CHAIN ENDS AND THE MULLINS EFFECT IN RUBBER*

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ABSTRACT

It has been suggested that "Mullins softening", which is the anomalously low stress found in crosslinked rubbers that have been subjected to a reversing deformation history, might be caused by retraction of the chain ends along their primitive paths. Using natural rubber networks made from precursors of varying molecular weight, and an end-linked polytetrahydrofuran rubber, the fraction of chain ends was varied. From stress-strain relationships measured on these rubbers, it is concluded that Mullins softening is unrelated to the presence of chain ends, or to polydispersity in the lengths of network strands.

INTRODUCTION

Neat crosslinked rubber exhibits "linear" viscoelastic behavior over a broader range of deformation than most materials. However, similar to results on polymeric liquids[1], mechanical stresses are found to be anomalously low when elastomers are subjected to reversing strain histories[2-7]. This phenomenon is well-known and the term "Mullins softening" was originally coined to describe it (notwithstanding that nowadays it is commonly used in specific reference to the large hysteresis of carbon black reinforced rubber). The hysteresis is anomalous in that it exceeds that which can be accounted for from the linear relaxation spectrum, but is unrelated to irreversible changes in the rubber network[2-7].

Recently it was determined that unfilled rubbers of widely varying network structure exhibit comparable degrees of Mullins softening[6,7]. It was hypothesized that the phenomenon reflected relaxation processes transpiring too rapidly to be included in the linear relaxation spectrum. Specifically, as first proposed for polymeric liquids[1,8], contraction of the primitive path of network chain ends was suggested as the mechanism underlying the anomalous hysteresis. Such an effect would be manifested only when the sign of the strain function is reversed.

Assessment of Mullins softening requires quantitative evaluation of the viscoelastic contribution to the hysteresis. In order to describe the mechanical relaxation of a material subjected to an arbitrary strain history, a constitutive equation is required. Several single integral constitutive equations have been developed from both molecular and phenomenological models for the rheology of polymeric liquids or networks. One class of constitutive equations is based on the phenomenological Kaye–Bernstein–Kearsley–Zapas (K–BKZ) theory[1,9], whose memory kernel is not limited to any particular molecular model but is derived from an empirical assumption involving the strain energy. In general, nonlinear models have been found to yield unsatisfactory results, particularly for deformation histories involving a reversal in the sign of the strain.

While linear behavior in the strictest sense is rarely observed, separability of time and strain effects, wherein the relaxation function is independent of strain, allows calculation of the stresses for an arbitrary strain history. For example, the response of a sample initially in equilibrium to a shear deformation for a time t_1, followed by a second shear deformation, can be predicted from the measured stress relaxation for single step strains[1,9]; *i.e.*

$$\sigma(t, t_1, \gamma_1, \gamma_2) = \sigma(t, \gamma_2) + \sigma(t + t_1, \gamma_1 + \gamma_2) - \sigma(t + t_1, \gamma_2), \tag{1}$$

where γ_1, γ_2, and $\gamma_1 + \gamma_2$ refer to the first, second, and total strain deformations, respectively. All terms on the right side of Equation 1 denote the stress relaxation for single step strains, while $\sigma(t, t_1, \gamma_1, \gamma_2)$ refers to the response at time t after imposition of a second strain deformation. This expression does not place any restrictions on the magnitude of t or t_1, nor is any assumption made concerning the strain dependence of the strain energy.

If the deformation does not alter the structure of the material (*e.g.*, no disentanglement of chains in a polymeric liquid or no strain induced crystallization of a network), Equation (1) accurately predicts the stresses for a double step shear strain deformation experiment in which γ_1 and γ_2 are in the same direction. However, when γ_1 and γ_2 are of opposite sign, several investigations have shown that differences between theory and experiment exist; moreover, these differences increase as the time interval, t_1, decreases or the size of the first deformation, γ_1, increases[1,8-14]. Invariably, the prediction underestimates the extent of stress relaxation (*i.e.*, overpredicts the stress) following application of the reversing strain.

Several explanations have been suggested for the discrepancy between theory and experiment. An early hypothesis for the origin of anomalous softening in crosslinked rubber was nonaffine motion of the network[3-5]. However, it has been demonstrated that Mullins softening is at least unrelated to the extent to which the equilibrium displacement of network junctions is nonaffine[6,7]. Network inhomogeneity, in the form of a distribution in the length of the network strands, can give rise to nonaffine motion. If the network chain distribution is sufficiently broad, the shortest chains may approach an extended configuration at relatively modest macroscopic strains[15]. It has been suggested that this phenomenon may underlie Mullins softening[3-5].

