NETWORK RECOVERY FROM UNIAXIAL EXTENSION: II. THE ORIGIN OF THE MULLINS EFFECT*

C. M. ROLAND

NAVAL RESEARCH LABORATORY, CHEMISTRY DIVISION, CODE 6120, WASHINGTON, D.C. 20375-5000

INTRODUCTION

The process of return of a deformed polymeric network to a state of ease is usually associated with a reduced level of stresses relative to the magnitudes observed during extension[1]. Three mechanisms are known to give rise to this hysteresis. Deformation can effect irreversible alterations of structure, such as fracture of network chains[2,3] or their detachment from filler particles[4], that cause a permanent increase in network compliance. Large deformation can also bring about extended chain crystallization which, by decreasing the number of elastically effective network strands and diminishing the microscopic strain of the remaining amorphous material, will reduce the stress associated with a given macroscopic strain amplitude[5,6]. Such crystallinity can persist even after removal of the external deformation because of the greater stability of crystallites formed with a paucity of crystal stem reentry sites. A third origin of strain softening arises from retardation in the response of network chains due to their interaction with the surrounding viscous medium.

The stresses observed during retraction have long been considered to be lower in magnitude than can be accounted for from the aforementioned considerations. This phenomenon is referred to as the Mullins effect (although the term is commonly applied to general stress softening in filled rubbers). Nonaffine displacement of the network junctions has been proposed as the origin of the purportedly anomalous behavior[1,7-9], but corroboration of this assertion is lacking. In the absence of quantitative assessment of the known contributions, particularly viscoelasticity, to the hysteresis, the origin and even the existence of Mullins softening remain to be demonstrated. The study described herein was directed toward this end.

BACKGROUND

DISSIPATION OF MECHANICAL ENERGY

The equilibrium response of an elastomeric material represents only a part of the overall mechanical behavior. The stress observed upon deformation typically includes a significant contribution from dissipative processes. These viscous effects can be rigorously quantified only by extraordinary methods. Ex-

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perimental characterization requires exceedingly fast displacement and observation of test specimens due to the rapid initial decay of stress. Despite this rapid initial dissipation, viscous contributions can persist with diminished magnitude for time periods extending many hours beyond imposition of the deformation. The simplest models of viscoelasticity assume a Newtonian (*i.e.*, invariant) viscosity, and therefore exhibit exponential stress relaxation. An infinite sum of exponentials is sometimes employed to fit relaxation data from polymeric materials, in consideration of the availability of a range of motions and corresponding relaxation processes. The long-time relaxation in crosslinked rubber is governed by the release of entanglement constraints on dangling network chains[10,11]. Since reptation of the network strands is suppressed, a principle release mechanism is fluctuations in the contour length. The dangling chain retracts and reemerges from the tube of entanglements and thereby can assume a relaxed configuration. The magnitude of the relaxing stress reflects the fraction of the chain segment remaining in the tube. An empirical stress-relaxation function, in which the stress has an inverse power-law dependence on time, has enjoyed wide success[10,12]. The form of this phenomenological relaxation function can be obtained by summing the diffusion times of the dangling chains on a network. These times are strongly dependent on the chain lengths, whose distribution in the network are a result of random crosslinking of the precursor chains[13].

In general, the magnitude of the dissipative stress depends not only on the nature of the material, but also on the details of the deformation process. The problem of analyzing viscoelastic mechanical behavior is greatly facilitated when the material exhibits linearity, which is strictly defined as the condition whereby stress and strain remain directly proportional to one another, and time invariance of the mechanical response is observed. The stress resulting from an applied strain, ϵ, is then described by the Boltzmann equation

$$\sigma(t) = \int_0^t E(t-u)[d\epsilon(u)/du]du, \tag{1}$$

where $E(t)$ is the stress-relaxation function. All polymeric materials obey this equation at sufficiently small strains. Limits for linearity are reputed to extend over a wider range for crosslinked elastomers than is realized for most materials[14]; however, strict adherence to Equation (1) is not necessarily made apparent from a single experiment[15]. Beyond the maximum strain for which the equation of linear viscoelasticity is valid, application of an integral constitutive equation can be attempted[14,16],

$$\sigma(t) = \int_0^t \{E[t-u, \epsilon(t-u)]\}[d\epsilon(u)/du]du. \tag{2}$$

The utility of this integral is limited by the strain dependence in the kernel. If the relaxation spectrum underlying the function $E(t)$ is independent of strain, the effects of time and of strain are uncoupled. Such time invariance permits the simplification,

$$\sigma(t) = \int_0^t E(t-u)g(\epsilon)[d\epsilon(u)/du]du. \tag{3}$$

The strain in a crosslinked rubber is defined in terms of the stretch ratio λ, as suggested by the statistical theories of rubber elasticity[17],

$$\epsilon \equiv f(\lambda) = \lambda - \lambda^{2}. \tag{4}$$

The presence of a damping function, $g(\epsilon)$, in Equation (3) reflects the fact that the material response does not remain proportional to the imposed deformation. This may be due to nonaffine motion of the polymer chains as the molecular deformation slips with respect to the motion of the continuum. Although the network motion may in fact not be affine even at very low strains, the slippage increases with extensional deformation due to increasing reduction of the steric constraints on the thermal motion of chains along the extension direction. The damping function is thus a decreasing function of the extent of deformation. For elastomeric networks, the form of the damping function consistent with experiments in uniaxial extension is obtained from the Mooney-Rivlin relation[17],

$$g(\epsilon) = 1 + (C_2/C_1)\lambda^{-1}, \tag{5}$$

which by custom is normalized to unity at $\epsilon = 0$. The elastic constant C_1 is a measure of the connectivity of network strands, thus

$$E(t = \infty) = C_1. \tag{6}$$

The magnitude of the C_2 term has often been associated with stress-relaxation behavior, consonant with the belief that this term reflects the contribution of trapped entanglements to the equilibrium modulus[10]. Attainment of equilibrium is inhibited by entanglements of the branched-chain segments in the network. One consequence of failure to allow for the completion of relaxation processes is obtaining an ostensibly larger value of C_2[18], although even under equilibrium conditions, C_2 usually is nonnegligible[17].

