

Stress Relaxation of Raw Natural Rubber

YUJI MINOURA and KAIJI KAMAGATA,* *Department of Chemistry,
Osaka City University, Kita-ku, Osaka, Japan*

Synopsis

The effects of mastication on stress relaxation of raw rubber was studied in the range of 20–120°C. The stress relaxation time became shorter with increasing mastication, and the modulus also decreased. The modulus decreased with increasing temperature of measurement. Moreover, it is found that mastication caused the solution viscosity of rubber to decrease, and on heating an intermolecular reaction and cleavage of molecules by oxidation appeared to occur at the same time.

INTRODUCTION

It has been reported that vulcanized rubber changes its physical properties as a result of thermal depolymerization accompanying crosslink formation.¹ We investigated the stress relaxation of unvulcanized rubber and determined (1) the effect of mastication on stress relaxation, (2) the dependence of stress relaxation on temperature in the range of 20–120°C., (3) the relationship between degree of mastication and solution viscosity, and (4) the decrease in solution viscosity of rubber on heating.

From the results, we could conclude that cleavage of rubber molecule took place in stress relaxation at high temperature, while decrease in degree of polymerization by mastication and change in degree of polymerization by heating were observed.

EXPERIMENTAL

Pale crepe deproteinized rubber and dry film from latex were used as the sample. Strips of sample of 5 mm. width were punched out from a sheet of testing material and the change of stress with time under a constant stretching was measured.

The measurement of stress relaxation was carried out by measuring the decrease in the stress, with time, necessary to maintain constant degree of deformation with a given stretching of the sample. The apparatus used for this experiment was the same one described in the preceding paper.² The viscosity of benzene solutions at 25°C. was measured by means of an Ostwald viscometer.

* Present address: Mitsubishi Petrochemical Co., Ltd., Japan.

RESULTS AND DISCUSSION

A. Effect of Mastication on Continuous Stress Relaxation

It is known that mechanical cleavage and oxidative depolymerization of rubber molecule occur when natural rubber is masticated in air and as a result, the solution viscosity decreases.

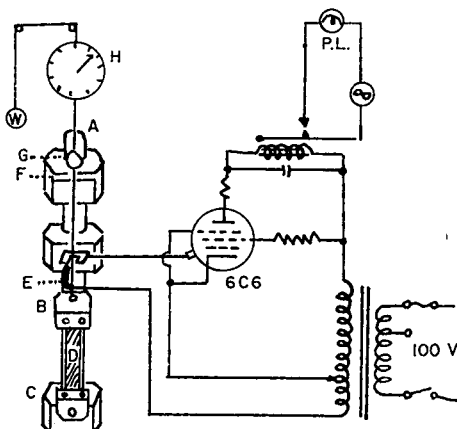


Fig. 1. Apparatus for measuring stress relaxation: (A) support; (B) clamp; (C) clamp; (D) rubber sample ($6-7 \times 0.5 \times 0.2$ cm.); (E) electrical contact point; (F) supported disk; (G) ring; (H) spring balance; (W) balanced weight; (PL) lamp.

In this study, pale crepe was thinned by rolling and heated at 141°C . under a press to form a film from which strips used in the measurement were punched out.

The effect of degree of mastication on stress relaxation was studied by the measurement of stress relaxation with the samples which had been subjected to different numbers of rolling operations in thinning. The results are shown in Figures 2 and 3. Figure 2 shows the results at 20°C . and Figure 3 gives those for 60°C .

It is shown that with unvulcanized rubber the stress required to maintain a certain deformation decreased rapidly with time.

As to the effect of mastication, the modulus was nearly halved by first five roll-thinning operations (Fig. 4). The relaxation time decreased with increasing time of mastication. From comparison of Figures 2 and 3, it is seen that with increasing temperature the relaxation time became shorter and the apparent modulus became smaller. These results indicate that the modulus of rubber was lowered by increasing time of mastication. The following are considered to explain this: (1) cleavage of the rubber molecule by mechanical force, (2) cleavage of the rubber molecule by oxidation, (3) cleavage of intermolecular weak bonds, and (4) effect of the relaxation of entangled molecules (entanglement relaxation).

