

Effect of Temperature on Sulfur Pre vulcanization of Natural Rubber Latex

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ABSTRACT: Sulfur pre vulcanization of natural rubber latex was conducted at 60, 70, 80, and 90°C for different periods. The extent of crosslinking was assessed. Tensile properties, water absorption, leaching, and stress-relaxation characteristics of the films were also evaluated. The volume fraction of rubber (V_r), which is a measure of crosslink density of the films, showed a maximum when pre vulcanization was conducted at 80°C for 2 h or at 90°C for 1 h. At lower temperatures, the rate of reaction was slow. At each temperature, tensile strength and elongation at break decreased when the pre vulcanization time increased, whereas the modulus increased up to a maximum crosslinking and thereafter decreased. Water absorption and leaching were more rapid in pre vulcanized film than in post vulcanized film. The rate of stress relaxation slightly increased as the extent of pre vulcanization increased. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1913–1920, 1997

Key words: natural rubber latex; pre vulcanization

INTRODUCTION

Pre vulcanized latex (PVL) is a very convenient raw material for the latex goods manufacturing industry. It is especially attractive for small-scale units since it can be used directly for the manufacture of latex products, thus eliminating the need for latex compounding other than the addition of antioxidant or pigment. The vulcanization of latex was first proposed by Schidrowitz.¹ The crosslinking of rubber in latex can be effected by the reaction with sulfur,^{2–6} sulfur donors,⁷ peroxides,⁸ or radiation.⁹ Production of sulfur PVL involves heating of raw latex with various compounding ingredients such as an accelerator and sulfur until the required degree of crosslinking is obtained. Drying of pre vulcanized latex produces a cross-linked film without the need for further vulcanization.

Several studies were reported on the sulfur pre-

vulcanized natural rubber (NR) latex. The rate of pre vulcanization varies with different vulcanization systems and the extent of pre vulcanization has a profound influence on the final vulcanizate properties. The crosslinking reaction in latex takes place over a range of conditions such as temperatures from 20 to 90°C for appropriate periods.¹⁰ As temperature is lowered, crosslinking takes place very slowly. By proper stabilization of latex, pre vulcanization conducted at higher temperatures reduces the vulcanization time appreciably. This study reports the effect of temperature and duration of heating on sulfur pre vulcanization of NR latex. The extent of crosslinking, tensile properties, water absorption, leaching, and stress-relaxation characteristics of the films prepared therefrom were evaluated.

EXPERIMENTAL

Materials and Methods

Centrifuged latex conforming to the specifications of the Bureau of Indian Standards (BIS), IS:5430-

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Table I Formulation of Latex Compound

Ingredients	Parts by Weight (Wet)
Centrifuged latex (60%)	167.0
Potassium hydroxide solution (10%)	2.5
Potassium laurate solution (20%)	1.3
Sulfur dispersion (50%)	3.0
Zinc diethyldithiocarbamate dispersion (50%)	2.0
Zinc oxide dispersion (50%)	0.4

1981, was used for the study. The other compounding ingredients were of commercial grade. The vulcanizing agents were used as 50% dispersions in water, prepared by ball milling.

Prevulcanization and Film Preparation

A latex compound was prepared as per the formulation given in Table I. Prevulcanization was conducted at temperatures of 60, 70, 80, and 90°C. For this, the latex compound was heated under stirring in a water bath set at a constant temperature. The latex was withdrawn at appropriate time intervals and cooled to room temperature. On the next day, films were cast in shallow glass dishes to a thickness of ~ 1 mm. After drying for 48 h at room temperature, the films were leached in water for 24 h and again dried at room temperature.

Determination of Volume Fraction of Rubber

The volume fraction of rubber (V_r) in the swollen vulcanizate was determined from equilibrium swelling of the films in toluene at 30°C following the method suggested by Ellis and Welding.¹¹

Tensile Testing

Tensile test pieces were punched out from the films using a dumbbell die. The tests were carried out according to ASTM D 412 (1994) using a Zwick Universal Testing Machine, Model 1474.