TENSILE RETRACTION

The hysteresis engendered in deformed networks by crystallization or irreversible changes in network structure is well known and at least qualitatively understood; however, even in the absence of these effects, the reduction in stress during the tensile retraction of a rubbery network is reputed to exceed any decrease attributable to viscoelasticity[1,7-9]. This anomalous hysteresis is known as the Mullins effect, although the term is commonly employed to refer to the large-strain softening of carbon-black-reinforced elastomers. Actually, while stress softening effects specific to the interaction of a polymer with filler may become significant at large extensions, the hysteresis in filler-reinforced rubbers is found to equal that observed in pure rubbers when comparisons are made at equivalent degrees of microscopic strain[9].

Whenever the relaxation time of a material is comparable to the time scale of the deformation, the stresses during retraction will be less than during extension. This viscoelastic softening is demonstrated for a linear material by employing Equation (1) to calculate the tensile-retraction response of a three parameter Maxwell solid[19]. This consists of two parallel Hookean springs, one of which is in series with a Newtonian dashpot, yielding

$$\sigma(t) = E_1 + E_2 \exp(-t/\tau) \qquad (7)$$

where E_i and τ represent the moduli and relaxation time of the model respectively. Calculated tensile retraction curves are displayed in Figure 1 for three materials, all having equivalent equilibrium moduli but differing in their relaxation times. These data illustrate that strain softening can occur during the deformation of a linear viscoelastic material, with the extent of the hysteresis depending upon the relaxation time.

The Mullins effect refers to anomalous softening; that is, a reversible but nonequilibrium deformation will be accompanied by a level hysteresis exceeding that expected from linear viscoelasticity. Nonaffine network motion is reported to underlie the Mullins effect[1,7 9], but this has never been demonstrated.

EXPERIMENTAL

Elastomers with a variety of network types were employed. The sample designations, test dimensions, and description of their structure and elastic behavior can be found in the preceding paper[17]. The nonequilibrium deformation experiments were conducted at constant crosshead velocity and consisted of uniaxial extension of the test specimens to various maximum strains, followed by immediate retraction at the same rate to zero load. The repeatability of the retraction measurements was scrutinized by repeating experiments on the same test specimen (several days later to allow complete relaxation) and verifying

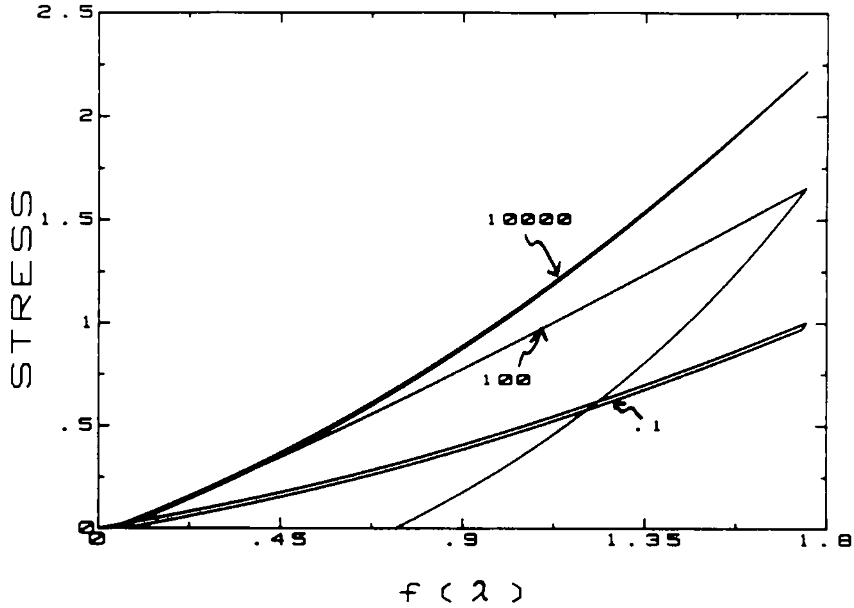

FIG. 1.—The reversing stress-strain curve for three Maxwell solids having equivalent equilibrium moduli. The ratio of the respective relaxation time of each solid divided by the extensional deformation rate is indicated.

that identical results were obtained. Such repeatability demonstrates that over the course of the extension no significant chain rupture had transpired.

Room-temperature stress relaxation was measured using a Imass Corp. Dynastat Mark II instrument. Following imposition of an instantaneous deformation (zero to full displacement in less than 70 ms), the stress was typically monitored over a time period of at least 10 ks. Due to sample geometry constraints and in order to minimize the displacement required to achieve measurable loads, planar extension (which is also known as pure shear in reference to the absence of rotation of the principal strain axes) was the approximate geometry employed for the stress-relaxation measurements. Specimen widths were typically more than 3 times their length. The time dependence of a network's response to a step strain is expected to be equivalent in planar extension, for which the principal stretch ratios are given by

$$\lambda_1 = \lambda_2^{1}, \qquad \lambda_3 = 1 \tag{8}$$

to that in uniaxial extension, for which

$$\lambda_2 = \lambda_3 = \lambda_1^{1/2}. \tag{9}$$

The responses to steady state or other more complicated deformations might however differ for these types of deformation. Ten stress measurements per decade of time were obtained. The numerical relaxation data were used directly, with double logarithmic interpolation employed between data points.

RESULTS AND DISCUSSION

Representative tensile-retraction measurements for the rubbers are displayed in Figures 2–7. The magnitude of the strain softening, as reflected for example by the ratio of strain energy during extension to that during retraction (referred to as the experimental hysteresis ratio in Table I), does not correlate with the magnitude of the elastic constants[17] either C_2 or the ratio C_2/C_1. It was seen in Figure 1 that the magnitude of strain softening depends upon the relaxation characteristics of the material; accordingly, it is necessary to quantify the magnitude expected for viscoelastically derived hysteresis in order to assess its contribution to the total energy dissipation.

