

Chemorheological Study of Vulcanized Rubbers under Mechanical Stress

TAKAE KUSANO, YUKIZI SUZUKI, and
KENKICHI MURAKAMI, *Chemical Research Institute of Nonaqueous
Solutions, Tohoku University, Sendai, Japan*

Synopsis

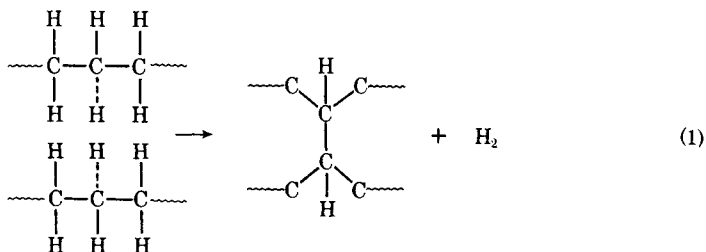
At lower than the glass transition temperature, the cleavage of the molecular chains of extended vulcanized rubbers will occur. The crosslinking density of vulcanized rubbers, which were placed at room temperature for about 4 hr in nitrogen atmosphere, increased about 17% after extension of 200% at -76°C . This may be due to the recombination of cleft chains, and this can be shown by the Maxwellian type of curves between crosslinking density and forced strain. Considering the decreasing proportion of crosslinking density by the radical acceptors included in the rubbers and the fact that crosslinking density increases because of recombination of cleft chains, this was attributed to the recombination of unstable chains produced by the added mechanical stimulus.

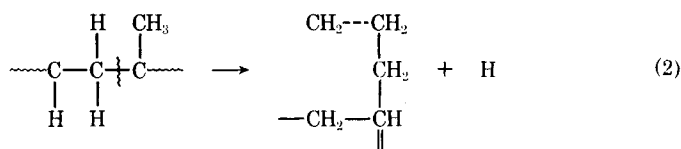
INTRODUCTION

Polymers can change their molecular structures under mechanical stimulus, and these changes result from cleavage of the polymers chains. Generally, the average molecular weight of masticated elastomers are smaller than those of unmasticated. If other reactive components exist, the unstable free radicals will combine with these reactive components, in so-called mechano-polymerization. The portions of polymer chains changed by mechanical stimulus are chemically unstable and always react to attain stable structures.

Some studies on mechano-polymerization have been reported, especially recently.¹⁻³ It is a well-known phenomenon that when polymers are irradiated, gaseous hydrogen is freed from the sites of cleft molecular chains and where crosslinking reactions are induced subsequently.

Similar phenomena have been found in the case of mechanical molecular cleavage, and these mechanisms can be shown by the following reactions:⁴





When vulcanized rubbers are forced to extend in the glassy state or near it (having nearly no mobilization and a large coefficient of friction of molecular chains), scissions will be considerable.

The recombination of scissioned main chains as in reaction (2),⁵ is considered as a new kind of crosslinking formation in the case of mechanical destruction.

We have observed changes in crosslinking densities through time by chemorheological methods of forcing extensional cured rubbers at low temperature.

EXPERIMENTS

The samples used were natural rubber (NR) (RSS #1) and nitril rubber (NBR) (Polyser #803).

The curing conditions are shown in Table I. The cured samples were extracted with hot acetone for 48 hr with a Soxhlet-type extractor, then maintaining them in a refrigerator after one day of drying under vacuum.

TABLE I
Mixing Detail and Curing Conditions

Sample	Rubber, parts	ZnO, phr	St—COOH, ^a phr	S, phr	M, ^b phr	DM, ^c phr	Curing temp., °C	Curing time, min
NR	100	5.0	1.0	2.0		1.0	145	10, 20, 30 40, 80
NBR	100	5.0	1.0	2.5	1.0		150	30, 40, 80

^a Stearic acid.

^b Mercaptobenzothiazole.

^c Dibenzothiazyl disulfide.

Operation of an Autograph (IM-100) at a speed of 2 mm per min to extend dumbbell-type specimens of 0.6 mm thickness, 5 mm width, and 20 mm length was carried out preextension to 21 mm length in order to avoid errors from length of specimens after cracking. Forced strains were then applied on the materials after setting for 10 min at -78°C .