Stress-Relaxation Measurements

The stress-relaxation measurements were carried out in Zwick universal testing machine, using dumbbell-shaped films. The samples were pulled to the required elongation at a strain rate of 0.03 s⁻¹ and the decay of stress as a function of time

was recorded, $f(t)$ being the stress at time t , and $f(0)$, the initial stress.

RESULTS AND DISCUSSION

Volume Fraction of Rubber

Figure 1 shows the volume fraction of rubber, which is a measure of the crosslink density of the films, obtained after prevulcanizing the latex at 60, 70, 80, and 90°C for different periods. It can be seen that when the prevulcanization was conducted at 60°C the volume fraction of rubber increased as the heating time increased from 0.5 to 6 h. But the rate of increase was very slow and the value of V_r obtained was much lower compared to that realized at the higher temperatures studied. When prevulcanization was conducted at 70°C, a higher V_r value was obtained, which was found to increase with the heating time, and the rate of

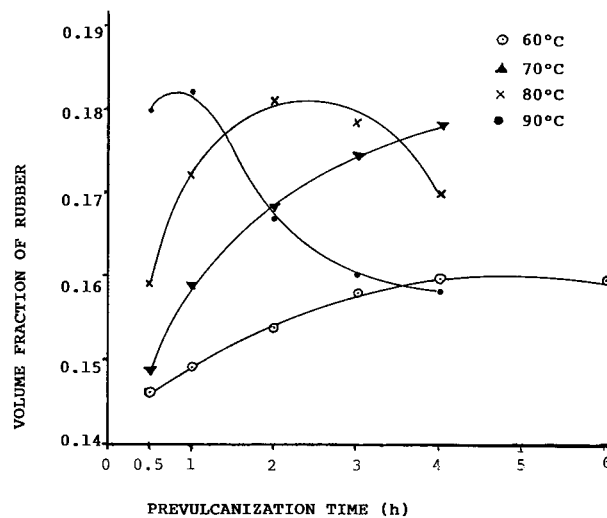


Figure 1 Effect of prevulcanization time and temperature on volume fraction of rubber.

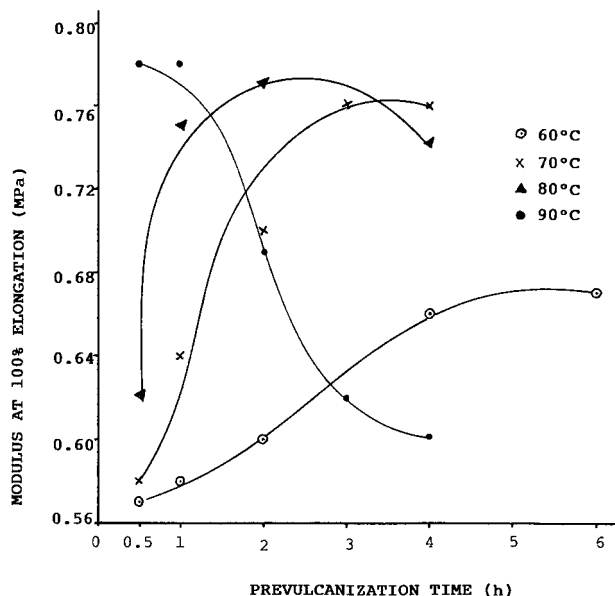


Figure 2 Effect of prevulcanization time and temperature on modulus at 100% elongation.

increase was also higher compared to that found at 60°C. When prevulcanization was conducted at 80 and 90°C, the V_r values further increased. A maximum was, however, observed at a definite period for each temperature after which a drop in the value was observed. At 80°C, the maximum V_r was obtained at 2 h of heating. On extending the heating time beyond 2 h, V_r decreased appreciably. At 90°C, the maximum V_r was obtained at 1 h of heating. On further heating, V_r dropped abruptly. The drop in V_r is due to overvulcanization of rubber particles. Crosslinks and pendent groups undergo a variety of further reactions which take place at the same time as does crosslinking, during overcure, and during the service life of the vulcanizate.¹² Crosslink shortening and crosslink decomposition are the two most important types of reaction occurring after crosslinking. The crosslink decomposition leads to an overall loss of crosslinks,¹³ which accounts for the observed drop in V_r values.

