

Mechanical Behavior of Some Lightly Crosslinked Rubbers

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Synopsis

The creep and dynamic mechanical properties of rubbers with a wide range of degree of crosslinking have been correlated with the swelling properties of the rubbers. Both butyl and styrene-butadiene rubbers were studied. Mechanical damping steadily decreases as the crosslinking increases. A damping test could replace the usual swelling tests as a measure of the tightness of the network structure. Lightly crosslinked rubbers have a minimum in the damping-temperature curve while highly crosslinked rubbers do not. Very small degrees of crosslinking dramatically decrease the creep rate, however, even for highly crosslinked rubbers, creep does not completely stop. The Nutting equation often gives a very good correlation between damping and creep rate.

Introduction

Although the mechanical properties of vulcanized rubbers and uncrosslinked polymers have been intensively studied, very little work has been reported on the mechanical behavior of very slightly crosslinked rubbers. Vulcanized rubbers have a tight network structure, so that even in a good solvent the swelling ratio is about five or less, and the amount of soluble polymer that can be extracted is very small. In this work much less perfect network structures were studied so that a large part of the rubbers remained soluble, and the swelling ratio might be as great as a hundred.

Creep and dynamic mechanical tests were made on the rubbers, and the results were correlated with the degree of crosslinking or swelling behavior.

Materials and Techniques

The base rubbers were a styrene-butadiene rubber (SBR) and three butyl rubbers. The SBR rubber contained about 25% styrene and had a molecular weight of 280,000 as measured by its intrinsic viscosity in benzene at 25°C. The butyl rubbers had molecular weights of about 315,000, 380,000, and 480,000 as measured by their intrinsic viscosities in cyclohexane. The values used in the equation^{1,2} $[\eta] = KM^a$ are given in Table I.

The 24 SBR formulations contained 1-3% sulfur and were cured for

TABLE I

Rubber	K	a
SBR	5.25×10^{-4}	0.67
Butyl	2.65×10^{-4}	0.69

10–60 min. at temperatures of 140–160°C. The butyl rubbers contained 1–3% sulfur, 2 phr zinc oxide, and 2 phr *p*-quinonedioxime; the specimens were cured for 10–60 min. at temperatures of 140–160°C. Mixing of the ingredients was done on a millroll.

Swelling data at 24°C. were obtained with the use of benzene as the solvent for the SBR materials and cyclohexane as the solvent for the butyl rubbers. The swelling ratio q is defined by

$$q = \frac{\text{Volume of swollen gel}}{\text{Volume of unswollen gel}}$$

The soluble part of the rubber or sol fraction is defined as

$$\text{Sol fraction} = \frac{\text{Weight of soluble polymer extracted}}{\text{Initial weight of rubber}}$$

The swelling experiments required about a week to carry out, and the solvent was changed several times until no more soluble polymer was extracted.

Creep tests were made on specimens $\frac{3}{8} \times 0.10 \times 2$ in. between clamps. The tests were made at 24°C. with a recording apparatus which gave a 10 in. deflection on the recorder chart for 0.4 in. stretch of the specimen. The loads on the specimens varied from 3 to 20 psi.

Dynamic shear modulus and mechanical damping (logarithmic decrement) were measured with a recording torsion pendulum.³ The frequency at 24°C. was roughly 0.5 cycle/sec.

Results and Discussion

The swelling results are summarized in Figure 1, where the sol fraction is plotted against the swelling ratio. For both types of rubbers there is a good correlation between these two quantities. As expected, the soluble fraction increases with the swelling ratio.

Typical dynamic mechanical results are illustrated in Figures 2–4. In each case a highly crosslinked specimen is compared with a lightly crosslinked one in these figures. Several dozen specimens were tested, and the results given here illustrate the general phenomena always found. Lightly crosslinked rubbers always have a minimum in the damping curve while the highly crosslinked rubbers give a damping curve which continuously decreases with temperature. At higher temperatures (say, at 50°C.) the lightly crosslinked rubbers have much greater damping than the more highly crosslinked ones. Also, at the higher temperatures the greater the degree of crosslinking the higher is the shear modulus.