More recently it was proposed that the anomalous hysteresis seen in polymeric liquids subjected to small (no loss of entanglements) reversing deformations reflects the contribution of chain ends[1,8]. Stress is dissipated by the rapid retraction of the chain ends; however, this relaxation is too fast to be measured and thus is omitted from the memory kernel of the constitutive equation. This omission results in a overestimation of the stress. Similarly, it has been suggested that the rapid chain end retraction mechanism may underlie the Mullins phenomenon in crosslinked rubber[6,7]. Of course, if any rapid relaxation processes are simply included in the constitutive description, improved agreement with experiment would result. Although the direct observation of chain end retraction has been reported[16], in general this is difficult to accomplish experimentally.

In this work, the contribution of chain ends will be assessed indirectly by the use of networks with varying concentrations of chain ends, obtained by crosslinking natural rubber of different initial molecular weights and by end-linking linear polytetrahydrofuran. Since the latter is monodisperse, the networks also provide an opportunity to examine the suggestion that network strand polydispersity engenders Mullins softening[3-5]. The elastomers were subjected to various strain histories and the measured stresses compared to predictions based on the superposition principle.

EXPERIMENTAL

The *cis*-1,4-polyisoprene (SMR-L type *Hevea Brasiliensis* from the Ore and Chemical Co.) was estimated to have an initial number average molecular weight of 3×10^5 [9]. Elastomers prepared from the polymer as received are designated NR-H. Two networks were also prepared from lower molecular weight precursors. The molecular weight of the SMR-L was reduced by annealing in air at 105°C for 240 min and alternatively by incorporation of 20%, by weight, of a low molecular weight synthetic *cis*-1,4-polyisoprene (Isolene 400 from Hardman Chemical Co.). These samples are designated as NR-L and NR-B respectively.

All rubbers were vulcanized for 48 min at 160°C, with 1.0 phr dicumyl peroxide as the curative. Thus, the crosslink density of the samples were equivalent, with the average molecular weight between crosslinks, M_c, estimated to be 19 600 (assuming depletion of the available peroxide[17]). The soluble fraction of each network, determined by extraction with cyclohexane, is listed in Table I. All mechanical results reported herein were obtained on the unextracted elastomers.

Network	M_c	Extractable weight %	Shear modulus MPa[a]	M_n[b]	Strength[c] MPa
NR-H	19 600	3.6	0.17	3.4×10^5	15.3 ± 2.7
NR-B	19 600	6.7	0.11	9.2×10^4	9.1 ± 1.2
NR-L	19 600	5.1	0.087	7.1×10^4	9.4 ± 2.0

[a] From the equilibrium strain measured at a shear stress = 0.43 MPa.

[b] Estimated from the chain end correction factor (the bracketed quantity in Equation 2) using M_c = 19 600.

[c] Average of ten tests.

The polytetrahydrofuran (PTHF) elastomer was prepared and characterized by Prof. R. S. Stein and Dr. L. Jong of the University of Massachusetts. An allyl terminated linear polymer (M_n = 8551) was crosslinked with a stoichiometric amount of pentaerythritol tetra-kis(3-mercaptopropionate)[18]. The exhaustive reaction of linear PTHF, of polydispersity less than 1.3, produces an essentially unimodal network. From NMR measurements it was estimated that the reaction was complete to within about 1%[18]; hence, the concentration of chain ends in the PTHF rubber is very small.

Double step strain deformation measurements were performed at 30°C with an Imass Corp. Dynastat Mark II instrument using a double sandwich shear geometry. The strain history was as follows: a sample in mechanical equilibrium was deformed instantaneously (full displacement in less than 60 ms) and the initial strain maintained for one second (t_1). A second deformation was then imposed and the stress measured for a period of five seconds. Single step stress relaxation measurements were also made at various strains.

Tensile strengths were measured at room temperature on the natural rubber networks. Ten measurements each were obtained on ring specimens elongated at 500 mm/min.