Tensile Properties

Figure 2 shows the modulus at 100% elongation of the films prepared from latex prevulcanized at different temperatures. At 60°C, as the heating time was increased, the modulus increased and the rate of increase slowed down after 4 h of heating. At 70°C, as the heating time increased, the modulus increased, the rate of increase being faster com-

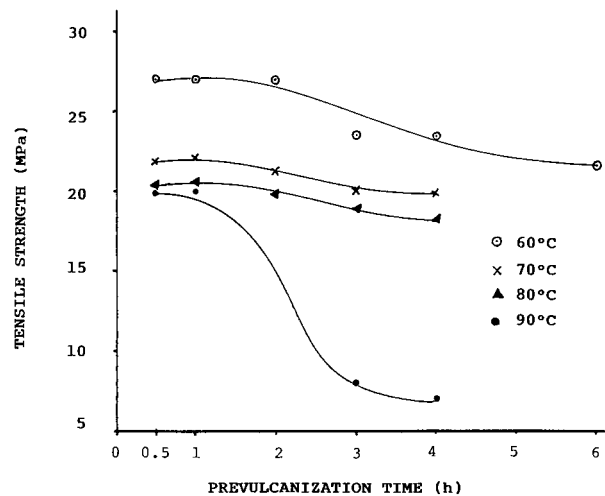


Figure 3 Effect of prevulcanization time and temperature on tensile strength.

pared to that at 60°C, attaining almost a maximum modulus at 3 h of heating, beyond which the increase was only nominal. At 80°C when the heating time increased from 0.5 to 1 h, a sharp increase in modulus was noticed. Afterward, the rate of increase slowed down, attaining a maximum at 2 h. On further heating, the modulus decreased steadily. This is in line with the changes in V_r values as shown in Figure 1. The maximum V_r value and the maximum modulus attained at 2 h of heating indicated that during this period maximum crosslinking had taken place. Beyond this period due to overvulcanization and the consequent restricted coalescence of the rubber particles, a decrease in V_r and the modulus was observed.

At 90°C, the maximum modulus was obtained at 1 h of heating. On extending the heating time, the modulus decreased and the rate of decrease was very fast beyond 1 h, which slowed down after 3 h of heating, showing that maximum crosslink-

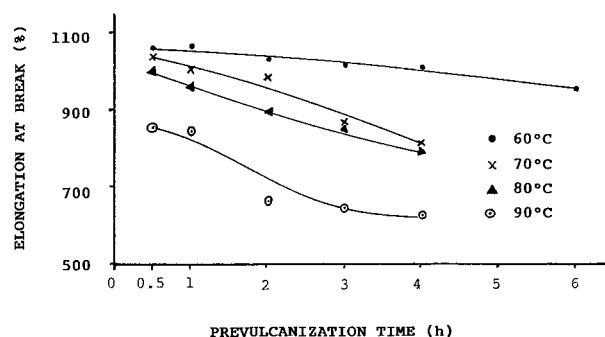


Figure 4 Effect of prevulcanization time and temperature on elongation at break.

