JOURNAL OF APPLIED POLYMER SCIENCE VOL. 21, 55–63 (1977)

# Chemorheological Studies on Polymer Degradation

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## Synopsis

The degradation of dicumyl peroxide-cured natural rubber was studied by the stress relaxation method. Experiments were carried out in air, in nitrogen, and by irradiation of UV light in the temperature range of 30–200°C. We attempted to divide factors of the degradation into two parts: that caused by heat and that by light, and to study the respective degradation quantitatively. The degradation caused by UV light in nitrogen was almost independent of temperature. However, the degradation caused by UV light in air increased with temperature and the rate of degradation caused by the interaction between light and oxygen was greater at high temperature than at low temperature. It was found that scission along main chains occurs for dicumyl peroxide-cured natural rubber by photo-oxidation as well as thermal oxidation.

## INTRODUCTION

As for the degradation of crosslinked rubber, studies on the scission mechanism by thermal oxidation, etc., from chemorheology[1,2] and investigations of reaction mechanisms by the kinetic method[3] and analysis by infrared methods,[4] etc., have been carried out.

However, no investigations have been undertaken to isolate each factor regarded as the cause of the degradation and to measure these factors quantitatively.

In this paper, the behavior of the degradation of dicumyl peroxide-cured natural rubber in air, nitrogen, and, in addition, UV light was observed. The rate constants and activation energy of natural rubber vulcanizates in degradation were investigated. Also, scission mechanism of crosslinked natural rubber caused by photo-oxidation was studied.

## EXPERIMENTAL

### Preparation of Crosslinked Rubbers

Natural rubber (NR-RSS-1) was milled with the curing ingredient dicumyl peroxide 3 phr under 50° ± 5°C of rolling temperature. Thin sheets (about 0.5 mm) of the milled polymer were pressed under 200 kg/cm$^2$ for 30 min at a curing temperature of 145°C. To remove nonreacted peroxide and reaction products, all the samples were extracted with hot acetone[5] and dried *in vacuo*. The sample was 5 mm wide, about 0.5 mm thick, and 20 mm long.



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### Measurement of Stress Relaxation

The stress relaxation apparatus used here was made in our laboratories; its mechanism is the usual strain-gauge system.[5] Measurements were conducted both in air and in nitrogen. As the nitrogen was not specially purified, it may be assumed that a very low partial pressure of oxygen would be present.

The ultraviolet light source was a 100-W high-pressure mercury lamp which emits strongly the wavelength 365–366 m$\mu$.

The extension ratio $\alpha$ used here is about 1.5. The stress relaxation results are plotted as $\log f(t)/f(0)$ against $t$, where $f(0)$ is the initial stress and $f(t)$ is the stress at time $t$.

## RESULTS AND DISCUSSION

### Chemical Stress Relaxation in Nitrogen

The stress relaxation curves in nitrogen in the range of 30° to 200°C are shown in Figure 1. In the range of 30° to 160°C, the stress relaxation curves of crosslinked natural rubber show that the rate of decay is almost the same, independent of temperature.

As the fact that the chemical reaction does not occur for dicumyl peroxide-cured natural rubber up to the vicinity of 100°C is known,[6] the approximate equal rates of relaxation in the range of 30° to 160°C in our experiment will indicate that the relaxation mechanism under this condition should be attributable to physical flow of the polymer chains.

At temperatures above 170°C the rates of relaxation become more rapid than those in the range of 30° to 160°C. This will be considered since thermal degradation begins to arise in addition to physical relaxation. In this regard, Takahashi and Tobolsky[7] reported that thermal degradation arises *in vacuo* at the about same temperature. In the range of 170° to 200°C the stress relaxation curves which were plotted as $\log f(t)/f(0)$ versus $t$ show approximate linearity at any temperature. This indicates that stress relaxation curves in nitrogen at these high temperatures are expressed by Maxwellian decay curves. So the following equation is obtained:

$$\frac{f(t)}{f(0)} = e^{-k_h t} \tag{1}$$

where $k_h$ is the rate constant for thermal degradation.

In the range of 170° to 200°C, the activation energy for thermal degradation was estimated as 30 kcal/mole from the Arrhenius plot. This value is smaller than that reported by Takahashi and Tobolsky.[7] This may suggest that it is due to the induction of the slight oxidation by traces of oxygen in nitrogen.