RESULTS AND DISCUSSION

NR NETWORKS

The broad molecular weight distribution[9] and presence of some gel makes determination of the respective molecular weights of the precursor natural rubbers difficult. The inability of chain ends to support stress causes the modulus of a rubber to be a function of the chain end content. In the limit of affine motion, the equilibrium shear modulus is given by[19]

$$G = \frac{\rho RT}{M_c}\left[1 - \frac{2M_c}{M_n}\right], \tag{2}$$

where ρ is density of the rubber and RT has its usual significance. Equation 2 is an oversimplification. Free radical crosslinked natural rubber deviates significantly from affine behavior[20] and G is actually a function of strain. However, if the bracketed quantity in Equation 2 is independent of strain, a measure of M_n can be obtained nevertheless. The equilibrium shear modulus was measured for each network at a stress equal to 0.43 MPa. Using M_c = 19 600 and the M_n estimated for NR-H[9], a value of M_n was determined for NR-L and NR-B. These results are listed in Table I.

At constant crosslink density, the strength of an elastomer reflects the concentration of chain ends[21]. To corroborate the variation in molecular weights of the three natural rubbers used to produce the networks, the tensile strength of the network was measured. As seen in Table I, the lower M_n of NR-L and NR-B is reflected in their substantially lower tensile strengths.

Since the crosslink densities are constant, the fraction of the polymer existing as a chain end will increase as the molecular weight of the precursor natural rubber decreases. If the hypothesis is correct—that dangling ends are a primary source of anomalous softening— variation in the number of chain ends in the three rubbers should lead to a variation in the magnitude of observed Mullins softening.

The strain history, along with the corresponding stresses, is shown in Figure 1 for NR-L subjected to a double step shear deformation for which γ_1 and γ_2 (equal to 81% and 41% respectively) are in the same direction. The stresses calculated *via* Equation 1 are in excellent agreement with the experimental data, consistent with all previous studies wherein γ_1 and γ_2 have the same sign[1,9].

Typical results obtained for a reversing shear deformation ($\gamma_1\gamma_2 < 0$) are shown in Figure 2. In these experiments, the same strain history was used for all rubbers: $\gamma_1 = 81\%$ with $t_1 = 1$ s, followed by $\gamma_2 = -41\%$ (the sign denoting deformation in the opposite direction). Only the data measured after imposition of the second strain are shown in the figure.

Using the time dependence for single step stress relaxation determined for each rubber in separate experiments, the response to the reversing double step deformation was calculated from Equation 1. These results are also displayed in Figure 2. While Equation 1 accurately predicts stress magnitudes during double step shear strain experiments in which γ_1 and γ_2 were in the same direction (as illustrated in Figure 1 for NR-L), the constitutive equation overpredicts the stress after a reversing strain. Of primary significance herein, the disagreement between the experimental and calculated curves is similar for all samples; that is, the
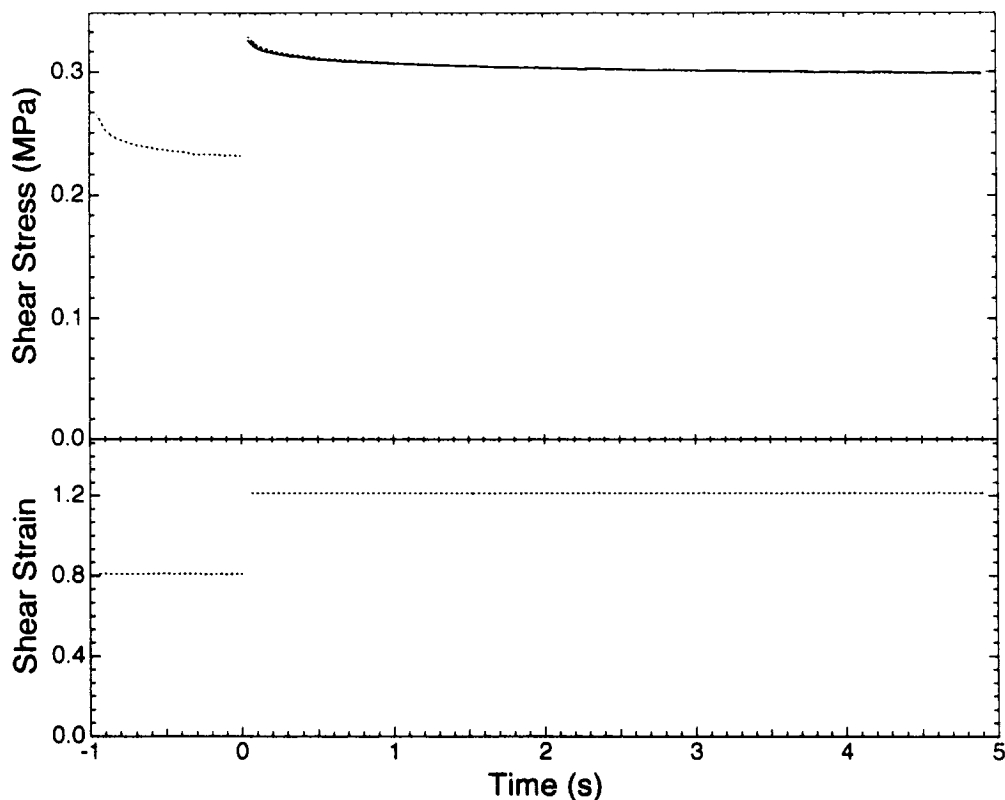