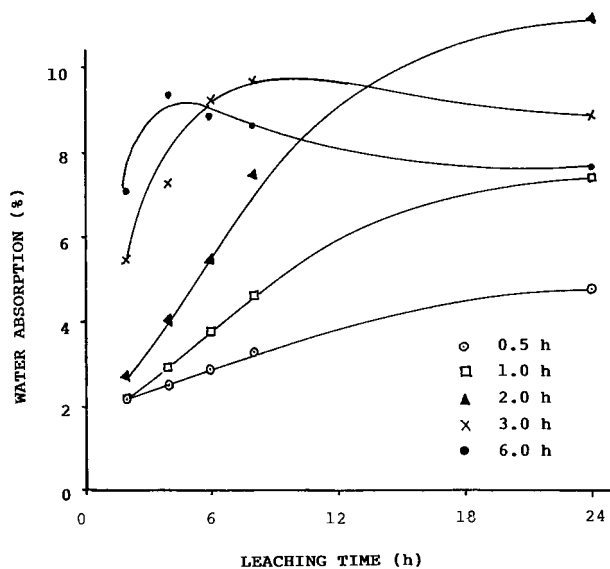


Figure 5 Effect of leaching time on water absorption of films from latex prevulcanized at 60°C for different periods.

ing had taken place during 1 h of heating, as evident from the V_r values given in Figure 1. At 90°C, beyond 1 h of heating, the latex particles become overvulcanized as stated earlier, which resulted in poor cohesion of the particles, thereby exhibiting a lower modulus.

Figure 3 shows the tensile strength of films prepared from latex prevulcanized at different temperatures. Unlike V_r and the modulus, high tensile strength was obtained when prevulcanization was

conducted at 60°C. For each temperature, better tensile strength was obtained at shorter periods of heating. As the heating was continued, tensile strength decreased. This is in line with the observation made by Gorton.³ At 90°C, a drastic decrease in tensile strength was obtained beyond 1 h of heating and the films exhibited very low tensile strength at 2–4 h of heating. This shows that the tensile strength of prevulcanized film is governed not only by the introduction of crosslinks but also by the ability of particles to coalesce among themselves. When latex is prevulcanized, the rubber particles are internally crosslinked. By increasing the temperature or increasing the heating time, the rubber particles become more and more crosslinked and, hence, become harder. Thus, when the film is prepared from a highly crosslinked latex, coalescence of the rubber particle becomes more and more difficult, resulting in lower tensile strength.

Figure 4 shows the elongation at break (EB) of the PVL films. EB was high when prevulcanization was conducted at 60°C. At each temperature, higher elongation was obtained at shorter times of heating. On prolonged heating, EB decreased. The maximum reduction was obtained when prevulcanization was conducted at 90°C for a heating time of 2–4 h. When the rubber particles are lightly crosslinked, the coalescence of particles is better, causing a higher elongation.

Water Absorption and Leaching Characteristics

Figure 5 shows water absorption during leaching of the films from latex prevulcanized at 60°C for

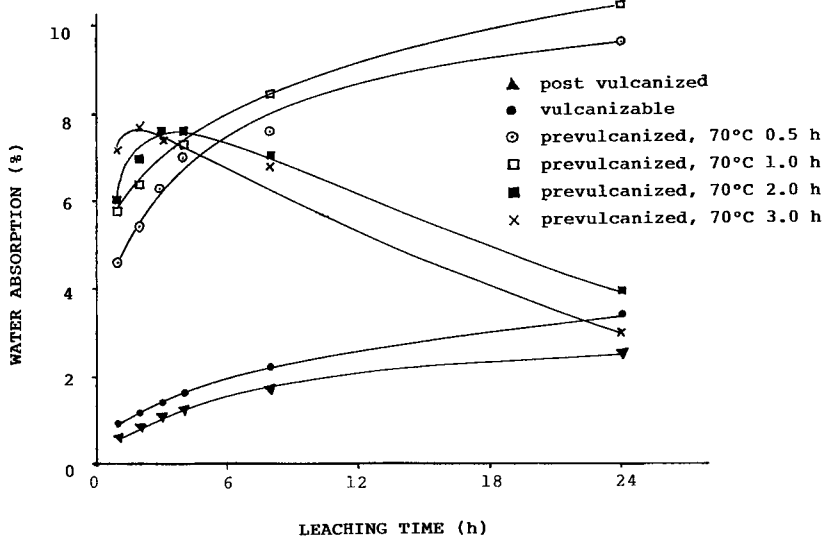


Figure 6 Effect of leaching time on water absorption of films from latex prevulcanized at 70°C for different periods in comparison with postvulcanized film and vulcanizable film.