DEFORMATION DEPENDENCE OF THE RELAXATION SPECTRUM

Previously reported attempts to separate out the contribution of viscoelasticity during tensile retraction of crosslinked rubbers relied on assuming their adherence to strict linear viscoelastic behavior[8,20]. When strict linearity is maintained, the stress after a time period $t - t_{rev}$ since reversal of the strain can be expressed as

$$\sigma(t) = \dot{\epsilon} t R(t) - 2\dot{\epsilon}(t - t_{rev}) R(t - t_{rev}), \tag{10}$$

where $\dot{\epsilon}$ is the (constant) strain rate and $R(t)$ contains the time dependence of the stress. With this approach, the validity of the assumption of linear viscoelastic behavior is not directly assessed. No comparison is made between the calculated and experimental extension data, because the latter are used directly

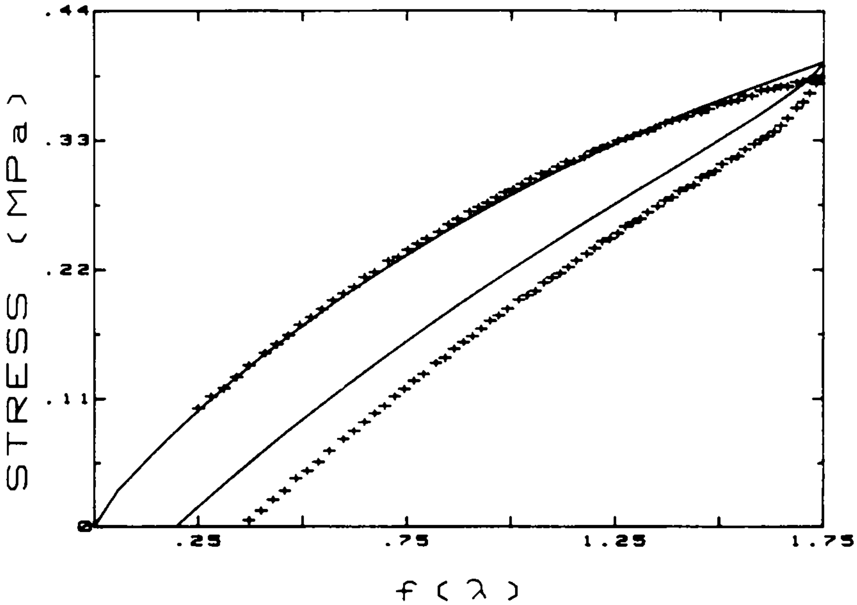

FIG. 2.—The reversing stress-strain data measured for the SBR05 (+++), along with the curve calculated assuming reversible damping. The nominal strain rate in this and Figures 3 through 7 was 0.083 sec^{-1}. The calculation employed the measured $E(t)$, with $E(0)$ serving as the sole fitting parameter. The strain dependence of $E(\infty)$ is obtained from Reference 17.

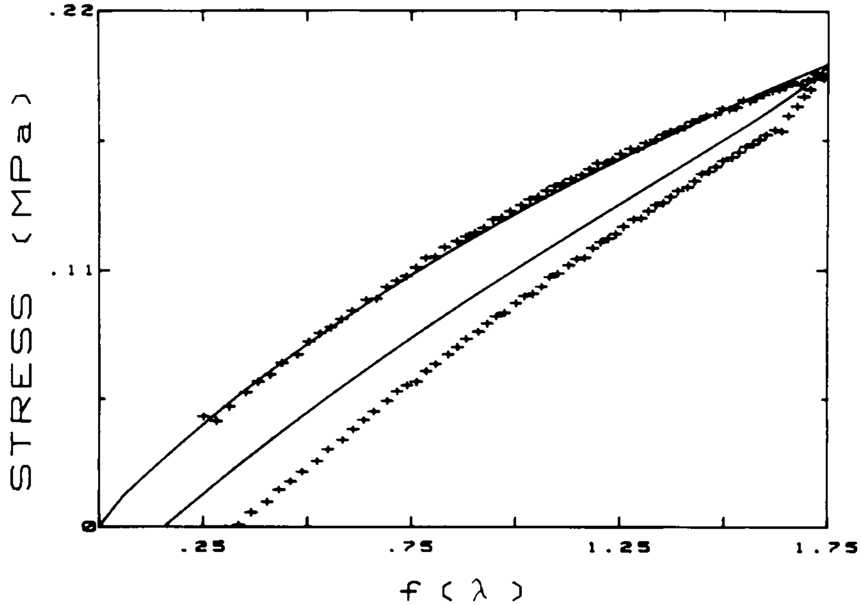

FIG. 3.—The reversing stress-strain data measured for the SBR05-S (+++), along with the curve calculated assuming reversible damping.

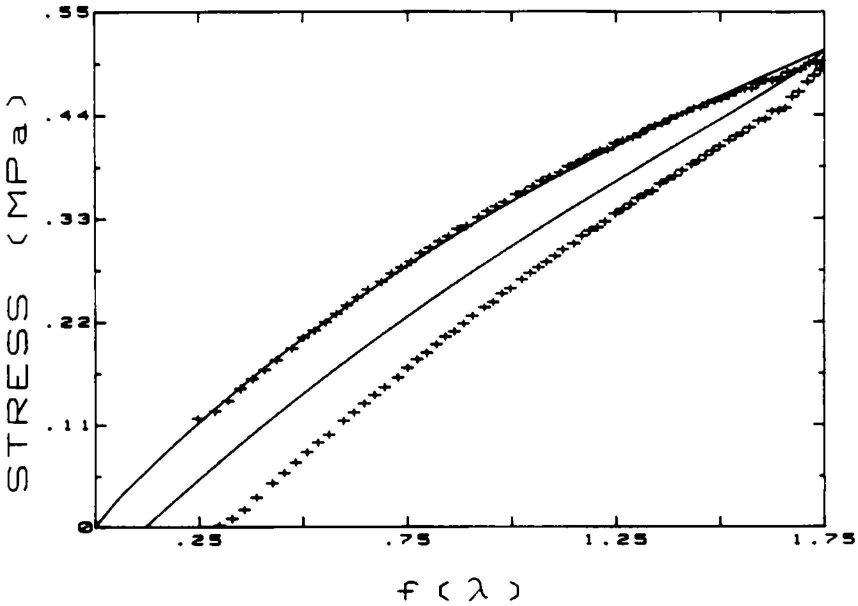

FIG. 4.—The reversing stress-strain data measured for the SBR10 (+ + –), along with the curve calculated assuming reversible damping.