Fig. 1.—The strain and stress history of NR-L subjected to a double step shear deformation (dotted lines). The respective values of γ_1 and γ_2 are 81% and 41%, with $t = 0$ corresponding to the imposition of the second deformation, γ_2. The theoretical stresses calculated from Equation 1 are shown (solid line) for $t > 0$.
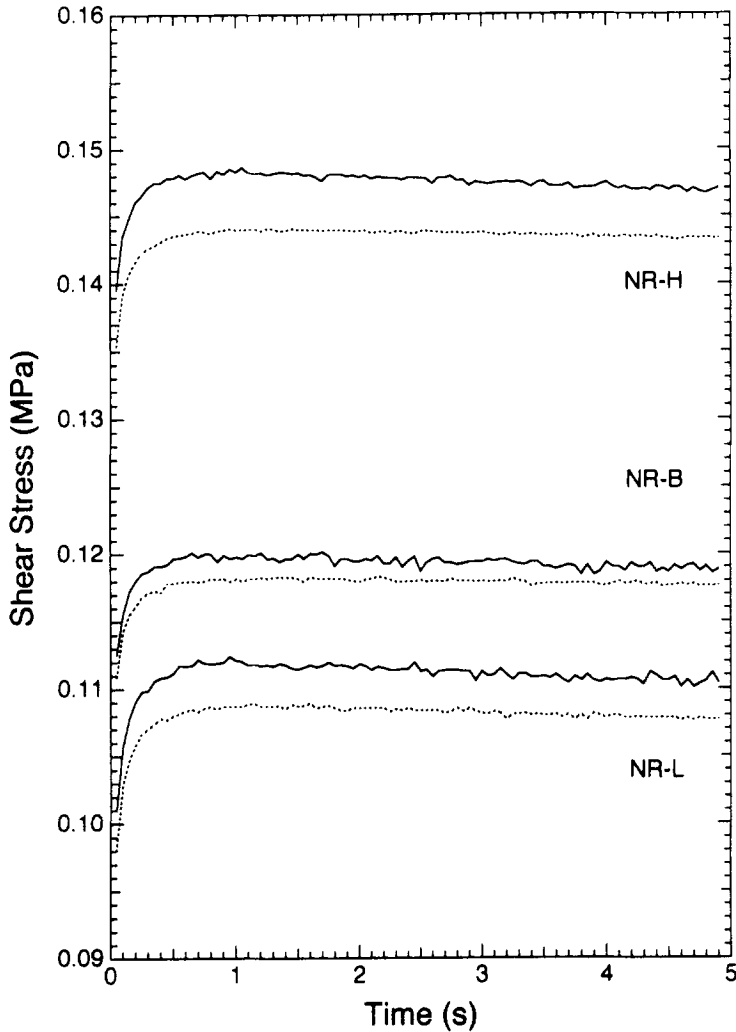
FIG. 2.—The experimental (dashed) and calculated (solid) stresses measured for $t > 0$ in NR-H, NR-B, and NR-L after a reversing double step shear deformation for which γ_1 and γ_2 are $+81\%$ and -41% respectively.

three NR networks exhibit comparable degrees of Mullins softening notwithstanding their differences in precursor M_n.

Actually the smallest degree of Mullins softening is seen for NR-B, the network formed from a blend of low and high molecular weight polymers. This may reflect its somewhat higher content of unattached polymer (cf. soluble fractions in Table I). Very relevant is the fact that NR-H, which contains the lowest concentration of dangling ends, is associated with not less, but actually slightly more anomalous hysteresis than the other two networks.

Although the strain histories were the same, the stresses during the experiments in Figure 2 were different for the NR-H in comparison to NR-L and NR-B. As discussed earlier, the different moduli of the rubbers are a reflection of equivalent crosslinking densities and dissimilar dangling chain end concentrations (see Table I).