### Chemical Stress Relaxation in Air

The stress relaxation curves in air in the range of 30° to 120°C are shown in Figure 2. In the range of 30° to 70°C, the relaxation decay of crosslinked natural rubber in air was almost independent of temperatures just like those in nitrogen in the range of 30° to 160°C. Therefore, the relaxation in air in the range of 30° to 70°C in Figure 2 will be due to physical relaxation.

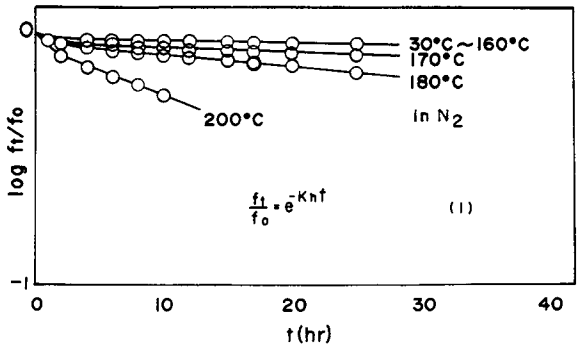


Fig. 1. Stress relaxation curves of crosslinked natural rubbers in nitrogen.

At temperatures above 80°C, the relaxation rate becomes faster, which may be caused by thermal oxidation. As can be seen from Figure 2, the stress relaxation curves show approximate linearity at any temperature except the initial stages. Therefore, the relaxation curves in air at higher temperatures are expressed by Maxwellian decay term described by the equation

$$\frac{f(t)}{f(0)} = e^{-k_{hox}t} \tag{2}$$

where $k_{hox}$ is the rate constant for thermal oxidation at high temperatures.

The activation energy was estimated as 28 kcal/mole for thermal oxidation, and this value was consistent with that which has been obtained elsewhere.[8,9]

## Photochemical Stress Relaxation with UV Light in Nitrogen

The sample was irradiated with UV light in nitrogen in the range of 30° to 200°C. The distance between the light source and the samples was 19 cm. The stress relaxation curves are shown in Figure 3.

The relaxation decay rate in this case is slightly faster than that in nitrogen. It indicates that chemical scissions are induced for dicumyl peroxide-cured natural rubber only by UV light. The relaxation velocity is nearly independent of temperature in the range of 30° to 160°C. This can be attributed to the fact

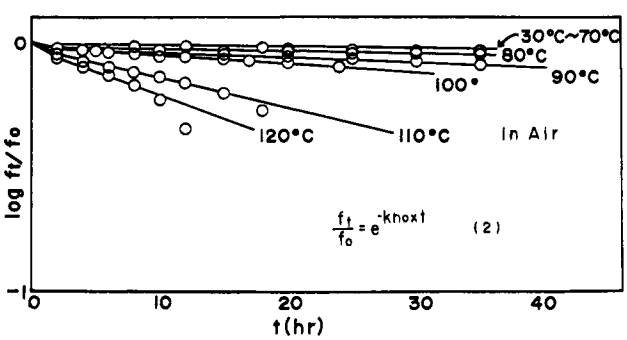


Fig. 2. Stress relaxation curves of crosslinked natural rubbers in air.

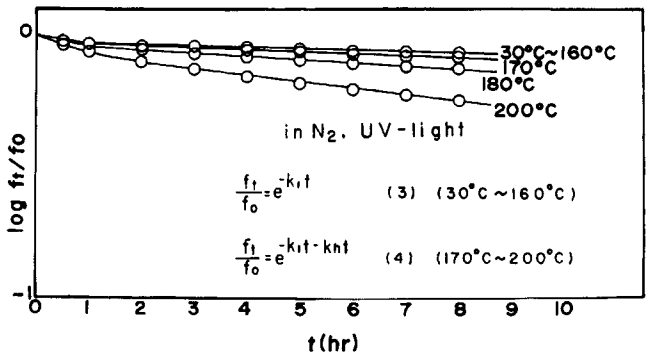


Fig. 3. Stress relaxation curves of crosslinked natural rubbers with UV light in nitrogen.

that the dissociation and excitation of molecular bonds are practically independent of temperature.

The relaxation curves which were plotted as $\log f(t)/f(0)$ versus $t$ also show linearity at any temperature except the initial stages. Therefore, as described in the previous section, the relaxation curves are expressed by the exponential term

$$\frac{f(t)}{f(0)} = e^{-k_l t} \tag{3}$$

where $k_l$ is the rate constant for photodegradation.