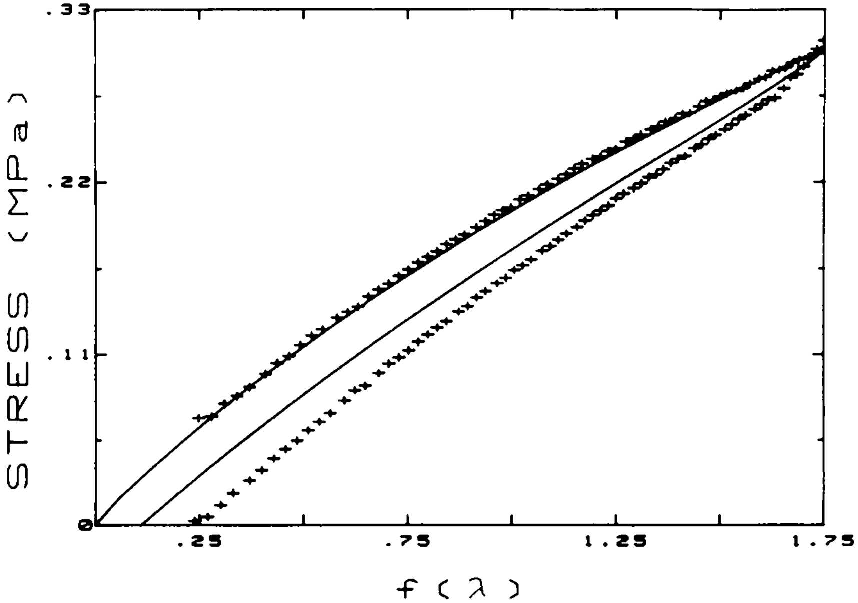

FIG. 5.—The reversing stress-strain data measured for the SBR10-S (+ + +), along with the curve calculated assuming reversible damping.

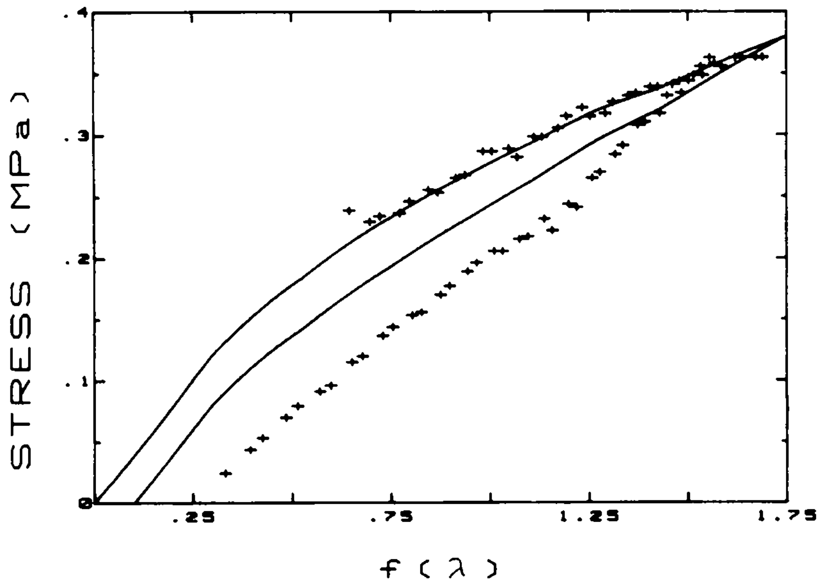

Fig. 6.—The reversing stress-strain data measured for the SBR-E (+++), along with the curve calculated assuming reversible damping.

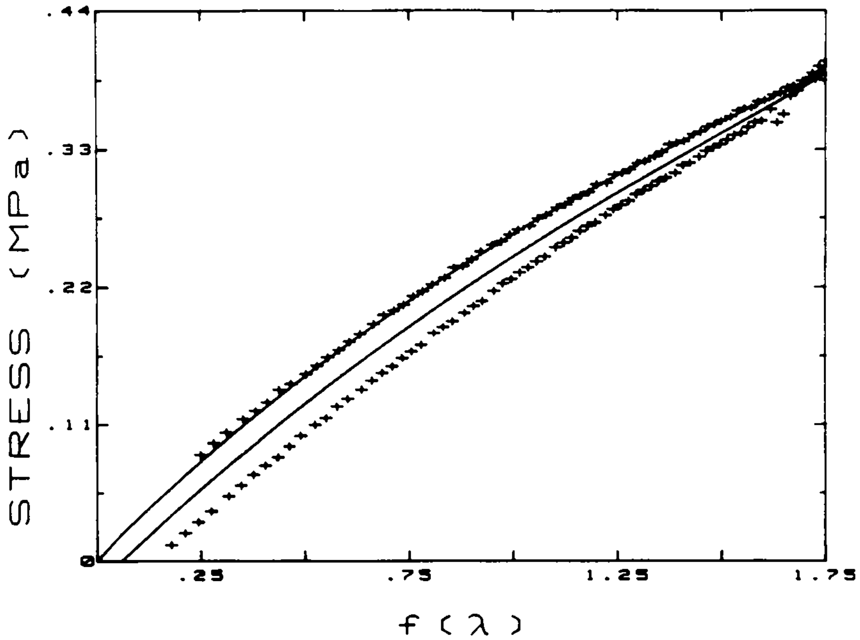

Fig. 7.—The reversing stress-strain data measured for the NR (+++), along with the curve calculated assuming reversible damping.

in the calculation of the retraction stresses. Divergence between theory and experiment in the results for retraction may therefore be an artifact of deviations from strict linearity. Inferences drawn from such a procedure[8,20] are consequently of uncertain value until such linearity is demonstrated.

