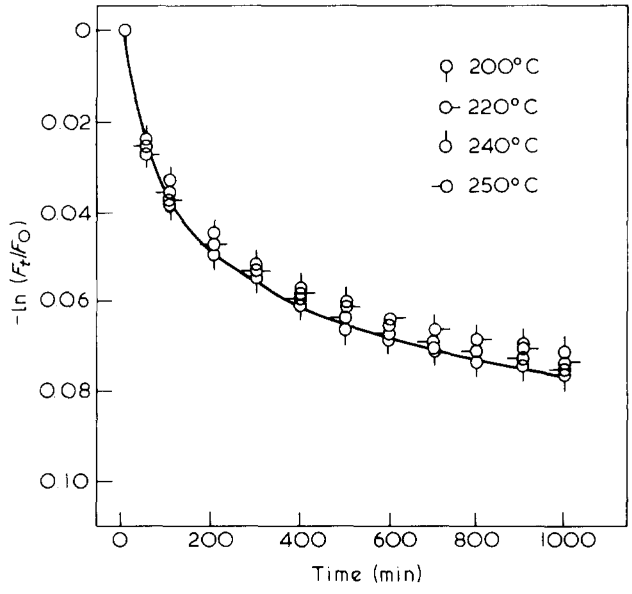

Figure 6 Physical stress relaxation at various temperatures calculated from master curve. The line is for 200°C

Figure 7 shows the relaxation curves at various temperatures in nitrogen. The decay curves are found to be Maxwellian for a certain period of time and the rate of decay is defined by equation (1). The activation energy is 2.5 kcal mol^{-1}. The rates of chemical stress relaxation are obtained by subtracting the decay rates in nitrogen (K_{nit}) from the rates in air (K_{air}). *Table 1* shows each of the rates.

Separation by the technique of atmosphere change. This method was developed by Murakami *et al.* to study the rate of oxygen diffusion in rubber[4]. Firstly the stress relaxation is carried out in nitrogen atmosphere. The stress decay in nitrogen may be ascribed to the relaxation of trapped entanglements. After a certain period of time, the nitrogen atmosphere is replaced by air. Chemical stress relaxation is observed from this time.

Here, after the stress decay in nitrogen is observed for 1000 min, the atmosphere is changed from nitrogen to air. *Figure 8* shows the chemical stress relaxtion curves after the time at which the atmosphere is changed. As the decay curves are found to be Maxwellian from a certain period of time, the rate of chemical stress relaxation (K_{tac}) is calculated by equation (1) and shown in *Table 1*.

DISCUSSION

Figure 9 shows the relationship between the rates of chemical stress relaxation obtained by various methods and reciprocal of temperature. *Table 2* shows the activation energy of the rates obtained by each method for the temperature range 200°–250°C.

The activation energy of chemical stress relaxation

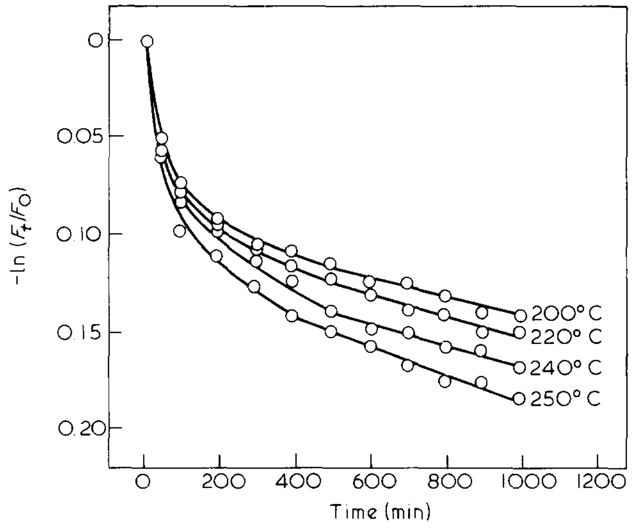

Figure 7 Stress relaxation at various temperatures in nitrogen atmosphere

Table 1 Separation of chemical component of stress decay by various methods

Temperature (°C)	$K_{air} \times 10^4$	$(K_{air} - K_{mc}) \times 10^4$	$(K_{air} - K_{nit}) \times 10^4$	$K_{tac} \times 10^4$
200	2.18	1.31	0.59	0.72
220	2.71	1.88	0.01	1.13
240	3.23	2.41	1.36	1.45
250	4.08	3.22	2.03	1.99

K_{air}, stress relaxation rate in air. K_{mc}, stress relaxation rate obtained by master curve. K_{nit}, stress relaxation rate in nitrogen. K_{tac}, rate of stress decay after atmosphere change from nitrogen to air