Table II Weight Loss After Leaching Films in Water for 24 h at Room Temperature

Prevulcanization Time at 60°C (h)	Weight Loss of Films (%)	Prevulcanization Time at 70°C (h)	Weight Loss of Films (%)
0.5	1.08	0.5	1.57
1.0	1.10	1.0	2.04
2.0	1.15	2.0	2.58
3.0	1.93	3.0	2.75
4.0	2.04	4.0	2.86
6.0	2.14	—	—
Postvulcanized film	0.2		
Vulcanizable film	0.5		

different periods. It can be seen that in the case of samples prevulcanized for 0.5–2 h the percentage of water absorbed by the films slowly increased during 24 h leaching time. When the prevulcanization time was increased to 3 h, the films attained maximum water absorption in 8 h of leaching. On further extending the prevulcanization time to 6 h, the maximum water absorption was attained during 4 h leaching time.

Figure 6 shows the water absorption of films from latex prevulcanized at 70°C for different periods. This figure also shows that at shorter prevulcanization times equilibrium water absorption was attained slowly. As the period of prevulcanization increased, the films attained equilibrium water absorption faster. During 0.5–1 h of prevulcanization, the films did not attain equilibrium

even after 24 h of leaching, but when the time of heating increased to 2 h, the films attained equilibrium in 3 h. On extending the prevulcanization time to 3 h, equilibrium was attained at a still faster rate. For comparison, a postvulcanized film and a vulcanizable film were also included in this study. These films were obtained by casting a portion of the latex compound prepared for prevulcanization. The films were dried for 48 h at room temperature (vulcanizable films). Vulcanizable films were heated in an air oven at 100°C for 1 h (postvulcanized films). From the figure, it is seen that these two films showed a very low rate of water absorption and the films did not attain equilibrium, even after 24 h of immersion. Films from prevulcanized latex do not attain the level of coalescence which is possible in postvulcanized

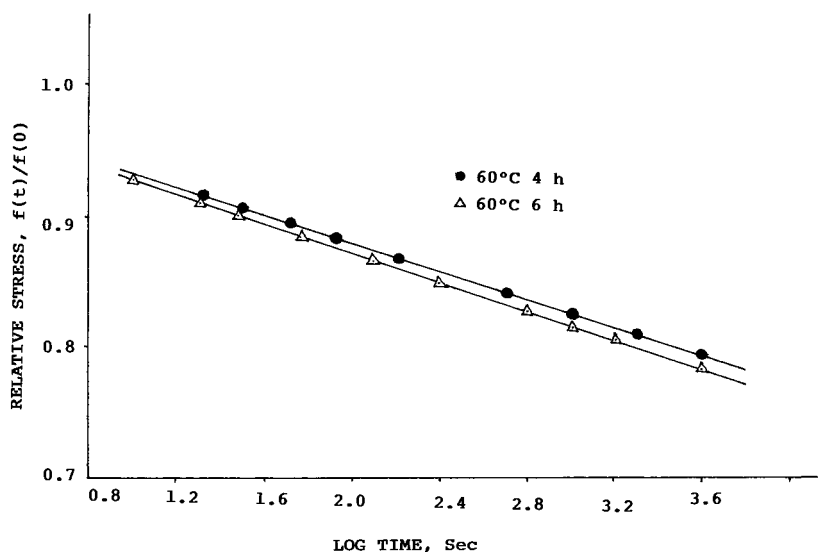


Figure 7 Semilogarithmic plots of stress decay as a function of time for the films from latex prevulcanized at 60°C for 4 and 6 h.