In fact, the nonlinearity of the elastic response in the present rubbers[17] clearly indicates that the Boltzmann superposition principle is inapplicable for these networks at $\lambda > 1$. If time invariance is maintained, however, recourse can be made to the superposition integral [Equation (3)] in attempting to ascertain the contribution of viscoelastic relaxation to the tensile-retraction data. Time invariance requires that the stress-relaxation function change by only a multiplicative constant when measured at different strains. The stress-relaxation function was characterized for the various materials. The faster relaxing rubbers were those with the looser network structure; that is, the presence of diluent or a lower density of crosslinks effected more rapid dissipation of stress. Of greater interest herein, however, is the dependence of the relaxation on strain.

Displayed in Figures 8 and 9 are representative stress relaxation results for two of the networks subjected to various elongations. Over the duration of these measurements, the stresses at various strains are seen to remain parallel to one another when the data are plotted in logarithmic form. This same proportionality is observed in Figure 10 between the stress relaxation after planar extension and after uniaxial extension. In fact, the only deviation from apparent constancy in the form of $E(t)$ for any of the rubbers was measured for the NR at very high elongations (see Figure 11). This deviation is not a reflection of

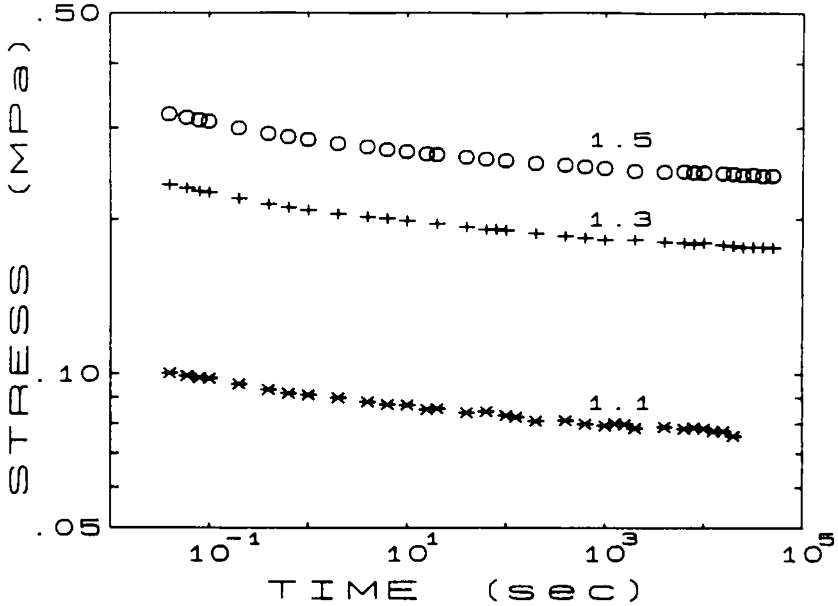

FIG. 8.—The stress relaxation measured for the NR after imposition of planar extensional strain of the indicated λ.

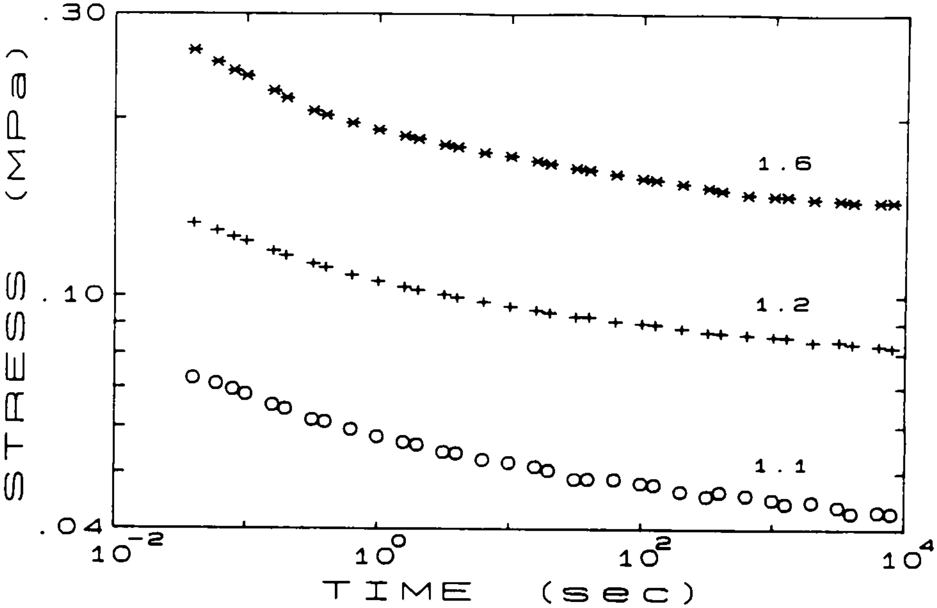

FIG. 9.—The stress relaxation measured for the SBR10-S after imposition of planar extensional strain of the indicated λ.

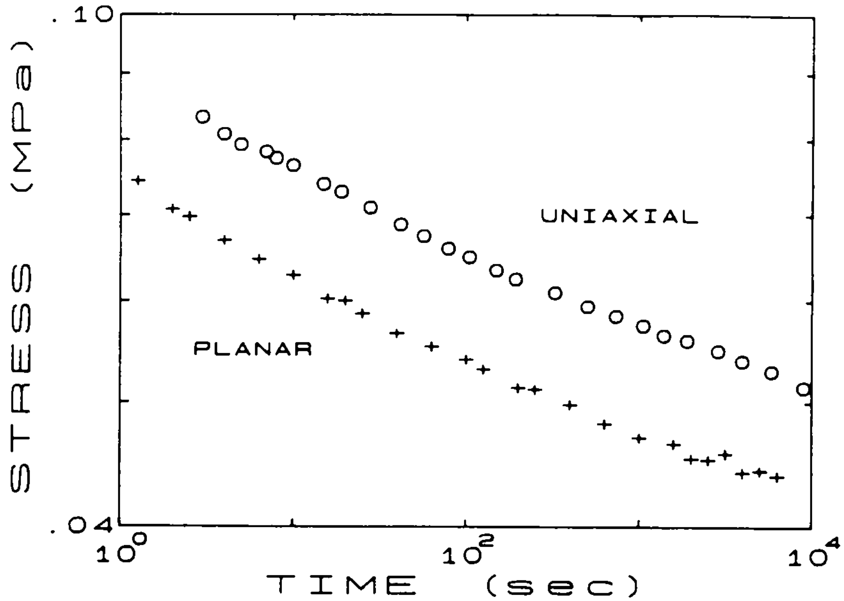

FIG. 10.—The stress relaxation measured for the SBR05-S in uniaxial extension (λ = 1.25) compared to that in planar extension (λ = 1.20).