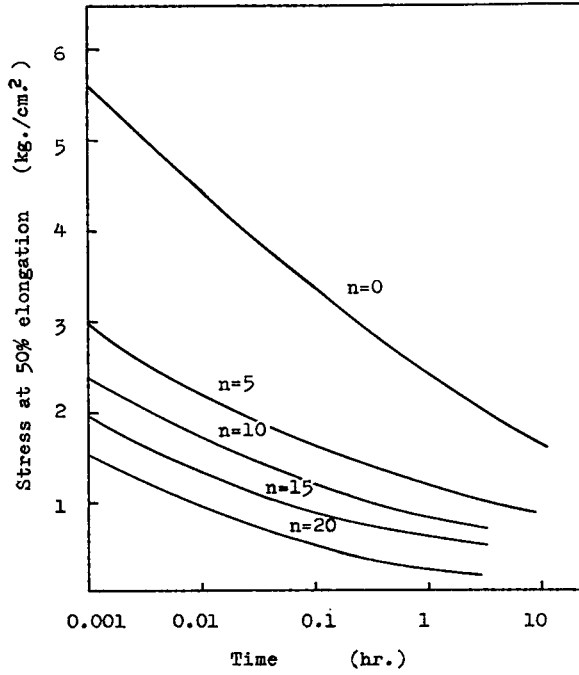


Fig. 2. Effect of number of roll-thinning operations n on stress relaxation at 20°C.

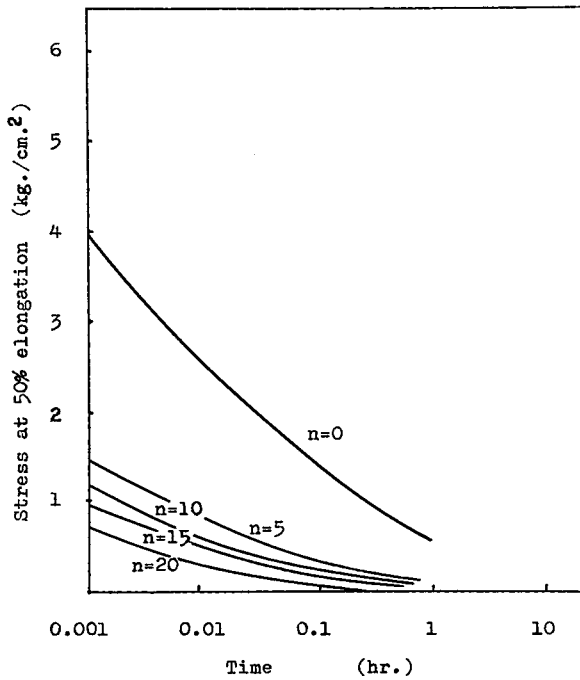


Fig. 3. Effect of number of roll-thinning operations n on stress relaxation at 60°C.

The fact that modulus is greater at lower temperature is not in agreement with an entropy effect according to the theory of rubber elasticity. This indicated that the flow effect is larger than the entropy effect in the measurement of modulus of unvulcanized rubber.

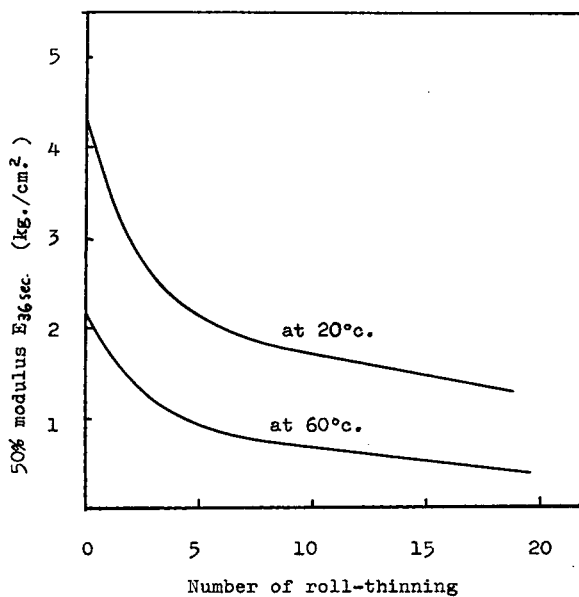


Fig. 4. Relationship between 50% modulus $E_{36 \text{ sec.}}$ and number of roll-thinning operations n .