We used intermittent stress relaxation to measure the changes in crosslinking density of examined samples in nitrogen atmosphere. To avoid shrinkage of samples under stress, the first recording stress was made at each noted temperature, after extension for 45 min.

RESULTS AND DISCUSSION

The stress-strain curve shown in Figure 1 was the resultant of forces extended rubber at low temperature. The maximum stress will be found in a narrow range of α values (about 1.05). While the stress is decreasing, α is increasing; at last the stress will be constant and parallel to the α axis when α is more than 1.5. This is meant by the slide of molecules of rubbers, which has passed the yield point accompanying the mobilization of molecular chains. This forced extensional ratio can be performed to about $\alpha = 2$.

With change in extensional velocity, there was also a change in destructive extensional ratio, and the lower the deformation, the larger the destructive extensional ratio.

Gaseous hydrogen molecules, which were freed from destructive molecules, have been observed on the surface of deformed specimens.

Figure 2 was obtained at -78°C with an extensional velocity of 2 mm/min to extend the NR specimens to $\alpha = 1.3$, then using intermittent stress relaxation to measure them after 45 min of leaving them at each temperature (66°C , 70°C , and 83°C). It was shown that the lower the measured temperature, the larger the relative stress, and vice versa. The higher the temperature, the faster the recombination of cleft chains. On the preheated specimens, there are quantities of active radicals capable of recombination if the temperature is low.

The same experiments were carried out for NBR and the results showed the same tendency as those with NR. As can be seen from Figure 3, generally the same temperature stabilities of free radicals produced by mechanical destruction obtained for NR and NBR.

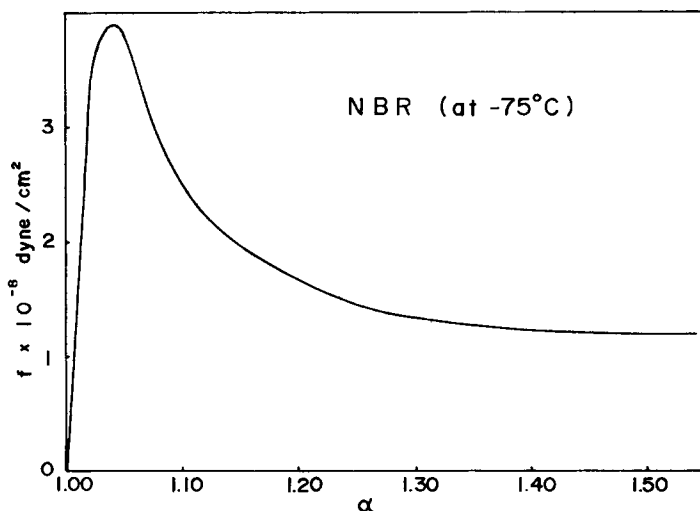


Fig. 1. Stress-strain curve obtained by forcible extension of nitril rubber (NBR) at low temperatures.

From the relation of relative stress versus time in Figures 2 and 3, we found that the measured relative stress by the intermittent method increased fast at first and then approached a constant value gradually, a value of equilibrium. That is, after a certain time has elapsed, no more radicals will be contributed to new crosslinking reactions.

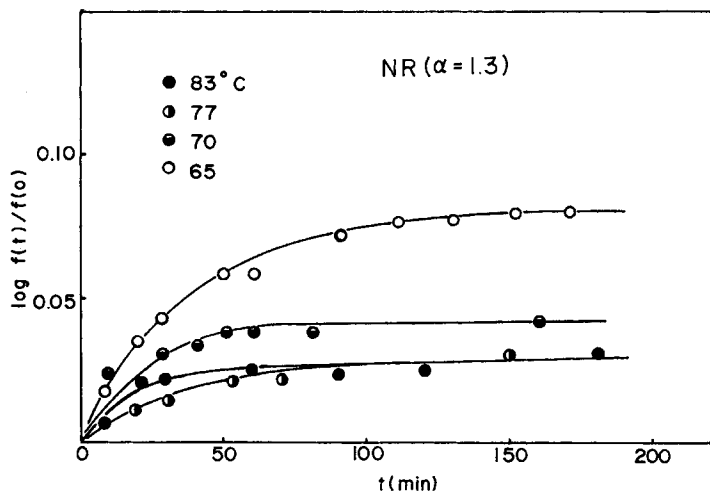


Fig. 2. Intermittent stress relaxation curves for natural rubber (NR).