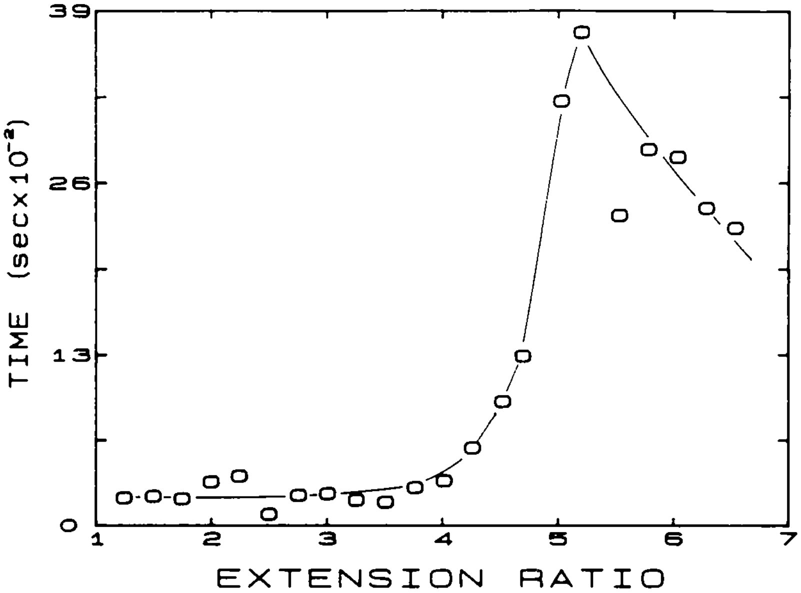

Fig. 11.—The time period required for cessation of stress relaxation in NR as a function of the uniaxial extension ratio. The increases at the higher strains coincide with deviations in the strain dependence of the elastic modulus from the Mooney-Rivlin equation.

alterations in the viscoelastic relaxation spectrum *per se*, but is due to the onset of orientational crystallization. The crystallization transpires over a time scale longer than the longest relaxation time, so that the time required for invariance of the stress to be observed increases for strains sufficient to induce crystallization. At the particular crosslink density of the NR network, orientational crystallization is induced only at extension ratios greater than about 5. From the parallelism observed over the strain range of interest, time invariant mechanical behavior is indicated. The factorization of time and strain effects is justified herein.

MULLINS SOFTENING

Using the time dependence of the stress relaxation taken from the experimentally measured relaxation functions, stress–strain data were calculated for the various networks using Equation (3). The scale factor for the $E(t)$ served as the sole fitting parameter and these are listed in Table I as $E(0)$. For the damping function, $g(\epsilon)$, Equation (5) was employed, with values for the elastic constants taken from Reference 17. These computations are summarized in Table I, with representative results superimposed on the experimental data in Figures 2 through 7. It is seen that while the calculations are, as expected, in good agreement with the experimental data during extension, the retraction stresses diverge significantly from the computed values. This discrepancy between the curves during retraction is a direct measure of the hysteresis in excess of linear

TABLE I

EXTENSION–RETRACTION RESULTS

				Hysteresis ratio, %			
Sample	λ_{max}	$\dot{\epsilon}$, sec^{-1}	E_{in}, MJ/m^3 [a]	$E(0)$	exp.	Eq. (3)	Mullins[b]
SBR05	1.54	8.3×10^{-2}	0.092	1.56	16	11	5
SBR05	1.79	8.3×10^{-2}	0.165	1.56	21	10	11
SBR05	2.04	8.3×10^{-2}	0.183	1.56	23	15	8
SBR05	2.52	8.3×10^{-2}	0.467	1.56	26	14	12
SBR05	2.03	8.3×10^{-4}	0.183	0.81	18	3	15
SBR05-S	2.04	8.3×10^{-2}	0.127	1.12	19	9	10
SBR10	1.54	8.3×10^{-2}	0.113	0.88	9	4	5
SBR10	2.05	8.3×10^{-2}	0.331	0.88	16	5	11
SBR10	2.54	8.3×10^{-2}	0.634	0.88	18	11	7
SBR10	2.03	8.3×10^{-4}	0.275	0.81	11	3	7
SBR10-S	2.04	8.3×10^{-2}	0.195	0.79	11	6	5
SBR-E	2.09	8.3×10^{-2}	0.261	0.53	31	11	20
SBR-E	2.02	8.3×10^{-4}	0.172	0.63	23	7	16
NR	2.04	8.3×10^{-4}	0.251	0.44	15	8	7

[a] The area under the extensional stress–strain curve.

[b] The percent experimental energy dissipation in excess of that calculated for linear relaxation.

viscoelastic losses. The extent of this anomalous strain softening (*i.e*, the Mullins effect) is listed in Table I for the SBR networks. These results are expressed in terms of the hysteresis ratio, defined as the irrecoverable strain energy divided by the energy expanded during extension.

Even though their elastic response encompasses a range of behaviors[17], the various rubbers exhibit roughly similar Mullins softening. As the reversal strain is increased, the fraction of the input mechanical energy that is dissipated, as well as the contribution to the hysteresis ratio from linear viscoelastic relaxation, increases in all cases. On the other hand, the magnitude of the Mullins effect itself (as gauged from the difference of these two quantities) is found to have no significant dependence on the reversal strain, at least over this limited range.