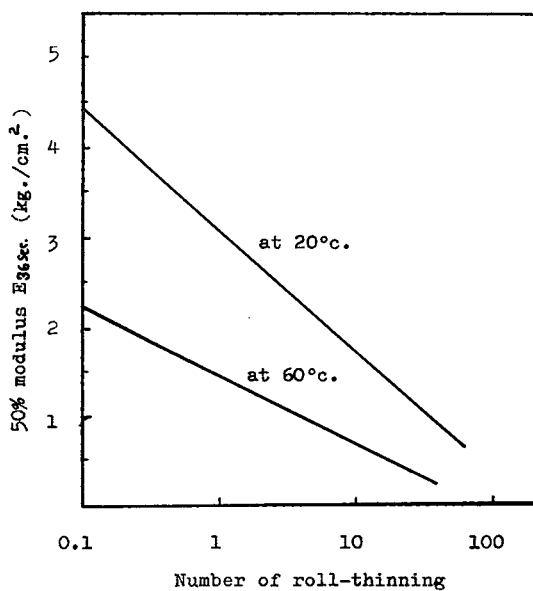


Fig. 5. Relationship between 50% modulus $E_{36 \text{ sec.}}$ and $\log n$.

Figure 5 shows the relationship between degree of mastication and modulus (stress at constant elongation). As the modulus, $E_{36 \text{ sec.}}$, the value at 36 sec. after 50% stretching was taken. From this, the effect of mastication could be considerable at early time of mastication. In Figure 5, the ordinate shows $E_{36 \text{ sec.}}$ and the abscissa shows the logarithm of the number of roll-thinning operations. From Figure 5, it is clear that the decrease in modulus was proportional to the logarithm of number of roll-thinning operations at the early period of mastication, and the following eq. (1) was established:

$$E = a - b(T) \log n \quad (1)$$

where E is the modulus, n is the number of roll-thinning operations, T is temperature, and a and b are constants.

B. Temperature Dependence of Stress Relaxation

Figure 6 shows the results from stress relaxation measurement of masticated pale crepe at various temperatures. As described previously, the modulus decreased with increasing temperature. However, on reaching

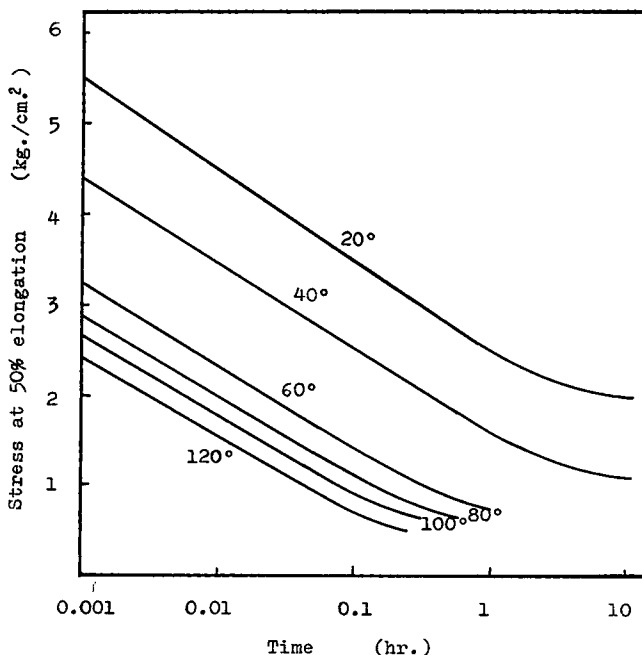


Fig. 6. Effect of temperature on stress relaxation of masticated pale crepe.

a certain temperature, the change in modulus became small; namely, up to about 70°C. the modulus decreased, but at temperatures above 70°C. the temperature dependency became less.

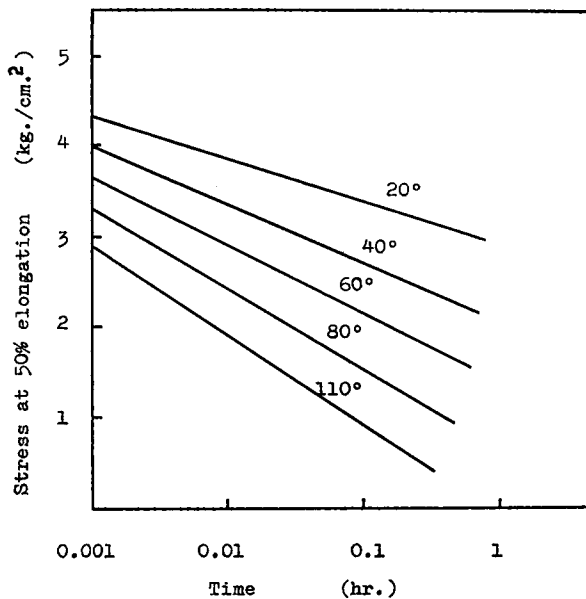


Fig. 7. Effect of temperature of stress relaxation of latex film.