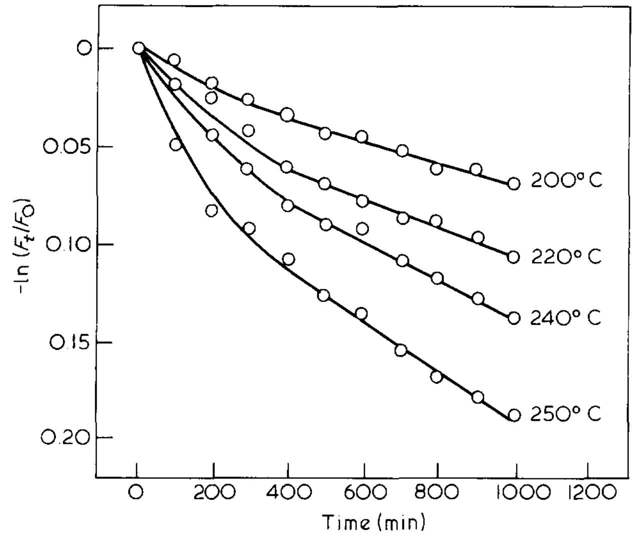

Figure 8 Stress decay after the atmosphere is changed from nitrogen to air

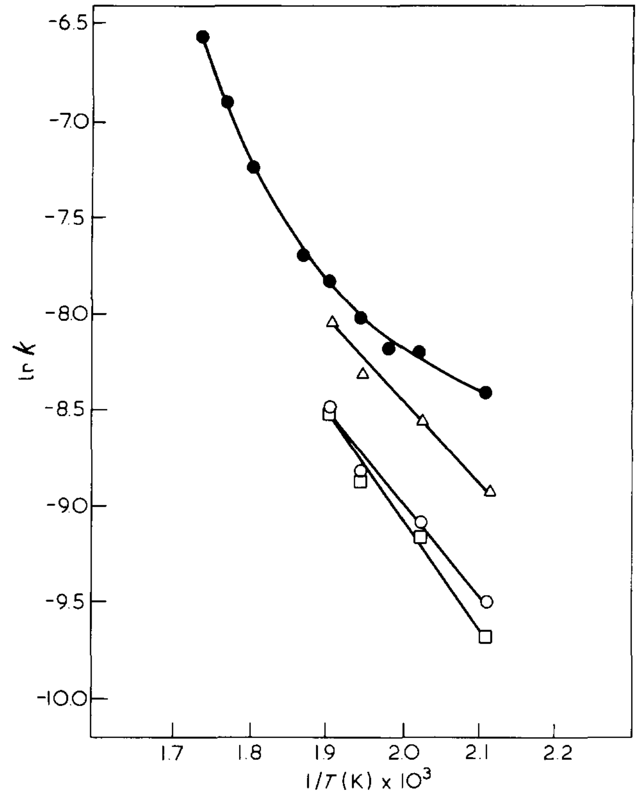

Figure 9 Arrhenius plot of rate of chemical stress relaxation obtained by various methods. ●, K_{air}; △, $K_{air}-K_{mc}$; □, $K_{air}-K_{nit}$; ○, K_{tac}

calculated from K_{air} is markedly different from others because of the lack of subtraction of the physical component. Other methods give similar values. The value obtained from $K_{air}-K_{mc}$ and $K_{air}-K_{nit}$ are 8.4 and 10.4 kcal mol^{-1}, respectively. The difference is caused by differences in the methods for estimating physical decay rates. The rate of physical decay is regarded as K_{mc} in the former and is regarded as K_{nit} in the latter. K_{nit} is larger than K_{mc} as shown in *Table 1* and the rate of physical decay will be overestimated by regarding it as K_{nit}. Murakami *et al.* studied the influence of oxygen content in the atmosphere on chemical stress relaxation of natural rubber vulcanization[5]. They showed that even 0.04% oxygen in atmosphere increased the stress decay at 140°C. Thomas studied[6] heat aging in fluoroelastomer and found out that the rate of decay in nitrogen was more rapid than *in vacuo*. These results suggest that the trace amount of oxygen even in nitrogen atmosphere increases the rate of stress decay. This should also be referred to as the chemical stress relaxation. Therefore, the rate of the physical decay is thought to be over estimated if K_{nit} is regarded as the rate of physical decay, since the purity of nitrogen gas used in this experiment is 99.99%.

Table 2 Activation energy of chemical stress relaxation obtained by various methods

Rate of chemical stress decay	Activation energy (kcal mol^{-1})
K_{air}	5.7
$K_{air}-K_{mc}$	8.4
$K_{air}-K_{nit}$	10.4
K_{tac}	9.4

See the footnote of *Table 1* for the symbols

There are a few differences between the activation energy obtained by the technique of atmosphere change (9.4 kcal mol^{-1}) and the value obtained by the proposed method (8.4 kcal mol^{-1}). It may be due to the difference in physical condition of the samples. As the sample is expanded for 1000 min before measurement in the atmosphere change technique, there are fewer chain entanglements and a part of polymer chain may be oriented before measurement. The chemical stress relaxation originates from the stress decay by the flow of polymer chains which are chemically scissioned. The rate of chemical stress relaxation and its temperature dependence are influenced by the physical state of the polymer.

Even though each method has some advantages and inevitably gives some errors in obtaining the values of activation energy, the values which are obtained by two methods (the atmosphere change technique and the new method) almost agree. The rate and activation energy of chemical stress relaxation obtained by the new method will therefore be reasonable.

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