The observation of comparable Mullins softening in all the networks confutes the assertion that the Mullins effect is due to nonaffine junction motion[1,7-9]. The most affinely deforming of these rubbers, the SBR10, displays about the same relative Mullins softening as does the SBR05-S, which, due to its lower crosslink density and the presence of diluent, behaves much more like a phantom network[17]. It is evident that Mullins softening is apparently unrelated to the degree to which the elastic displacement of individual network junctions parallels the macroscopic strain.

The stresses during return from uniaxial extension are overpredicted when only linear relaxation and the nonlinear elastic modulus are considered. It is evident that another relaxation mechanism is operative. It is this relaxation which underlies the Mullins effect.

IRREVERSIBILITY OF THE DAMPING

Similar to the Mullins softening of rubber, in reversing deformations of polymeric liquids, it is found that the stresses after reversal of the strain are less than the values calculated assuming linear viscoelasticity[16]. The motion of a highly entangled polymer chain is inhibited by restrictions imposed by other chains. The group of conformations consistent with these topological constraints defines a so-called primitive path; a primitive chain represents the real chain without its small-scale fluctuations[11]. In an uncrosslinked polymer melt, relaxation after the application of a strain will proceed *via* two processes. The first involves rapid retraction of the primitive chain back to its original contour length. The second relaxation process consists of disengagement (primarily *via* reptation for linear chains) from the deformed tube of constraints. Only this slower process, however, is usually included in the measured linear viscoelastic relaxation spectrum[11,16]. The differential modulus of polymeric melts decreases over the course of a steady-state deformation, reflecting slippage of the chain molecules with respect to the macroscopic continuum. This softening in polymeric fluids has its origin in different physical phenomena than the hysteresis effects described herein for rubber networks; nevertheless, it has been similarly accounted for in the constitutive equation by introduction of a damping function. The mechanism underlying the attenuation of the damping function in polymeric fluids is not reversible; that is, as the strain is returned to zero, the damping function does not increase back to unity[16,21]. Introduction of irreversibility into the damping function reduces the relative magnitude of the calculated stresses during retraction, in qualitative agreement with experiments. The origin of this irreversibility is the dissipation of stress due to relaxation processes not included in the linear relaxation spectrum, in particular the retraction of the primitive chain[16,22]. The chain ends assume a more random conformation upon contraction, and the consequent loss of microscopic deformation reduces the strain energy. These losses occur sufficiently fast that they can be neglected in the constitutive description. However, neglect of these relaxation mechanisms causes overestimation of the stress in calculations for a reversing strain history[16,22]. In recognition of the failure of superposition integrals with separable time and (nonlinear) strain functions to describe reversing strains, it has been proposed that, after a strain reversal, $g(\epsilon)$ assumes the minimum value it had attained during the extension portion of the strain history[21]. This implies that the structure breakdown (*e.g.*, disentanglement of the chain molecules in a polymeric fluid) is not recovered upon strain reversal.

Distinct differences exist in the nature of the phenomena represented by the damping function for networks with that for uncrosslinked polymers. Nevertheless, the Mullins effect in rubber may have an origin similar to that underlying the irreversibility of the damping function for polymeric liquids. In a network, the tethered chains are incapable of reptation. Dangling chain ends primarily equilibrate by fluctuation in their contour length. Prior to this, however, retraction of their primitive path contour lengths will transpire. In addition, upon deformation, the segments of a chain are initially stretched or compressed along their primitive path depending on their particular instantaneous direction. Although these local imbalances are rapidly adjusted, they cause a variation in force along the chain. Due to the rapid nature of this adjustment and of the contraction of the primitive path, these dissipative processes are omitted from linear relaxation behavior as exemplified in Figures 9–11. A consequence of this omission is the failure of Equations (2) and (3) to describe the stresses measured during tensile retraction of rubber. This omission is accordingly seen to be the origin of the Mullins effect.

Tensile retraction curves for the rubbery networks were calculated employing an irreversible damping function. It was assumed that, while the damping function during extension is given by Equation (5), after change in sign of the strain,

$$g(\epsilon) = (1 + (C_2/C_1)\lambda_{max}^{1}, \qquad (11)$$

where λ_{max} is the extension ratio upon reversal of the strain. The resulting recoverable strain energy calculated for the networks is displayed in Table II for various values of λ_{max}. It can be seen that the assumption of an irreversibility significantly improves the agreement between experimental and calculated retraction results; however, the description of the experimental behavior for all samples under all deformations conditions is not quantitative. The form assumed for the irreversibility was empirical. Better agreement with experimental data could be obtained by adjusting the nature of the irreversibility of the damping function. In fact, a fundamental difficulty exists with the form of irreversibility given in Equation (11). The problem is illustrated in Figure 12, in which the computed retraction cycle for complete relaxation (that is, a strain history conducted infinitely slowly) is shown. This calculated stress–strain curve, which, when measured experimentally, corresponds to equilibrium results obtained in a step-wise fashion, diverges from the elastic results. Although not necessarily

TABLE II

REVERSIBLE AND IRREVERSIBLE DAMPING

			Recoverable strain energy, MJ per m^3		
Sample	λ_{max}	$\dot{\epsilon}$, sec^{-1}	Measured	Equation (5)	Equation (11)
SBR05	1.54	8.3×10^{-2}	.077	.082	.073
SBR05	1.79	8.3×10^{-2}	.130	.149	.128
SBR05	2.04	8.3×10^{-2}	.205	.227	.191
SBR05	2.52	8.3×10^{-2}	.344	.402	.327
SBR05	2.03	8.3×10^{-4}	.150	.178	.154
SBR05-S	2.04	8.3×10^{-2}	.103	.115	.102
SBR10	1.54	8.3×10^{-2}	.103	.108	.098
SBR10	2.05	8.3×10^{-2}	.279	.314	.273
SBR10	2.54	8.3×10^{-2}	.519	.562	.478
SBR10	2.03	8.3×10^{-4}	.246	.266	.236
SBR10-S	2.04	8.3×10^{-2}	.174	.184	.166
NR	1.54	8.3×10^{-2}	.075	.087	.080
NR	1.80	8.3×10^{-2}	.138	.165	.149
NR	2.04	8.3×10^{-2}	.241	.250	.223
NR	2.54	8.3×10^{-2}	.413	.459	.402