Also at temperatures above 170°C, because of thermal degradation in addition

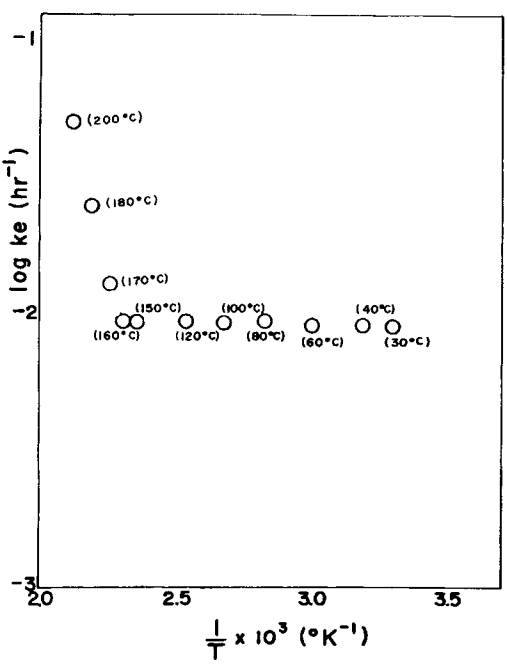


Fig. 4. Arrhenius plot for the reaction of crosslinked natural rubbers with UV light in nitrogen.

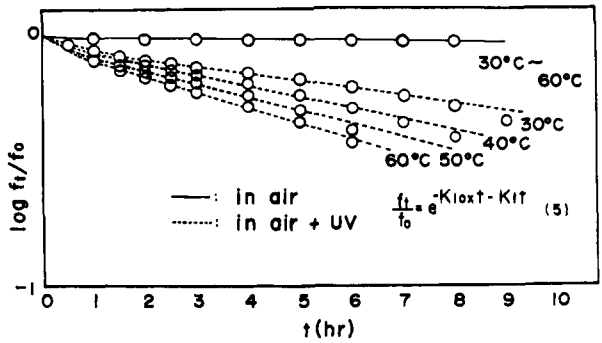


Fig. 5. Stress relaxation curves of crosslinked natural rubbers with UV light in air (30–60°C).

to photodegradation, the relaxation curves are represented by eq. (4), which added the rate constant of thermal degradation to that of photodegradation.

$$\frac{f_t}{f_0} = e^{-k_h t - k_l t} \tag{4}$$

As for such additivity for the rate constants, Mochuloky and co-workers[10] performed the experiment for polysulfide rubber and found such additivity reasonable. They measured the chemical stress relaxation in air under UV light, in the temperature range of 40° and 80°C.

The Arrhenius plots of the above reactions irradiated with UV light in nitrogen are shown in Figure 4. In the range of 30° to 160°C, it is seen that the rate constant is almost independent of temperatures and the activation energy is about zero, whereas at temperatures above 170°C, the Arrhenius plot is established, and, accordingly, 18 kcal/mole was obtained. It shows that this value naturally becomes smaller than that of thermal degradation in nitrogen because of irradiation.

## Photochemical Stress Relaxation with UV Light in Air

In the range of 30° to 60°C, the stress relaxation curves on exposure to UV light in air with a light source-to-sample distance of 19 cm are shown in Figure 5. In

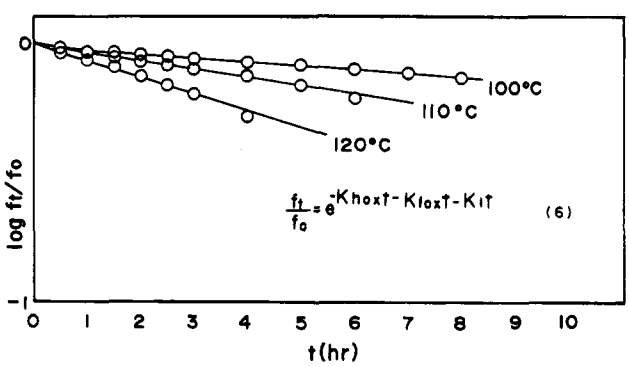


Fig. 6. Stress relaxation curves of crosslinked natural rubbers with UV light in air (100°–120°C).

