

Dynamics of Loosely Crosslinked Polymer Networks*

F. BUECHE

Department of Physics, University of Wyoming, Laramie, Wyoming

INTRODUCTION

An ideal vulcanized rubber (or crosslinked plastic in the rubbery state) is expected to reach an equilibrium elongation soon after a constant load has been applied to it. This behavior is closely approached in the case of natural rubber vulcanizates provided the rubber has not been milled extensively. Very seldom does one observe that a synthetic rubber approaches this ideal situation. This fact is the chief reason for the inferior hysteresis properties of synthetic rubbers.¹

It is the purpose of this paper to show what molecular factors influence the shape of the tensile creep curve of crosslinked polymers. Particular attention will be directed toward the behavior at long times. Our approach will be to examine the rubbery state creep curves for polyethyl methacrylate crosslinked with various amounts of ethylene dimethacrylate. A theoretical treatment of this problem will then be presented which gives insight into the reasons for the observed behavior.

EXPERIMENTAL

The polymers were prepared by polymerizing the required proportions of monomers in sealed tubes at 70°C. The ethyl methacrylate had been purified of inhibitor but the ethylene dimethacrylate was used in the form received from the manufacturer (Monomer-Polymer Laboratories, dental grade). After machining to a convenient size and shape, the resultant plastic was heat treated for several hours at up to 130° C. so as to remove residual monomer.

The tensile creep measurements were carried out in the usual way.¹ The data were reduced to a composite curve for the polymers at 70°C. by using the customary temperature-time superposi-

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tion method. These curves are shown in Figure 1. The composition of each of the polymers is given in Table I.

TABLE I
Composition of Polymers Used in This Study

Polymer	A	B	C	D	E	F	G
Volume % ethylene dimeth- acrylate	0.000	0.0064	0.033	0.067	0.100	0.133	0.200

At first sight one might think that the relative heights of the curves are not in proper relation. These have all been carefully checked, however, and the height variations are real. They arise because of two competing factors.

First, it will be noticed that the noncrosslinked polymer is of very high molecular weight, and the plateau resulting from entanglements is clearly visible. However, as crosslinker is added, the equivalent "primary" molecular weight appears to decrease. This means that the more highly crosslinked systems appear as though they had been made from the crosslinking of much lower molecular weight primary molecules. For these materials the entanglement plateau will be so short as to be nonexistent. Second, the larger the number of crosslinks, the lower the curves will tend to be at long times.

The combined effect is for the height of the curves at intermediate times to vary in the following way. The curves rise in height with increasing crosslinker because the "primary" molecular weight (and therefore the entanglement effect) is being reduced. Eventually, though, the crosslinks become dense enough so that the compliance decrease from that effect is overpowering.

It will be noticed that these curves show all the typical variants found in the case of the usual vulcanized rubbers. Considerable insight into

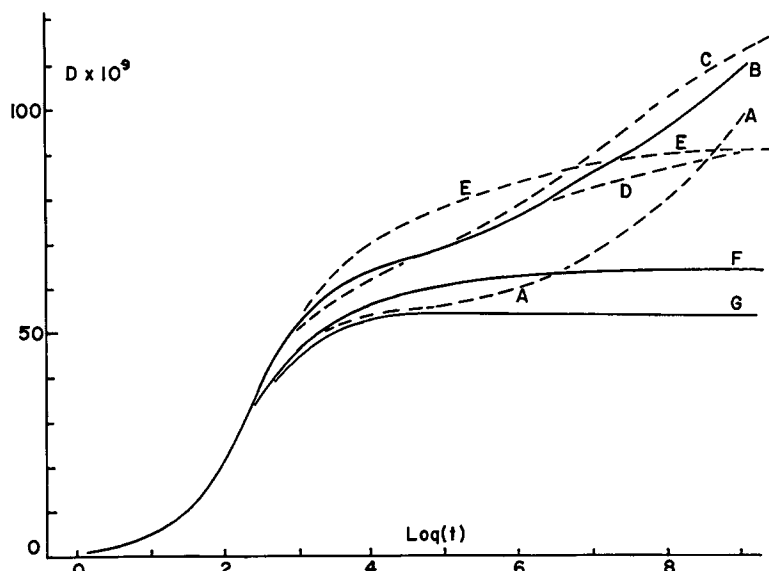


Fig. 1. Tensile creep compliance for the polymers given in Table I. D is expressed in cm^2/dyne and t is in minutes.

this behavior can be obtained from an examination of these curves. We shall only mention two features which are clearly visible, leaving the more abstruse consequences until the theory for the curves has been developed in a later section.