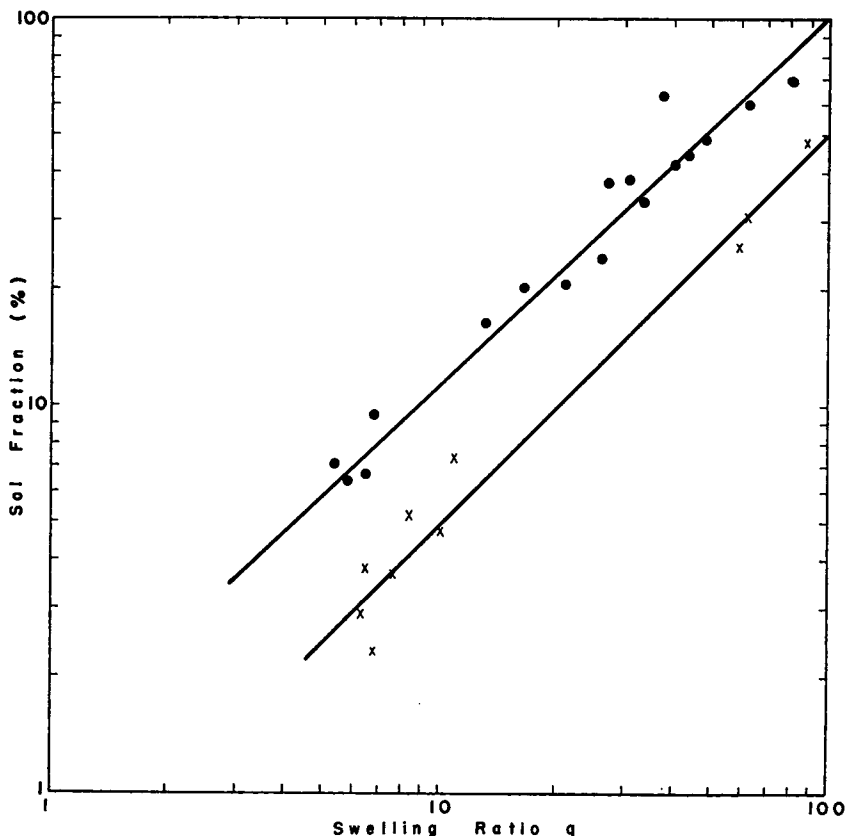


Fig. 1. Relation of sol fraction to swelling ratio at 24°C.: (●) SBR measured in benzene; (×) butyl rubbers measured in cyclohexane.

In the range of crosslinking studied here, the glass transition temperature (as measured by the maximum in the damping peak) is raised only slightly by the crosslinking process. At higher degrees of crosslinking it is well known that the glass temperature increases with degree of crosslinking.⁴⁻⁶

Typical creep results are given in Figures 5 and 6. The results show that very small amounts of crosslinking have a dramatic effect on reducing the rate of creep. Increasing the molecular weight of a linear polymer does not have near the effect of a little crosslinking in reducing creep. However, even highly crosslinked rubbers still show some creep even at long times.

A number of interesting correlations between the swelling properties and the mechanical properties has been found. Figure 7 shows that the logarithm of the swelling ratio is approximately a linear function of the damping at 50°C. On the basis of Figure 1, a similar relationship exists between damping and the sol fraction. The relation between damping and swelling ratio is so good that damping rather than laborious swelling

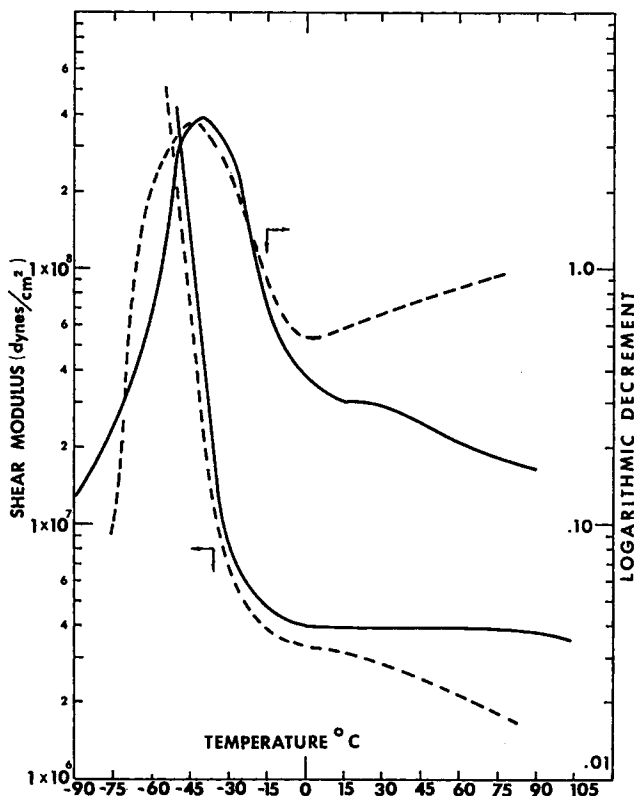


Fig. 2. Dynamic mechanical properties of butyl rubbers: (—) highly crosslinked rubber, $q = 6.29$; (---) lightly crosslinked rubber, $q = 66.2$.