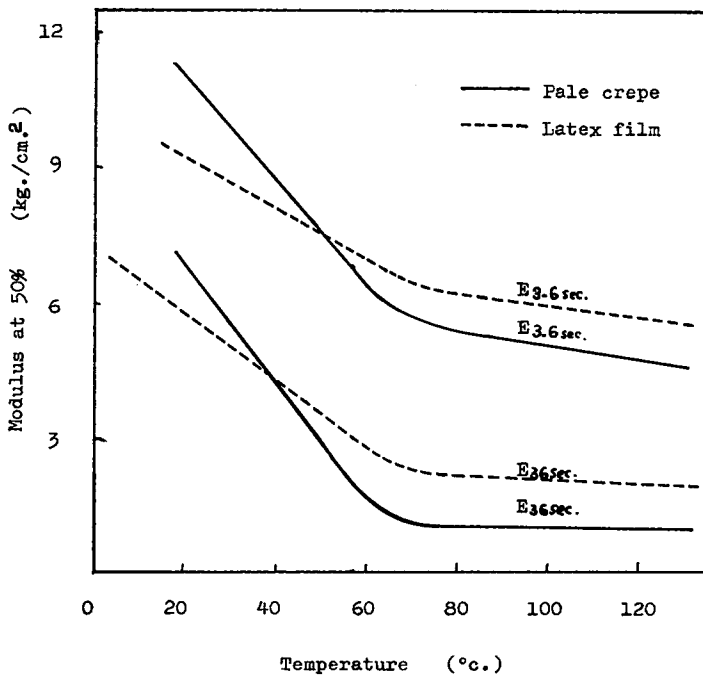


Fig. 8. Relationship between modulus ($E_{3.6 \text{ sec.}}$ and $E_{36 \text{ sec.}}$) and temperature: (—) pale crepe; (---) latex.

C. Stress Relaxation of Film from Latex

A sample made of a sheet or film from 60% latex was subjected to stress relaxation. The results are shown in Figure 7. In the temperature range of 20–100°C., the stress showed a linear relationship with logarithm of time. The slope for this sample was smaller than that for the pale crepe sample. This indicates that the flow of segments took place with more difficulty than that in pale crepe. Figure 8 shows the relationship between elasticity and temperature for the samples of latex and pale crepe films. The flow temperature was found to be in the vicinity of 70°C. Temperature coefficients of pale crepe with latex films were also compared; that of latex film was smaller up to the flow temperature.

D. Change in Solution Viscosity of Pale Crepe due to Mastication

Pale crepe was thinned down by rolling and dissolved in benzene. The viscosity of the solution was measured, and the relation between number of rolling operations and the relative viscosity η_{rel} was studied. Measurements were carried out on samples subjected to 3, 6, 10, 20, 30, and 60 rollings. Results are shown in Figure 9. The relative viscosity was determined at concentrations of 1.0, 0.75, 0.58, and 0.25 g./100 ml. Pale crepe which was not subjected to rolling had some insoluble portion in solvent. As shown in Figure 8, the decrease in solution viscosity was considerable in the early period of mastication and became less after cer-

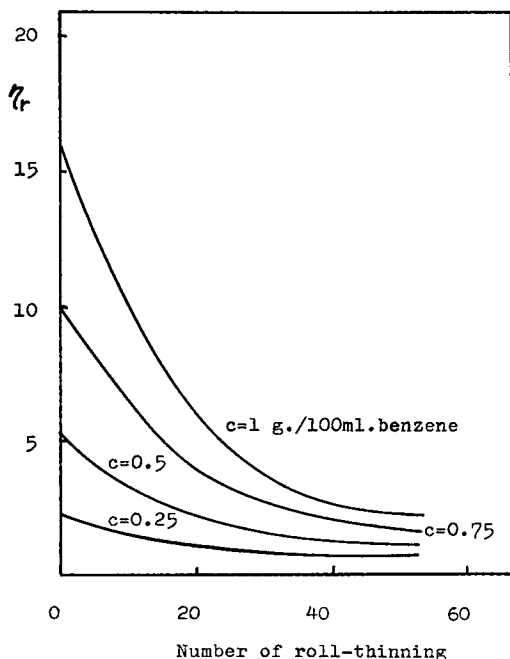


Fig. 9. Effect of n on η_r at 25°C.

tain extent of mastication. The logarithm of the number of rolling operations and the relative viscosity had an approximately linear relationship in the early period of mastication.