First, the two most highly crosslinked samples can be used to compute the molecular weight between crosslinks, M_c , from the familiar relation

$$D(\infty) = M_c/3\rho RT \quad (1)$$

where $D(\infty)$ is the equilibrium compliance. One finds M_c values of 6500 and 5200. If one computes M_c directly from the number of chemical crosslink monomers (making no corrections for cyclization and chain ends), one finds values of 7500 and 5100. A possible reason for the discrepancy found in the less highly crosslinked case will be pointed out after the theory has been developed. The observed agreement is perhaps only the result of the fortuitous cancellation of the effects of entanglements and chain ends.

Second, it should be noticed that M_c must be of the order of 7000 before the curves level off reasonably rapidly. This is probably much smaller than the molecular weight of the "primary" molecules. In addition, the slopes of the long time portions of the curves become quite large if the value of M_c is doubled.

THEORY

Qualitatively, one can easily explain the slopes of the observed creep curves. For example, if

the number of crosslinks is so low that each molecule is linked directly to only two other molecules, as shown in Figure 2(a), then the whole sample will consist of one huge linear molecule. Upon stretching, such a molecule will show a nearly infinite retardation or response time, and consequently the creep curve will trend rapidly upward until exceedingly long times.

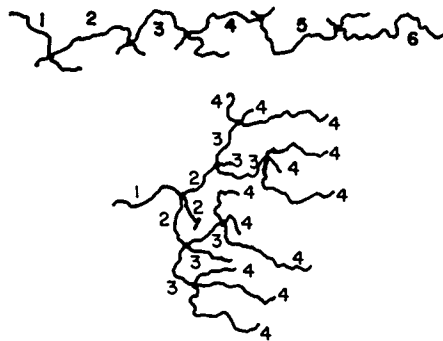


Fig. 2. Schematic diagrams for sections of polymer networks.

On the other hand, a more highly crosslinked system, such as is shown in Figure 2(b), will behave somewhat more sluggishly. If one pulls toward the left on chain 1, then chains 2 will also move toward the left and so will chains 3 and chains 4. However, each succeeding set of chains will respond less rapidly because of the larger friction associated with each group. (We are, of course, assuming these chains to be immersed in a viscous matrix.) Consequently, the response of the more

distant chains will be so far delayed that the observer will find that, after the response of the first chain, the further creep is much less rapid than it used to be. Indeed, if the crosslink density is high enough, the creep curve may actually appear to become flat.

These ideas may be developed quantitatively, and this is done in the Appendix. It turns out that the important quantities involved are the response time, τ , of a single network chain, such as chain 1 in Figure 2, and a parameter β defined as follows: β is the average number of the #2 chains in Figure 2 which contain at least one other crosslink. For example, in Figure 2(a) one has $\beta = 1.00$ while in Figure 2(b) $\beta = 2.00$.

It is found in the Appendix that the ratio of "the slope of the logarithmic creep curve" to "the compliance of the network at $t \rightarrow \infty$ computed from the simple theory of elasticity assuming affine deformation of the crosslinks" is given by the following relation for $t \gg \tau$:

$$[1/D_0(\infty)] [dD/d(\ln t)] \cong (\pi\tau/16t)^{1/2}/\ln\beta \quad (2)$$

The value of β depends, of course, on the ratio M_c/M_n , where M_c is the average molecular weight of a network chain and M_n is the number-average molecular weight of the primary molecules. The exact form of β varies from one system to another.

An approximate form for β can be found in the following way. In Figure 2(b), one of the #2 chains is a continuation of the #1 chain. If it is to contain a second crosslink, then a length of chain $2M_c/M_0$ monomer units long must be free of chain ends. We are assuming that each network chain is exactly M_c/M_0 units long. The probability that no chain ends exist in this length is

$$(1 - 2M_0/M_n)^{2M_c/M_0} \cong \exp\{-4M_c/M_n\}$$

Similarly, the probabilities that the 2nd and 3rd chains in the #2 group contain crosslinks are $\exp\{-2M_c/M_n\}$ and $\exp\{-4M_c/M_n\}$. Therefore β will be

$$\beta = \exp\{-2M_c/M_n\} + 2 \exp\{-4M_c/M_n\} \quad (3)$$

Values of β for various values of M_c/M_n are given in Table II.