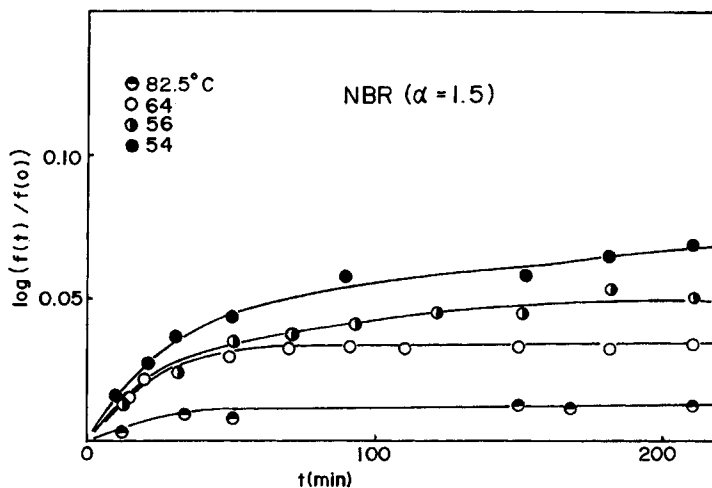


Fig. 3. Intermittent stress relaxation curves for nitril rubber (NBR).

In Figure 4, the relation between equilibrium network $n(\infty)$ and temperature was plotted. The $n(\infty)$ was obtained for samples left for 3 hr at each temperature. The figure suggests that those radicals induced by chain scission recombine at a constant ratio regardless of the temperature. That

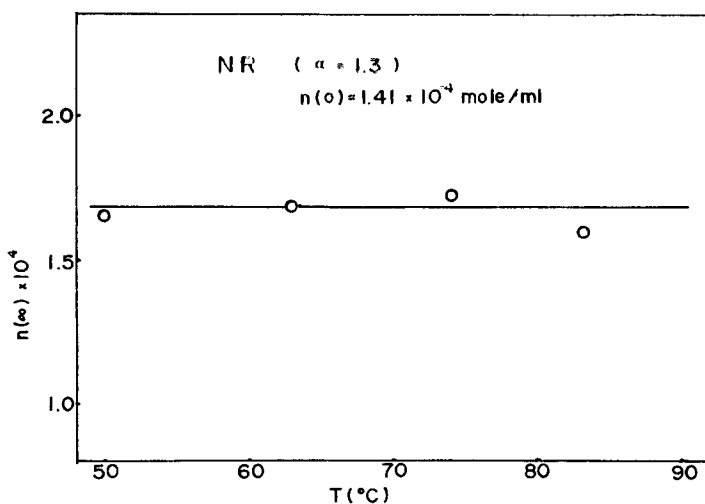


Fig. 4. Equilibrium crosslinking density $n(\infty)$ vs. temperature for natural rubber.

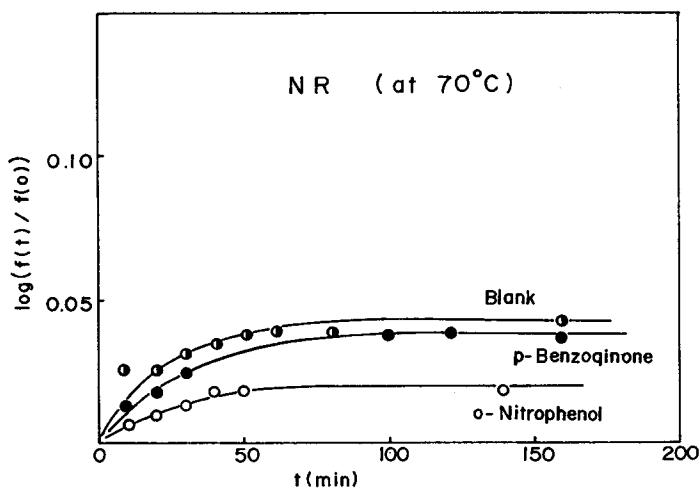


Fig. 5. Intermittent stress relaxation curves for natural rubber including radical acceptors.

is to say, the number of unstable radicals induced by a constant extension is independent of temperature measured under stress and nearly constant.