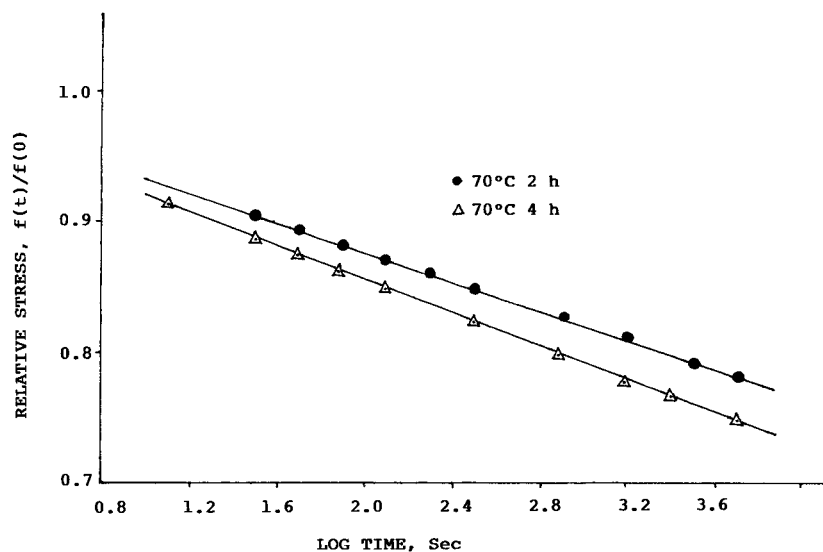


Figure 8 Semilogarithmic plots of stress decay as a function of time for the films from latex prevulcanized at 70°C for 2 and 4 h.

films and this lack of proper interparticle coalescence results in capillary action, leading to larger water uptake. The extent of capillary flow would be relatively small in lightly crosslinked particles where the constraints on particle coalescence are less. In such a network, the water-absorption rate is low. When the level of prevulcanization is increased, the rubber particles become harder and the films prepared therefrom become discontinuous and porous. Thus, equilibrium is attained more rapidly when the extent of prevulcanization is increased.

When the films are immersed in water, absorption and leaching occur simultaneously. The weight loss after leaching the films in water for 24 h is shown in Table II. It can be seen that leaching proceeded more rapidly from prevulcanized film than from a postvulcanized/vulcanizable film. When the extent of prevulcanization was increased by increasing the temperature or extending the heating time at a particular temperature, the amount of materials leached out from the films also increased. This can be attributed to the structural differences as explained earlier.

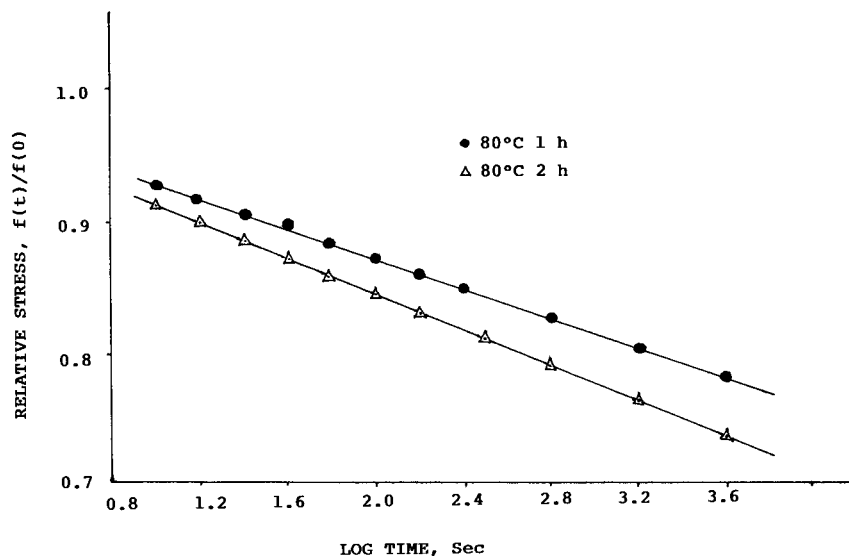


Figure 9 Semilogarithmic plots of stress decay as a function of time for the films from latex prevulcanized at 80°C for 1 and 2 h.