Displayed in Figure 3 are the results of an alternative set of experiments in which the strains were adjusted for each rubber to yield equal stresses. For NR-L and NR-B the strains are identical to those in Figure 2, whereas for NR-H, γ_1 and γ_2 were decreased to $+60\%$ and
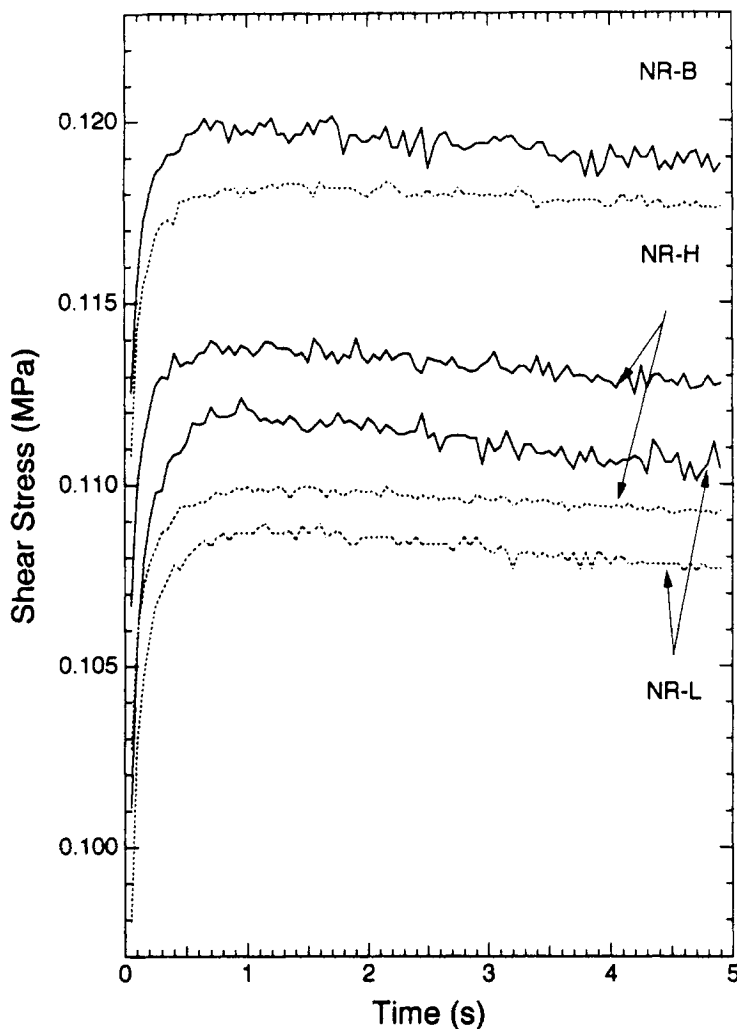
FIG. 3.—The experimental (dashed) and calculated (solid) stresses measured for $t > 0$ in NR-H, NR-B, and NR-L subjected to a reversing double step shear deformation. The strains for NR-B and NR-L are given in Figure 2, while for NR-H $\gamma_1 = +60\%$ and $\gamma_2 = -30\%$.

−30%, respectively. The observed behavior conforms to that in Figure 2. NR-H exhibits a moderately larger Mullins softening, although the strain softening is very similar for the three rubbers.

The results in Figures 2 and 3 are unexpected if chain and retraction is responsible for Mullins softening. At least for crosslinked rubber, the hypothesis that the Mullins effect arises from the rapid relaxation of chain ends appears to be invalidated.

END-LINKED PTHF

The random crosslinking used to produce the NR networks gives rise to a distribution in the lengths of the polymer chain between network junctions. End-linking of monodisperse linear polymer, on the other hand, yields networks whose strands are essentially equal in length. In addition, the end-linking procedure minimizes the amount of chain ends. The conformance to equation for reversing strain histories of a PTHF elastomer produced in this fashion was examined.

Similar to the results for NR described above, the response of the PTHF to a double step strain deformation in which γ_1 and γ_2 are in the same direction is accurately predicted by Equation 1 (results not shown). Contrarily, the measured stress when γ_1 and γ_2 are of opposite sign is appreciably less than the K–BKZ calculations. In Figure 4, the observed and calculated stresses for several reversing strain histories are shown for the PTHF rubber. This data demonstrates clearly that neither chain ends nor network strand dispersity can be invoked to rationalize the Mullins effect.