To further investigate these recombination reactions,^{2,6} cured natural rubbers were immersed in benzene solutions containing the radical acceptors *p*-benzoquinone, 3.47 mg, and *o*-nitrophenol, 0.48 g per gram of NR. Then, the specimens were dried in vacuo for one day after keeping them in the laboratory for $\frac{1}{2}$ hr. The same experiments as in Figure 3 were carried out with these samples, and the results shown in Figure 5 were obtained. In the case of included radical acceptors, the results measured by intermittent

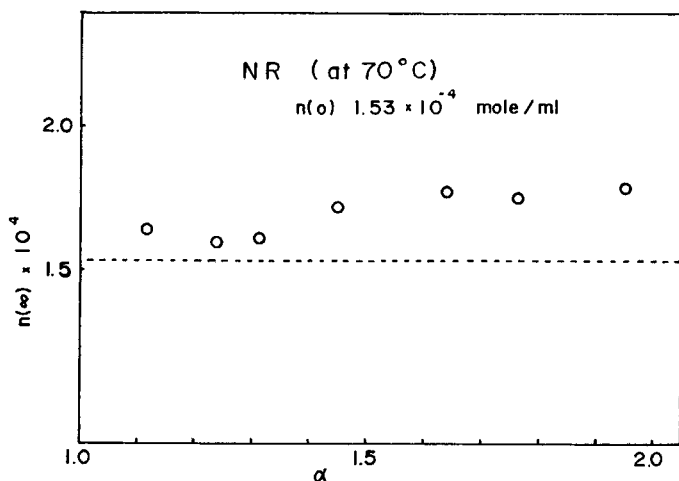


Fig. 6. Equilibrium crosslinking density $n(\infty)$ vs. forcible extension ratio α for natural rubber.

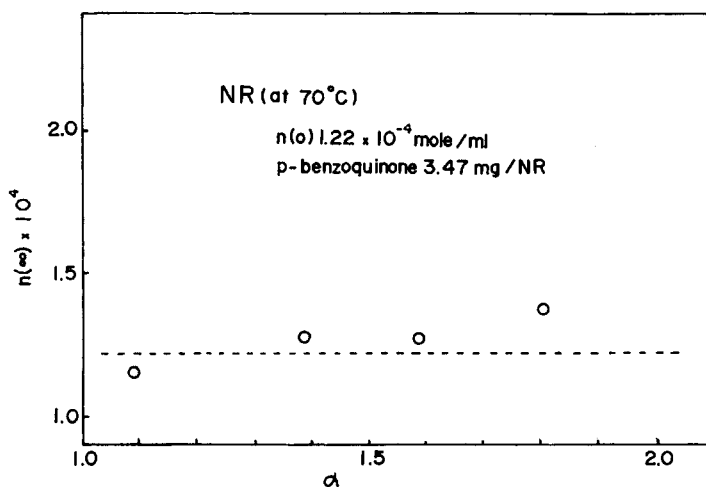


Fig. 7. Equilibrium crosslinking density $n(\infty)$ vs. forcible extension ratio for natural rubber including radical acceptors.

stress relaxation showed a little increase in relative stress compared to the controlled specimens. This was due to the reducing radicals which were the results of reaction with radical acceptors; thus, the increasing networks by recombination of cleft chains were also considered to be reduced sequentially.

The above-mentioned experiments were carried out at constant extension ratio.

Next the equilibrium densities are discussed for $n(\infty)$, which were measured after each temperature. With the same specimens mentioned above, the stress was measured by the same methods in nitrogen stream at 70°C

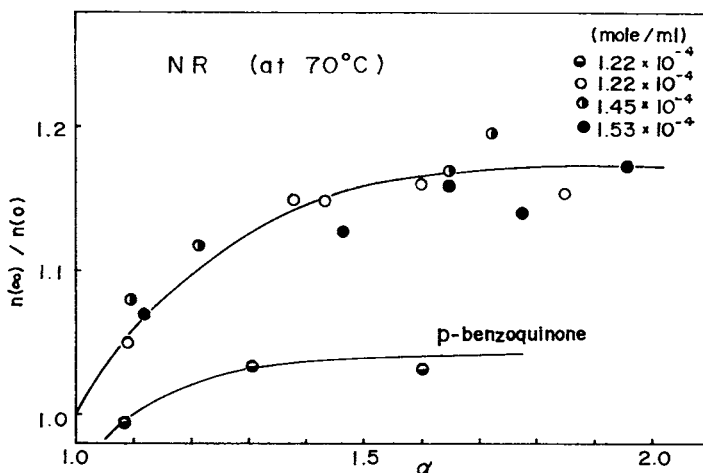


Fig. 8. Plot of $n(\infty)/n(0)$ vs. α for natural rubber.