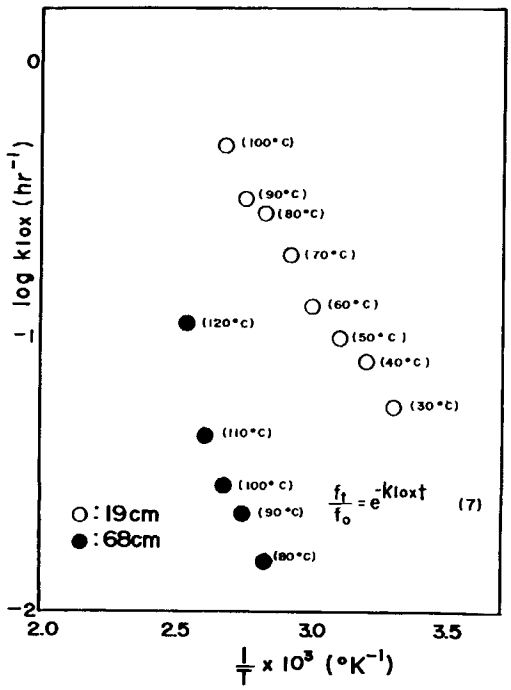


Fig. 7. Arrhenius plot for the reaction of the interaction between UV light and oxygen.

the range of these temperatures, the relaxation in air was only based on the physical relaxation; and when exposed to UV light in nitrogen, the samples exhibited a slight photodegradation, but the relaxation on exposure to UV light in air becomes markedly faster. While the relaxation velocity upon irradiation with UV light in nitrogen was found to be almost independent of temperature, that upon irradiation with UV light in air became faster with higher temperatures.

In this case, the relation of $\log f(t)/f(0)$ versus $t$ also indicates linearity, and the relaxation curves are expressed by Maxwellian decay. In the range of these temperatures, the rate constant of degradation on exposure to UV light in air is expressed by adding the term of photodegradation to that of the interaction

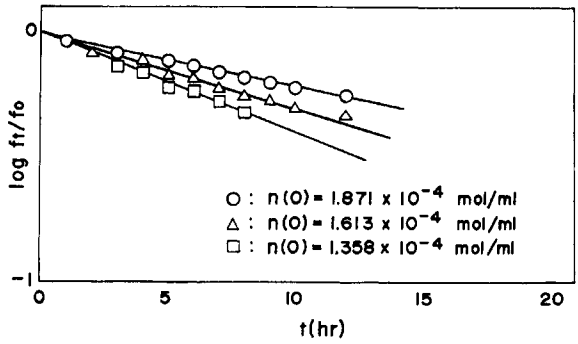


Fig. 8. Stress relaxation curves for three samples of different network chain densities with UV light in air (30°C).

TABLE I
Apparent Activation Energy and Rate Constant

| Atmosphere | Light source-to-sample distance, cm | Activation energy $E$, kcal/mole | rate constant $k$, $hr^{-1}$ (80°C) | (100°C) | (120°C) | |
|---|---|---|---|---|---|---|
| Air (80° ~ 120°C) | | 28 | $1.84 \times 10^{-3}$ (30°C) | $6.91 \times 10^{-3}$ (40°C) | $5.18 \times 10^{-2}$ (60°C) | $k_{hox}$ |
| Air + UV (30° ~ 60°C) | 19 | 5 | $6.79 \times 10^{-2}$ (100°C) | $9.44 \times 10^{-2}$ (110°C) | $1.43 \times 10^{-1}$ (120°C) | $k_l + k_{lox}$ |
| Air + UV (100° ~ 120°C) | 68 | 22 | $3.57 \times 10^{-2}$ (30°C) | $6.91 \times 10^{-2}$ (100°C) | $1.64 \times 10^{-1}$ (160°C) | $k_{hox} + k_l + k_{lox}$ |
| $N_2$ + UV (30° ~ 160°C) | 19 | nearly 0 | $7.83 \times 10^{-3}$ (170°C) | $10.1 \times 10^{-3}$ (180°C) | $9.67 \times 10^{-3}$ (200°C) | $k_l$ |
| $N_2$ + UV (170° ~ 200°C) | 19 | 18 | $1.52 \times 10^{-2}$ (170°C) | $2.90 \times 10^{-2}$ (180°C) | $6.03 \times 10^{-2}$ (200°C) | $k_h + k_l$ |
| $N_2$ (170° ~ 200°C) | | 30 | $5.53 \times 10^{-3}$ (30°C) | $1.06 \times 10^{-2}$ (40°C) | $5.07 \times 10^{-2}$ (60°C) | $k_h$ |
| $\frac{\text{Air + UV}}{\text{UV}}$ (30° ~ 60°C) | 19 | 6 | $5.64 \times 10^{-2}$ (100°C) | $8.29 \times 10^{-2}$ (110°C) | $1.31 \times 10^{-1}$ (120°C) | $k_{lox}$ |
| $\frac{\text{Air + UV}}{\text{Air, UV}}$ (100° ~ 120°C) | 68 | 14 | $2.88 \times 10^{-2}$ | $4.38 \times 10^{-2}$ | $1.12 \times 10^{-1}$ | $k_{lox}$ |