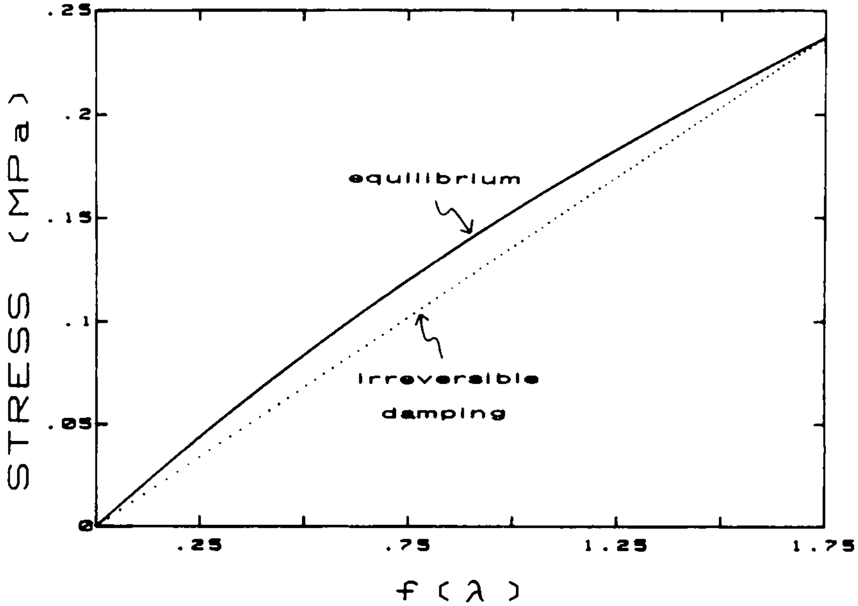

FIG. 12.—The stress during tensile retraction of the SBR10-S calculated assuming complete relaxation and irreversible damping, in comparison to the measured elastic equilibrium results.

the case with polymeric liquids, sufficiently slow deformation of networks is fully reversible, at least in the absence of chain rupture. The connectivity of the network requires complete strain recovery, since network chains and their junctions can not irreversibly change their relative positions. The fundamental difference between the behavior of liquids and networks during reversing strain histories is that the structure of the latter is not altered during a strain cycle. The eventual complete disappearance of any set reflects this fact[17].

SUMMARY

The Mullins effect refers to the dissipation in crosslinked rubber of mechanical energy beyond that due to linear relaxation processes or irreversible structural changes. Physically, Mullins softening probably arises from adjustment of local imbalances in segment density and from contraction of the primitive path of network chain ends. The resulting more random chain configuration contributes to the relaxation of the stress, but at a sufficiently rapid rate that it is omitted from the experimentally measured linear relaxation spectrum. This omission is made apparent upon reversal of the applied strain. The mechanism underlying the hysteresis can be modeled empirically by the introduction of irreversibility into the damping function. Although the Mullins effect is a reflection of nonaffine network motion during deformation of rubber, it is independent of the extent to which the junctions of the network are affinely displaced at elastic equilibrium. Randomly crosslinked networks of widely varying structure exhibited comparable degrees of Mullins softening. Corroboration that the network chain ends are a major source of Mullins softening could be obtained by a similar study using end-linked networks. Such experiments on end-linked polytetrahydrofuran rubber are currently in progress.

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REFERENCES

[1] L. Mullins, RUBBER CHEM. TECHNOL. **42,** 339 (1969).
[2] C. M. Roland and W. J. Sobieski, RUBBER CHEM. TECHNOL. **62,** 683 (1989).
[3] W.-N. Huang and J. J. Aklonis in "Chemistry and Properties of Crosslinked Polymers," S. S. Labana, Ed., Academic, New York, 1977, p. 453.
[4] F. Bueche, "Physical Properties of Polymers," Wiley, New York, 1962, p. 49.
[5] J. A. C. Harwood and A. R. Payne, *J. Appl. Polym. Sci.* **11,** 1825 (1967).
[6] P. J. Flory, *J. Chem. Phys.* **15,** 397 (1947).
[7] J. A. C. Harwood and A. R. Payne, *J. Appl. Polym. Sci.* **10,** 1203 (1966).
[8] J. A. C. Harwood and A. Schallamach, *J. Appl. Polym.* **11,** 1835 (1967).
[9] J. A. C. Harwood and A. R. Payne, *J. Appl. Polym. Sci.* **10,** 315 (1966).
[10] J. D. Ferry, "Viscoelastic Properties of Polymers," Wiley, New York, 1980.
[11] M. Doi and S. F. Edwards, "The Theory of Polymer Dynamics," Clarendon Press, Oxford, 1986.
[12] T. G. Nuttig, *J. Franklin Inst.* **191,** 679 (1921).
[13] J. G. Curro and P. Pincus, *Macromolecules* **16,** 559 (1983).
[14] I. V. Yannas, *J. Polymer Sci. Macromol. Rev.* **9,** 163 (1974).
[15] W. V. Chang, R. Bloch, and N. W. Tschoegl, *Rheol. Acta* **15,** 367 (1976).
[16] R. G. Larson, "Constitutive Equations for Polymer Melts and Solutions," Butterworths, Boston, 1988.
[17] C. M. Roland, RUBBER CHEM. TECHNOL. **62,** 863 (1989).
[18] A. Ciferri and P. J. Flory, *J. Appl. Phys.* **30,** 1498 (1959).
[19] A. V. Tobolsky, "Properties and Structure of Polymers," Wiley, New York, 1960, ch. III.
[20] F. S. C. Chang, *J. Appl. Polym. Sci.* **8,** 37 (1964).
[21] M. H. Wagner, *J. Non-Newtonian Fluid Mech.* **4,** 39 (1978).
[22] R. G. Larson and V. A. Valesano, *J. Rheology* **30,** 1093 (1986).