tests could be used to characterize the degree of crosslinking. Once a calibration curve has been established between damping and swelling ratio (or density of crosslinks) the tightness of the network structure can be accurately determined in a few minutes. Although the shear modulus increases with crosslinking, the modulus is not as sensitive as the damping in detecting changes in network structure.

Although the creep is related to the swelling index, a better correlation was found between the creep rate and q . This is illustrated in Figure 8, where the difference in creep compliance at 100 min. and 10 min. is plotted against the swelling ratio. In this plot it might be expected that the slopes of the lines would be $5/3$.⁷ This is true for the SBR, but for the butyl rubbers the slope is only slightly greater than one.

The Nutting equation^{8,9} holds for most of the creep curves, that is, nearly straight lines are found when log creep is plotted against log time. A simple equation has been proposed to relate creep and damping in such cases.⁹ This equation is

$$\Delta = \pi^2(d \log \epsilon)/2(d \log t) = 4.9n$$

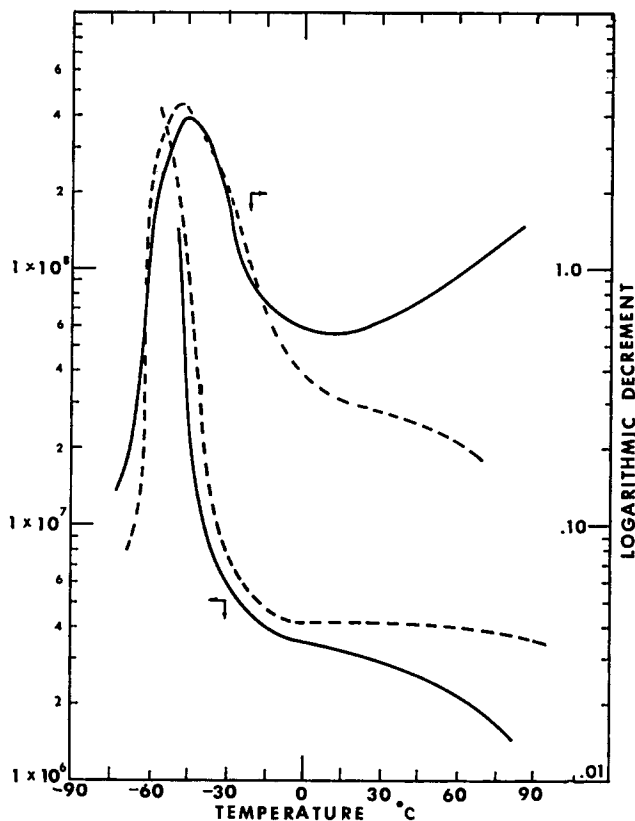


Fig. 3. Dynamic mechanical properties of butyl rubbers: (—) very lightly cross-linked rubber, $q \approx \infty$, sol fraction ≈ 1 ; (- -) highly crosslinked rubber, $q = 5.98$.

where Δ is the logarithmic decrement (damping), n is the slope of the creep curve on a log-log plot, ϵ is elongation, and t is time. In many cases the equation holds remarkably well. Table II gives a few examples chosen at random.

TABLE II
Calculation of Damping From Creep Measurements at 24°C.

Specimen no.	Damping Δ	
	Calculated from Nutting's equation	From torsion pendulum
SBR 1	0.91	0.88
SBR 3	0.24	0.43
SBR 8	1.11	1.25
SBR 13	0.19	0.36
Butyl 4	0.95	0.61
Butyl 5	0.41	0.43
Butyl 7	0.95	0.58
Butyl 10	0.29	0.35