On comparing these results with the results of stress relaxation measurement, it is considered that, since viscosity and molecular weight have a simple relation, molecular weight is decreased by mastication and, as a result, the flow of molecules in stress relaxation becomes easier and relaxation time becomes shorter.

E. Change in Solution Viscosity of Deproteinized Natural Rubber Due to Heating in Air

It is expected that a change in the molecular structure of unvulcanized rubber takes place when it is heated. In order to investigate what kind of change takes place in heated rubber molecules, deproteinized natural rubber was heated at various temperatures in air and the relationship between its relative viscosity in benzene solution and time of heating was studied. The results are shown in Figure 10. At temperatures, above 100°C. the solution viscosity decreased with duration of heating, and with an increase in temperature a marked decrease in solution viscosity was observed.

Figure 11 shows a plot of the data shown in Figure 10, the logarithm of time of heating being plotted on the abscissa and the ratio η_{rt}/η_{r_0} on the ordinate, where η_{r_0} is the relative viscosity of the unheated sample and η_{rt} is that of the sample which was heated for t hours. For samples which

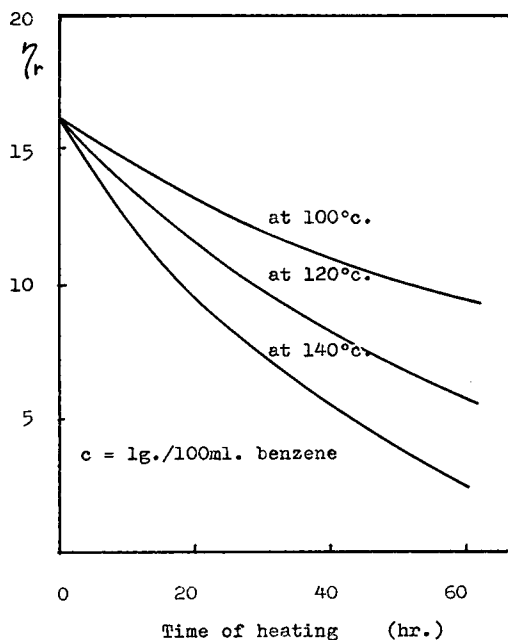


Fig. 10. Effect of heating on η_r at 25°C.

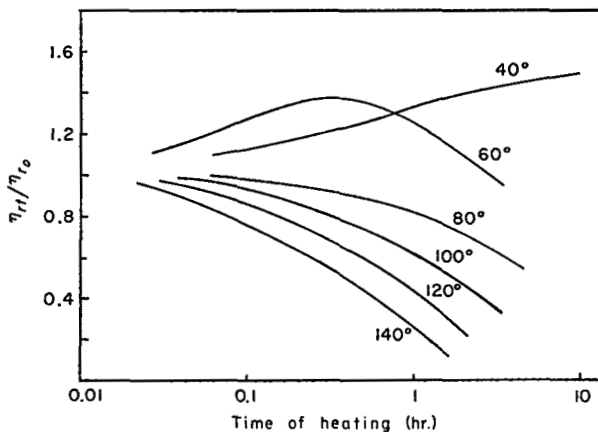


Fig. 11. Relationship between η_{rt}/η_{r0} and the logarithm of heating time.

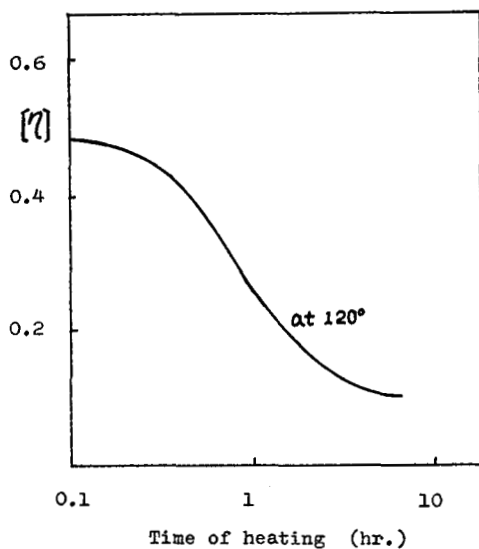


Fig. 12. Relationship between $[\eta]$ of deproteinized rubber and the logarithm of heating time.