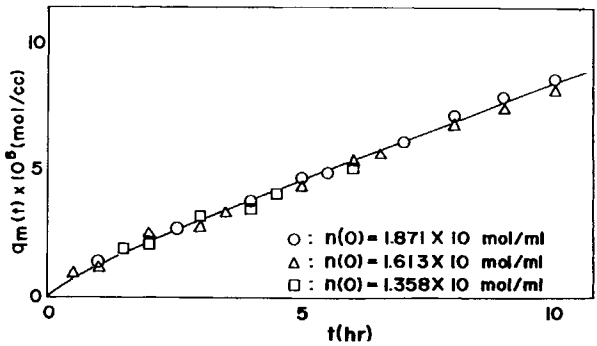


Fig. 9. Relation of $q(t)$ vs. $t$ for three samples with UV light in air (30°C).

between light and oxygen, or photo-oxidation. Therefore, the relaxation curves are expressed as follows:

$$\frac{f(t)}{f(0)} = e^{-k_{lox}t - k_l t} \tag{5}$$

where $k_{lox}$ is the rate constant for the interaction between light and oxygen. The activation energy in the range of these temperatures was calculated as 5 kcal/mole.

Next, in the range of 100° to 120°C, the stress relaxation curves on exposure to UV light in air with a light source-to-sample distance of 68 cm are shown in Figure 6. The relaxation curves are also represented by the Maxwellian decay term. The rate constants in this case are expressed by adding that of thermal oxidation ($k_{hox}$) as follows. The equation is

$$\frac{f(t)}{f(0)} = e^{-k_{hox}t - k_{lox}t - k_l t} \tag{6}$$

The activation energy in the range of these temperatures was calculated as 22 kcal/mole.

From eqs. (3) and (5), it is possible to calculate the relaxation curve of degradation based upon the interaction between light and oxygen which leads to the derivation of the value of $k_{lox}$. Another way of finding the same value of $k_{lox}$ is to estimate the same relaxation curve from eqs. (2), (3), and (6), finally obtaining the value of $k_{lox}$. Consequently, the equation is obtained as follows:

$$\frac{f(t)}{f(0)} = e^{-k_{lox}t} \tag{7}$$

Thus, the Arrhenius plot of $k_{lox}$ against $1T$ can be obtained for a wide range of temperatures using the two methods mentioned above, as shown in Figure 7. It can be seen from the figure that the degradation rate becomes greater at higher temperatures than at low temperatures.

Finally, the various kinds of degradation rate constants estimated from the above experiments were tabulated in Table I.

## Scission Mechanism of Dicumyl Peroxide-Cured Natural Rubber Caused by Photo-oxidation

It has been known that main-chain scission occurs for dicumyl peroxide-cured natural rubber in oxidative degradation.[2]

Here, the photo-oxidation mechanism was investigated for the same natural rubber. The stress relaxation of three crosslinked natural rubbers differing in initial crosslinking densities $n(0)$ was measured on exposure to UV light in air at 30°C.

Judging from the relaxation decay lines indicating the relation of $\log f(t)/f(0)$ versus time depending upon $n(0)$ (in Fig. 8) and the relation of $q(t)$, the number of scissions at $t$ versus time which is independent of $n(0)$ (in Fig. 9), it is concluded that the scissions of dicumyl peroxide-cured natural rubber caused by photo-oxidation also indicate those along main chains of rubber networks.

The cooperation and useful suggestions by Mr. Saburo Tamura in our laboratories are deeply appreciated.

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Received September 10, 1975
Revised January 30, 1976