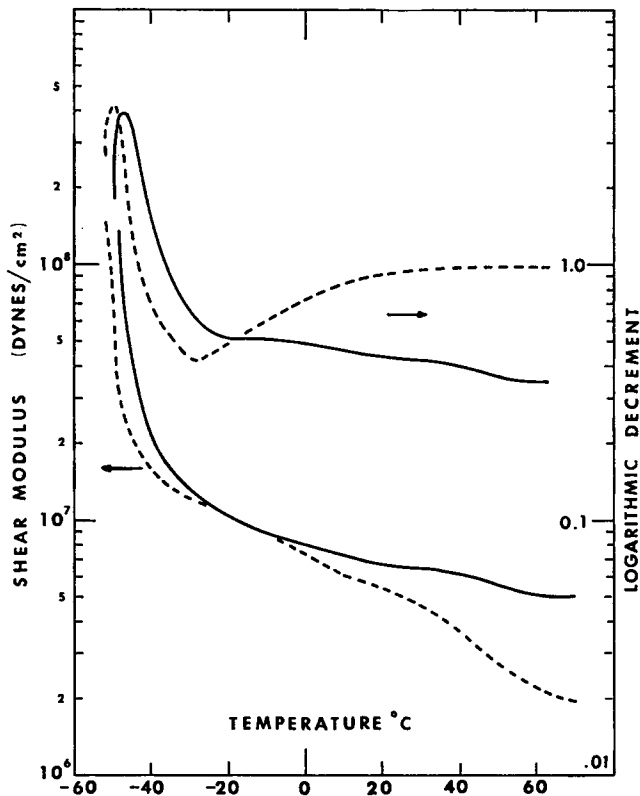


Fig. 4. Dynamic mechanical properties of SBR rubbers; (—) highly crosslinked rubber, $q = 6.2$; (- -) lightly crosslinked rubber, $q = 42.1$.

The molecular weight of chain segments between crosslinks was estimated from the swelling data.⁷ The values of the interaction parameter χ_1 used in these calculations were 0.398 for benzene-SBR and 0.436 for cyclohexane-butyl rubber.¹⁰ These values of \bar{M}_c (molecular weight

TABLE III
Effect of Extracting Sol Fraction on Creep of a SBR Rubber^a

Time, min.	Elongation, %	
	Unextracted rubber	Extracted rubber
1	6.85	5.98
5	7.77	6.53
10	8.25	6.78
20	8.72	7.00
35	9.24	7.24

^a Sol fraction extracted with benzene; sol fraction = 39%, $q = 28$; stress = 10 psi.

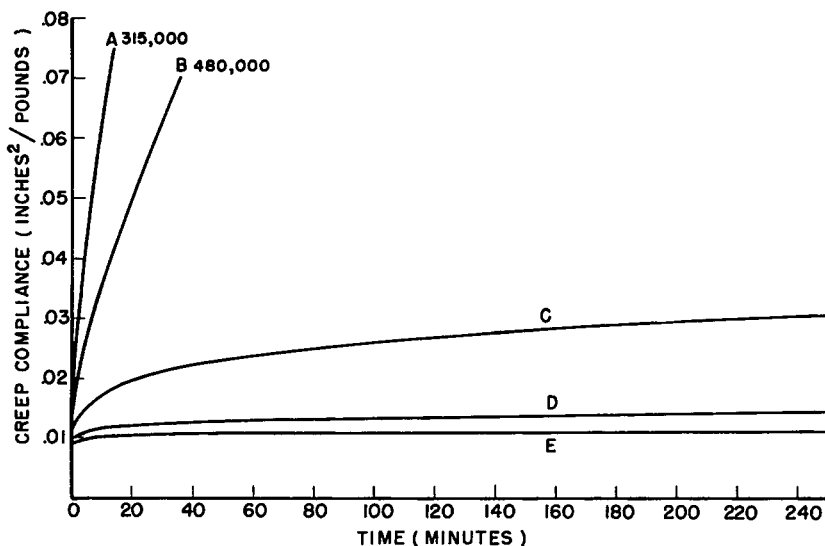


Fig. 5. Creep of butyl rubbers at 24°C.: (A) uncrosslinked rubber of molecular weight 315,000; (B) uncrosslinked rubber of molecular weight 480,000; (C) lightly crosslinked rubber, $q = 88.5$, sol fraction = 48.5%; (D) moderately crosslinked rubber, $q = 10.1$, sol fraction = 4.8%; (E) highly crosslinked rubber, $q = 6.8$, sol fraction = 2.4%.