TABLE II
Dependence of β on M_c/M_n

M_c/M_n	0	0.10	0.20	0.25	0.30	0.33	0.347
β	3.00	2.26	1.57	1.34	1.15	1.05	1.00
$1/\ln\beta$	0.91	1.23	2.2	3.4	7.2	20	∞

At any given value of time after the start of a creep experiment, the slope of the creep curve will vary as $1/\ln\beta$. This value is also shown in Table II. Clearly, for $M_c/M_n = 0.347$, the creep curve will rise exceedingly rapidly. (We are here neglecting the effect of entanglements. This may be done if M_w is not too large or if one is concerned only with very long times.) As M_c decreases, the slope of the curve decreases very rapidly until $M_c/M_n = 0.20$ after which the curves will have an exceedingly small slope provided $\tau/t \gg 1$.

These facts are amply substantiated by the experimental curves of Figure 1. In fact, the discrepancy between the values for M_c found in the case of the next to flattest curve there may merely be a reflection of the small but finite slope still present for that curve.

APPLICATION TO RUBBER

In usual rubber practice one does not vulcanize to obtain an M_c much below about 6000. Since in order for a mechanically stable network to be formed $M_c/M_n < 0.347$ as shown above, this means M_n must be larger than 17,300. If a near zero slope to the creep curve is required (and it is if good hysteresis properties are desired), then $M_c/M_n < 0.20$. That is, M_n should be at least 30,000.

In the case of natural rubber, this limit on M_n is easily satisfied since M_n of the unmilled rubber is above 30,000. However, for GR-S one is at a far greater disadvantage. The unmilled rubber usually has an M_n near or below 30,000.² (Its exact value is not known with any certainty. Values for M_n higher than this quoted in the literature are almost certainly the result of failure to measure the very low molecular weight species present.) It is this fact which gives rise to the observed high slope found for the creep curves of these materials and results in poor hysteresis properties.

APPENDIX

We shall attempt here to work out the compliance of a system such as that shown in Figure 2(b). Consider a tetrahedral branch system at each crosslink. Then chain 1 with friction constant λ per unit length and elasticity modulus e per unit length will be joined to a secondary set of chains as shown. If we replaced these three chains by an equivalent one it would have a modulus of elasticity e also but its friction coefficient would be larger than λ . Take it to be $\beta\lambda$ where β is defined in the

text. (This action neglects the usually short chains which do not further crosslink.) Similarly, the third set of chains will have constants e and $\beta^2\lambda$ and the n th set, e and $\beta^{n-1}\lambda$.

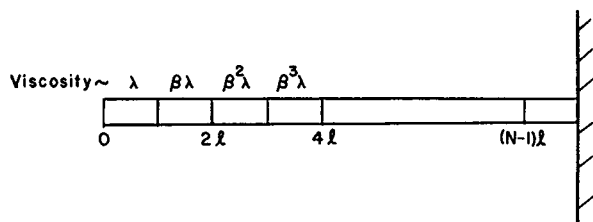


Fig. 3. A mechanical model used for calculations in the text.

The response of such a system is analogous to that of rod immersed in a liquid of varying viscosity as shown in Figure 3. This system is solvable using the method of Gross and Fuoss,³ extending it to multiple regions. Their method consists of solving the following differential equation for a rod with modulus of elasticity e and friction coefficient λ when subjected to a tensile stress in the x direction $\sigma = \sigma_0 \exp\{zt\}$:

$$(\partial^2 \sigma / \partial x^2) = (\lambda/e)(\partial \sigma / \partial t) \quad (4)$$

In our particular case we must find solutions to eq. (4) which make σ and the displacement continuous along the rod. It turns out that the compliance function is given by the following expression (using the notation of Gross and Fuoss):

$$J(z) = \frac{1}{e\gamma_1 z^{1/2}} \sum_{n=1}^N \frac{(\gamma_1/\gamma_n) \tanh(l\gamma_n z^{1/2})}{\prod_{p=1}^{n-1} \cosh(l\gamma_p z^{1/2})} \quad (5)$$

with $\gamma_n^2 = (\lambda/e)\beta^n$ and N being the number of sections in the bar.

Following the procedure of Gross and Fuoss further we can find the retardation spectrum from the poles of the compliance function. For simplicity we will ignore all the poles given by $iz > \pi^2(2l\gamma_n)^2$. The poles we have neglected give rise to the higher overtone vibrations of the individual network chains and should not be important for creep experiments at long times.