SUMMARY

The principal conclusion herein is that anomalous strain softening is unrelated to the presence of chain ends, or to dispersion in the network strand lengths. Dissipation of stress by the rapid relaxation of chain ends is a reflection of nonaffine network motion in crosslinked rubbers, but retraction of dangling chain ends can not significantly contribute to the anom-
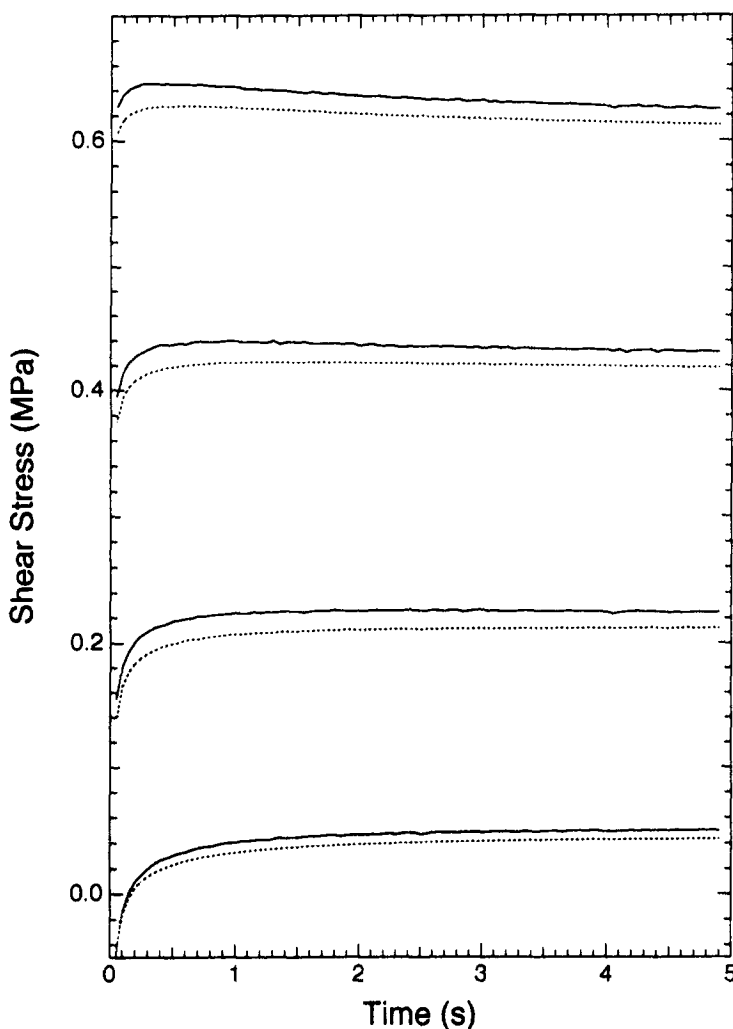

FIG. 4.—The experimental (dashed) and calculated (solid) stresses measured in end-linked PTHF after various reversing double step shear deformations. From top to bottom: γ_2 equals -20%, -41%, -63%, and -79%. The value of γ_1 was $+83\%$ for all cases shown and $t = 0$ corresponds to imposition of the second step.

alous relaxation of crosslinked rubber. From earlier work[6,7] it was concluded that nonaffine elastic behavior in networks is not manifested as Mullins softening. The fact that crosslinking in solution does not ameliorate the Mullins effect[6,7] argues against any contribution of trapped entanglements.

The question remains concerning why stresses during retraction are lower in magnitude than can be accounted for from consideration of linear relaxation. The obvious rejoinder, that deformation takes the material beyond the bounds for linearity, ignores the fact that Equation 1 works well absent strain reversal. Improved predictions for reversing strain histories can be achieved by the introduction of irreversible damping functions into the constitutive description. These empirically account for the structure breakdown ostensibly causing the extraneous hysteresis[1,22]. Although this approach is plausible for polymeric liquids in which disentanglement of the chain molecules during flow is not recovered on the time scale of the strain reversal, no microscopic mechanism can be identified as responsible for the anomalous hysteresis in crosslinked rubber. Since their modulus (equilibrium or isochronal) is invariably a function of strain, crosslinked rubbers are not linearly viscoelastic in the strictest sense. Hence, the Mullins effect can simply be viewed as a consequence of nonlinearity, and the anomaly is perhaps the surprising success, for nonreversing deformations, of approaches such as Equation (1).

ACKNOWLEDGMENTS

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