for 4 hr after extension at low temperature. Assuming that the crosslinking density calculated from the formula

$$f = nRT(\alpha - \alpha^{-2})$$

is the equilibrium density, Figure 6, in which radical acceptors were not included, and Figure 7, in which radical acceptors were included, were obtained. The broken line shown in both figures indicates the initial crosslinking density of the specimens before molecular destruction.

For the purpose of comparing both figures, Figure 8 was obtained by plotting the ratio $n(\infty)/n(0)$ versus α . It was shown that in the case of included radical acceptors the ratio $n(\infty)$ was smaller than that of unincluded radical acceptors. Figure 8 elucidates that the relation between $n(\frac{1}{2})/n(0)$ and α approached Maxwellian curves independent of $n(0)$ for three kinds of specimens having different initial crosslinking density. That is, molecular destruction, which was induced by forced extension, depends upon the extensional ratio α and is shown by appropriate Maxwellian curves. Thus the change in properties induced by mechanical stimulus depends closely on the strain ratio. The phenomena have been found not only in molecular destruction at low temperature, but also in the large deformation experiments involving stress relaxation of cured rubbers, at temperatures above room temperature.⁷

The relation between $f(\infty)/f(0)$ and time can be shown by Maxwellian relationship in the ordinary stress relaxation curves; and in the case of molecular destruction induced by forced extension at low temperature, as shown in Figure 8, by substituting time for the α axis, the same type of curves are obtained.

The time measured for stress relaxation within the region of linear be-

havior of strain can be considered to be equivalent to the strain ratio of large deformation.

In Figure 8, the increasing ratio of crosslinking density in the large range of α , as shown by Maxwellian curves, becomes small. That is, as mentioned in Figure 1, the mobilization of molecular chains becomes large according to the magnitude of extensional forces and its cleavage effect will be minimal.

It is well known that the stability of free radicals induced by mechanical shear differs with the kind of polymer. Poly(methyl methacrylate) and polystyrene will retain their stability even at comparatively high temperatures.^{8,9} The stability of these radicals is also closely related to their glass transition temperature.¹⁰

From the results measured by the intermittent stress relaxation method as shown in Figures 2 and 3, the increasing stress has been maintained for a considerable time at the temperature. These phenomena are believed to demonstrate the comparative stability of radicals induced by the cleavage of chains from forced extension at low temperature.

References

1. K. Goto, *Kogyokagaku Zasshi*, **71**, 1319 (1968).
2. S. Yamashita, *Kogyokagaku Zasshi*, **71**, 1331 (1968).
3. A. A. Berlin, G. S. Petrov, and V. F. Prosvirkina, *Zhur. Fiz. Khim.*, **32**, 2565 (1958).
4. K. Shinohara and K. Kashiwabara, *Hoshasen To Kobunshi*, Makisyoten, 1968.
5. E. H. Andrews and P. E. Reed, *Polymer Letters*, **5**, 317 (1967).
6. G. Ayrey, C. G. Moor, and W. F. Watson, *J. Polym. Sci.*, **14**, 1 (1956).
7. T. Kusano and K. Murakami, Paper presented at 18th Annual Meeting of the Society of Polymer Science of Japan, Kyoto, 1969.
8. P. Yu. Butyagin, I. V. Kolbarev, A. M. Dubinskaya, and M. V. Kisluk, *Vysokomol. Soedin.*, **10**, 2265 (1968).
9. S. E. Bresler, S. N. Zhurkov, S. N. Kazbekov, E. M. Saminski, and E. E. Tomashevski, *Zhur. Tekh. Fiz.*, **29**, 358 (1959).
10. D. K. Backman and K. L. Devries, *J. Polym. Sci. A-1*, **7**, 2125 (1969).

Received March 31, 1971

Revised June 23, 1971