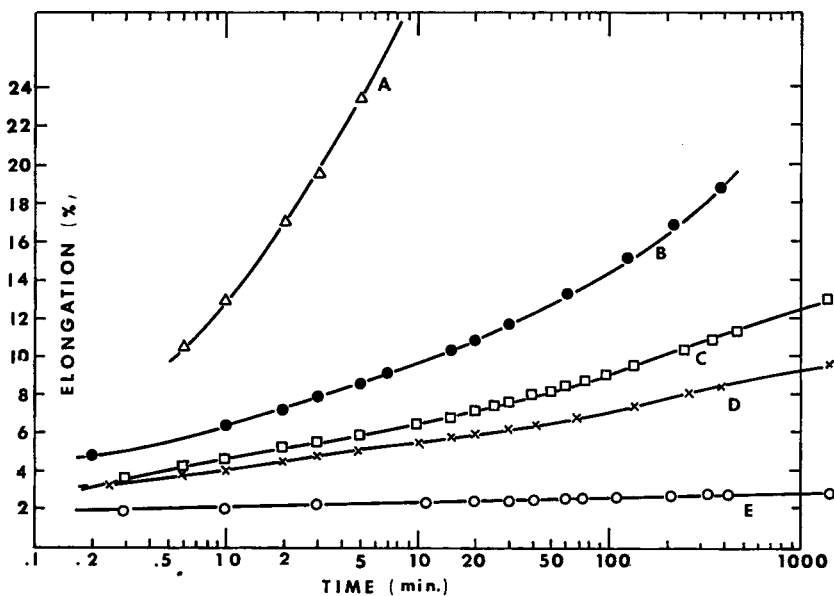


Fig. 6. Creep of SBR rubbers at 24°C.: (A) uncrosslinked rubber; (B) lightly cross-linked rubber, $q = 33.5$, sol fraction = 34.0%; (C) moderately crosslinked rubber, $q = 25.8$, sol fraction = 24.1%; (D) moderately crosslinked rubber, $q = 20.9$, sol fraction = 20.4%; (E) highly crosslinked rubber, $q = 6.8$, sol fraction = 9.5%.

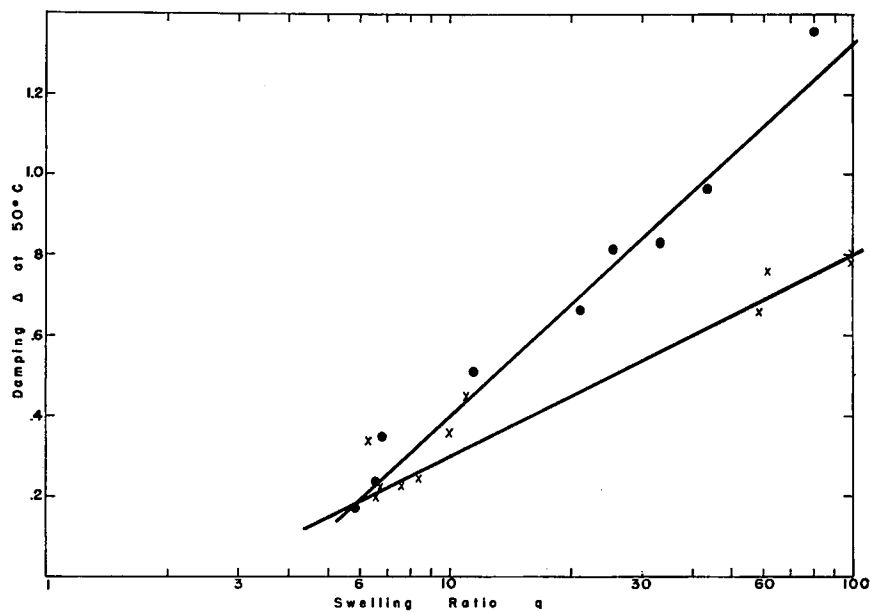


Fig. 7. Relation of mechanical damping (log decrement) at 50°C. to swelling ratio: (●) SBR, benzene as swelling solvent; (×) butyl rubber, cyclohexane as swelling solvent.