The derivative of the creep displacement of the end of the rod pictured in Figure 3 may then be written as

$$\frac{d\psi(t)}{dt} = \frac{2Q}{el} \sum_{n=1}^{\infty} \frac{\exp\{-\pi^2 t/4l^2 \gamma_n^2\}}{\gamma_n^2 \prod_{p=2}^n \cos(\pi/2\beta^{(p-1)(p-1)/2})} \quad (6)$$

where we have let $N \rightarrow \infty$.

Q is a complex function of β of the order of unity. The exact value of Q is seriously dependent upon the way in which the rod of Figure 3 is sectioned. Properly one should average it over all the various sample network chain lengths. For our purposes we shall be satisfied to consider it a constant.

Since we are interested in t large, the important terms will occur for n large. With that in mind one finds

$$\psi(t) \sim \sum_{n=0}^{\infty} [1 - \exp\{-t/\tau\beta^{2n}\}] \quad (7)$$

where

$$\tau = 4l^2\lambda/\pi^2 e$$

Suppose β was a very large number. This would be equivalent to placing a solid wall at the end of the first section of the bar. Or, this would be equivalent to considering chain 1 of Figure 2 to be fastened to a solid object. Since only the term with $n = 0$ in the above expression for $\psi(t)$ is of importance under these conditions, this term must represent the kinetic theory response of a single chain.

Actually we are interested in the response of the whole sample, and not in this particular system. The first term of the above sum is, as pointed out, the primary response of the individual chain. The second term is the secondary response of the β attached chains and so on. If we tried to obtain the sample response by merely multiplying by the number of chains we would count the second term too many times and it would be β times too large. In fact the n th term would be β^{n-1} times too large. The sample response will therefore be proportional to

$$D(t) \sim \sum_{n=0}^{\infty} \beta^{-n} [1 - \exp\{-t/\tau\beta^{2n}\}] \quad (8)$$

Calling the first term $D_0(t)$, it is now a simple matter to compute $[1/D_0(\infty)][dD/d(\ln t)]$ provided one assumes $t/\tau \gg 1$. When this is done, one finds the expression given as eq. (2) in the text.

References

1. See, for example, F. Bueche, *J. Polymer Sci.*, **25**, 305 (1957).
2. F. Bueche and S. W. Harding, Unpublished work.
3. B. Gross and R. M. Fuoss, *J. Polymer Sci.*, **19**, 39 (1956).

Synopsis

An ideal crosslinked rubber will reach an equilibrium elongation soon after a constant tensile stress has been ap-

plied to it. Actual materials never reach an equilibrium strain in many cases. This fact is clarified by studying the creep curves for molten polyethyl methacrylate crosslinked with varying amounts of ethylene dimethacrylate. A quantitative theory for the observed effects is presented. It shows that the slope of the long time portion of the creep curve is dependent primarily on a parameter which characterizes the number of effective chains emanating from a network branch point. Reasonable agreement between theory and experiment is found.

Résumé

Un caoutchouc ponté idéal atteindra une élongation d'équilibre aussitôt après qu'une tension constante lui aura été appliquée. Les matériaux actuels n'atteignent pas un équilibre de tension dans la plupart des cas. Ce fait est expliqué en étudiant les courbes de contraction pour des polyméthacrylates de méthyle fondus ramifiés avec des quantités variables de diméthacrylate d'éthylène. Une théorie quantitative des effets observés est avancée. Elle montre que la pente de la partie lente de la courbe de contraction dépend en premier lieu d'un paramètre caractérisant

le nombre de chaînes effectives partant d'un point du réseau. On trouve un accord satisfaisant entre la théorie et l'expérience.

Zusammenfassung

Ein idealer, vernetzter Kautschuk wird bald nach Anlegung einer konstanten Zugspannung eine Gleichgewichtsdehnung erreichen. Die realen Stoffe erreichen in vielen Fällen niemals eine Gleichgewichtsverformung. Dieses Verhalten wird durch Untersuchung der Kriechkurven für geschmolzenes Polyäthylmethacrylat aufgeklärt, das mit wechselnden Mengen von Äthylendimethacrylat vernetzt ist. Eine quantitative Theorie der beobachteten Effekte wird vorgelegt. Sie zeigt, dass die Neigung des Teiles der Kriechkurve, der für langzeitige Änderungen charakteristisch ist, in erster Linie von einem Parameter abhängt, der für die Zahl der von einem Verzweigungspunkt des Netzwerkes ausgehenden Ketten kennzeichnend ist. Es wurde eine befriedigende Übereinstimmung zwischen Theorie und Experiment festgestellt.

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