were heated above 100°C., the ratio of the relative viscosities η_{rt}/η_{r0} changed exponentially time of heating t .

$$\eta_{rt}/\eta_{r0} = e^{-kt} \quad T > 100^\circ\text{C.} \quad (2)$$

This viscosity was measured at the concentration of 1 g./100 ml. benzene at 25°C. Table I shows the values of k for eq. (2) at various temperatures.

With heating at temperatures below 100°C., the ratio of relative viscosities increased at early period of heating and gradually decreased on further heating. This may be explained on the basis of intermolecular crosslinking

TABLE I
Relationship between Heating Temperature and k

Heating temp., °C.	k
100	0.252
120	0.398
140	0.721

by free radicals formed by heating, and the decrease in viscosity may be attributed to a decrease in degree of polymerization due to cleavage of molecules by oxidation. With unvulcanized rubber, also, the intermolecular reaction and cleavage reaction seem to occur on heating in air; below 80°C. the former seems to be dominant, and above 100°C., the latter. However, even above 100°C. the sample heated for some 10 hr. formed a partially insoluble gel in solvent. Figure 12 shows the change of intrinsic viscosity of deproteinized natural rubber heated in air in relation with time. The heating temperature of the sample was 120°C. Up to a heating period of 3 hr. the intrinsic viscosity was gradually lowered and then the rate of lowering became slower. This also indicates that heating causes a decrease in degree of polymerization.

SUMMARY

The stress relaxation of unvulcanized rubber was determined, and at the same time, η was measured. Changes in unvulcanized rubber due to mastication and heating and their effect on stress relaxation were investigated. Unlike vulcanized rubber, in the stress relaxation curve of unvulcanized rubber, the stress initially decreased linearly with the logarithm of time. As to the effect of mastication on stress relaxation, the relaxation time decreased with increasing period of mastication; the modulus also decreased (especially in the first several hours of mastication the modulus decreased rapidly). An approximate linear relationship was demonstrated between modulus and logarithm of number of rolling operations.

As to the effect of increasing temperature of measurement, a decrease in stress and rapid shortening in relaxation time were observed. However, a decrease in modulus $E_{36 \text{ sec.}}$ was shown at temperatures up to about 70°C., while at higher temperatures, the stress stayed nearly constant. This can not be explained by the entropy effect from the point of view of theory of rubber elasticity and is rather similar to the temperature dependence of the modulus of plastics.

Measurements of the effect of mastication on solution viscosity of unvulcanized rubber showed that mastication caused a decrease in solution viscosity; this is attributed to lowering of the molecular weight in rubber molecules. Comparison of this result with the stress relaxation curve for decrease in relaxation time due to mastication shows that the change in molecular weight seems to be a major factor.

Raw natural rubber showed structural changes on heating. Intermolecular reaction and cleavage of molecules by oxidation seem to occur at the same time. These are the main conclusions reached on the effects of mastication and heating on stress relaxation of unvulcanized pale crepe deproteinized natural rubber and latex.

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References

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Résumé

On a étudié les effets de la mastication sur la relaxation de tension du caoutchouc brut entre 20° et 120°. Le temps de relaxation de tension diminue pour des temps de mastication plus importants et le module décroît également. Quant à l'effet de la température où s'effectue la mesure, une augmentation de la température fait diminuer le module. De plus, on trouve que la mastication a pour effet de faire décroître la viscosité de la solution de caoutchouc et que par chauffage la réaction intermoléculaire et la cassure des molécules par oxydation semblent se produire en même temps.

Zusammenfassung

Der Einfluss der Mastizierung auf die Spannungsrelaxation von Rohkautschuk wurde im Bereich von 20–120° untersucht. Mit zunehmender Mastizierungsdauer wird die Relaxationszeit kürzer und der Modul nimmt ab. Ausserdem nimmt der Modul mit steigender Messtemperatur ab. Durch die Mastizierung wird die Lösungsviskosität des Kautschuks erniedrigt. Beim Erhitzen treten anscheinend intermolekulare Reaktion und oxydative Spaltung von Molekülen gleichzeitig auf.

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