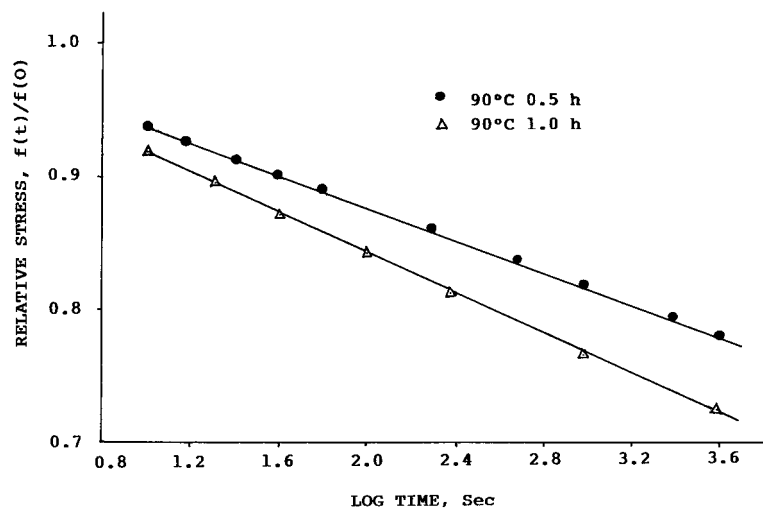


Figure 10 Semilogarithmic plots of stress decay as a function of time for the films from latex prevulcanized at 90°C for 0.5 and 1 h.

Stress-Relaxation Characteristics

Figures 7–10 present the stress-relaxation curves of films cast from PVL prepared at different conditions. The relaxation pattern of the samples were studied at 700% elongation. Table III shows the slope of these lines. It is seen that when the extent of prevulcanization increased the rate of stress relaxation also slightly increased. There are two important mechanisms which can lead to stress relaxation in a crosslinked elastomer¹⁴: (1) physical stress relaxation due to molecular rearrangements requiring little primary bond formation or breakage and (2) chemical stress relaxation due to chain scission, crosslink scission, or crosslink formation. Under normal conditions, both physi-

cal and chemical stress relaxation will occur simultaneously. However, at ambient temperature, the rate of chemical stress relaxation in a rubberlike NR is very low and the relaxation behavior is dominated by physical processes except for very long periods. From Table III, it can be seen that the slope of the lines increases with increase in the extent of prevulcanization. When the extent of prevulcanization is increased, there is only limited interdiffusion of the rubber particles, which accounts for the slightly higher rate of stress relaxation.

CONCLUSION

Maximum crosslinking was obtained when prevulcanization was conducted either at 80°C for 2 h or at 90°C for 1 h. At lower temperatures, the rate of reaction was slow. After attaining maximum crosslink density on extending the prevulcanization time, a decrease in crosslink density was observed. The modulus of the films varied in line with the V_r values. Tensile strength and elongation at break were better when prevulcanization was conducted at lower temperatures and, at each temperature, with a shorter heating time. Water absorption and leaching were more rapid in prevulcanized film than in postvulcanized film. The rate of stress relaxation slightly increased when the extent of prevulcanization increased.

Table III Effect of Prevulcanization Conditions on Stress Relaxation of Films

Prevulcanization		
Temperature (°C)	Time (h)	Slope of the Lines
60	4.0	0.0535
60	6.0	0.0568
70	2.0	0.0566
70	4.0	0.0625
80	1.0	0.0578
80	2.0	0.0653
90	0.5	0.0609
90	1.0	0.0788

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