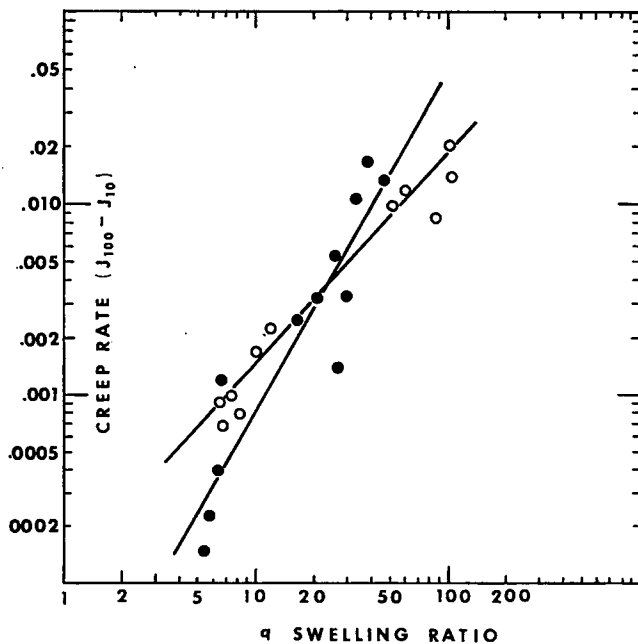


Fig. 8. Relation of creep rate (compliance at 100 min. minus compliance at 10 min.) to swelling ratio q at 24°C.: (●) SBR, benzene as swelling agent; (O) butyl rubber, cyclohexane as swelling agent.

between crosslinks) were then substituted into the equation for Young's modulus E derived from the kinetic theory of rubber elasticity:⁷

$$E = (3 \rho RT / \bar{M}_c) (1 - 2\bar{M}_c/M)$$

where M is the molecular weight of the rubber before crosslinking, and ρ is the density of the rubber. The calculated values of the modulus were less than the experimental values generally by at least a factor of two or more. It is believed that this difference between theory and experiment is largely due to the effect of chain entanglements. Chain entanglements, in addition to the chemical crosslinks, are effective in increasing the experimental modulus, but in the swelling experiments the entanglements can relax out and thus make no contribution.

Several attempts were made to assess the role of the soluble fraction of the polymer in creep experiments. The specimens were used as prepared. After extracting out the soluble polymer and drying the specimens, the creep test was repeated. The load on the specimens was adjusted so that the same stress was applied in the two cases. The very lightly crosslinked rubbers were too fragile when swollen to give good specimens after the extraction process, so only moderately or highly crosslinked rubbers could be studied. The extracted polymers always gave less creep than the unextracted ones, but the effect was not large. Typical results are given in Table III. It appears that even in lightly crosslinked rubbers, the creep behavior is determined primarily by the network structure rather than by the soluble polymer not incorporated in the crosslinked network.

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Résumé

La rétraction et les propriétés mécaniques dynamiques de caoutchoucs dont le degré de réticulation varie dans de larges proportions, ont été comparées aux propriétés de gonflement des caoutchoucs. On a étudié simultanément les caoutchoucs butyle et styrène-butadiène. L'amortissement mécanique diminue progressivement avec une augmentation du degré de réticulation. Un test d'amortissement peut remplacer les tests usuels de gonflement comme mesure de la rigidité de la structure du réseau. Les caoutchoucs faiblement réticulés présentent un minimum dans la courbe amortissement-température tandis que les caoutchoucs hautement réticulés ne présentent pas de minimum. Des degrés de réticulation très faibles diminuent très considérablement la vitesse

de contraction, tandis que, même pour des caoutchoucs hautement réticulés, le fluage ne s'arrête pas complètement. On peut établir une très bonne corrélation entre l'amortissement et la vitesse de fluage.

Zusammenfassung

Das Kriechverhalten und die dynamisch-mechanischen Eigenschaften von Kautschukproben mit einem weiten Bereich an Vernetzungsgrad wurden mit ihren Quellungseigenschaften in Beziehung gebracht. Sowohl Butylals auch Styrol-Butadien-kautschuk wurden untersucht. Die mechanische Dämpfung nimmt mit steigender Vernetzung stetig ab. Ein Dämpfungstest könnte den üblichen Quellungstest als Mass für die Dichte der Netzwerkstruktur ersetzen. Schwach vernetzte Kautschukproben besitzen ein Minimum in der Temperaturabhängigkeitskurve der Dämpfung, während das bei hoch vernetzten Proben nicht der Fall ist. Sehr kleine Vernetzungsgrade setzen die Kriechgeschwindigkeit stark herab; es kommt das Kriechen aber selbst bei hoch vernetzten Proben nicht völlig zum Stillstand. Die Gleichung von Nutting liefert oft eine sehr gute Korrelation zwischen Dämpfung und Kriechgeschwindigkeit.

Received November 7, 1962