The Mullins Effect in Crosslinked Rubber*

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Synopsis

The Mullins effect refers to the dissipation in cross-linked rubber of mechanical energy in apparent excess of that due to linear relaxation processes or irreversible structural changes. Although it reflects nonaffine network motion in response to an applied deformation, contrary to previous assertions Mullins softening is found to be independent of the extent to which the junctions of the network are affinely displaced at elastic equilibrium. Rubbers of widely varying network structure were observed to exhibit comparable degrees of Mullins softening. Physically this softening arises from equilibration of local imbalances in the force along the network chains and from contraction of the primitive path of network chain ends. These mechanisms, which transpire too rapidly to be included in the linear relaxation spectrum, can be modeled empirically by the introduction of irreversibility into the damping function in the constitutive equation.

INTRODUCTION

When a condition of elastic equilibrium does not prevail, the stresses during the return of a stretched rubber to an unstrained state are less than the corresponding stresses during the extension. This hysteresis, or "strain softening," is observed even in the absence of any structural changes, such as extended chain crystallization or the detachment of chains from filler particles. Although viscoelasticity obviously underlies this phenomenon, the stresses observed during the retraction of cross-linked rubber are considered to be lower in magnitude than can be accounted for by measurable relaxation processes, a phenomenon known as the Mullins effect.[1] Nonaffine displacement of the network junctions has been proposed as the origin of the anomalous behavior,[2-4] but such a hypothesis has never been examined. 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.

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BACKGROUND

Limits for linear viscoelastic behavior, as defined by adherence to the Boltzmann equation,

$$\sigma(t) = \int_0^t E(t-u)\, de(u)/du\, du \tag{1}$$

are reputed to extend over a wider range for cross-linked elastomers than is realized for most materials.[5] In this equation σ and e are the stress and strain, respectively, and $E(t)$ the stress–relaxation function. Beyond the maximum strain for which Eq. (1) is valid, an integral constitutive equation may be employed[5,6]

$$\sigma(t) = \int_0^t \{E(t-u, e(t-u))\}\, de(u)/du\, du \tag{2}$$

whereby, if the relaxation spectrum underlying the function $E(t)$ is independent of strain so that the effects of time and of strain are uncoupled,

$$\sigma(t) = \int_0^t E(t-u) g(e)\, de(u)/du\, du \tag{3}$$

The definition of uniaxial strain in a cross-linked flexible chain polymer is suggested by statistical theories of rubber elasticity[7–9]

$$e(\lambda) = \lambda - \lambda^{-2} \tag{4}$$

where λ is the ratio of the final, l, and initial, l_o, specimen lengths. The presence of a damping function, $g(e)$, in Eq. (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 network motion may not be affine even at very low strains, in crosslinked rubbers the "slippage" increases with extensional deformation due to increasing reduction of the steric constraints on Brownian 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 suggested by the Mooney-Rivlin relation for the equilibrium stress[7–9]

$$\sigma_{eq} = v^{-1/3} v_x^{2/3} e(\lambda) \{2C_1 + 2C_2\lambda^{-1}\} \tag{5}$$

In this expression v and v_x are the respective volume fractions of the network during the deformation and during cross-linking. C_1 can be identified with N, the number density of elastically effective network strands, while the ratio C_2/C_1 is a measure of the magnitude of the constraints on fluctuations of the network junctions away from their equilibrium position. As deformation proceeds, the junctions become less constrained in the stretch direction due to dilution of neighboring chain segments along that dimension. A smaller ratio of C_2/C_1 implies less alteration from affine to phantom-like response as the strain increases, either because the junction behavior is relatively unconstrained initially (as in the case, for example, of a network swollen with diluent, $v < 1$) or because the severity and spatial domain of the constraints are of a more permanent nature (e.g., cross-links of high functionality).

From Eqs. (3) and (5)

$$g(e) = (1 + (C_2/C_1)\lambda^{-1}) \tag{6}$$

which by custom is normalized to unity at $e = 0$. Note that at equilibrium

$$E(t = \infty) = v^{-1/3} v_x^{2/3} C_1 \tag{7}$$

The long time relaxation in cross-linked rubber is governed by the release of entanglement constraints on dangling network chains.[10,11] Since reptation of the network strands is suppressed, a principal 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.

EXPERIMENTAL

The elastomers used in this study were a *cis*-1,4-polyisoprene (SMR-L type Hevea Brasiliensis) and a 23.5% styrene, 76.5% butadiene random copolymer (Duradene 706 from the Firestone Tire and Rubber Co.). Cross-linking was done at 160°C for 48 min with dicumyl peroxide as the curative. Four basic network types were prepared:

1. Polyisoprene with 1.0% by weight peroxide, along with 0.05% stabilizer to suppress degradation (PIP)
2. Styrene–butadiene copolymer cross-linked neat with, respectively, 0.05% (SBR05) and 0.10% (SBR10) peroxide
3. SBR05 and SBR10 swollen after cross-linking with 33% by volume of nonvolatile paraffin oil (these materials, desig-

nated SBR05-S and SBR10-S, respectively, were tested in the swollen state)

4. SBR with 0.2% peroxide cross-linked while in solution with 50% by weight of paraffin oil, the latter and any soluble polymer subsequently extracted with tetrahydrofuran prior to testing (this sample is referred to as SBR-E)

The soluble fraction of all rubbers, f_{sol}, along with the volume fraction of the insoluble network at equilibrium swelling, v_e, are given in Table I. The solvent for the determination of v_e was cyclohexane for the SBR samples and carbon tetrachloride for the PIP. The solubility parameter difference, $\Delta\delta$, between the solvent and polymer is in both cases 0.3 per $(\text{cal/ml})^{1/2}$.[12] Low network chain densities were used to minimize the occurrence of chain scission during mechanical deformation. Particularly for the higher strain experiments, an absence of significant network mechanical damage was confirmed from the reproducibility of results on reused test specimens.

Tensile measurements on the rubbers were carried out at room temperature using an Instron 4206. For equilibrium experiments, invariance of the stress for 15 min was taken to correspond to elastic equilibrium. Nonequilibrium deformation experiments were conducted at constant cross-head 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.

Room temperature stress–relaxation was measured using a Imass Corp. Dynastat Mark II instrument. Following imposition of a deformation the stress was typically monitored over a period of from 10^{-2} to 10^4 seconds. Ten stress measurements per decade

TABLE I
Rubbery Networks Employed

Sample	v_x	v	f_{sol}	v_e	N[a] $\times 10^4$	C_1	C_2
SBR05	1.0	1.0	.05	0.152	1.1	.064	.156
SBR05-S	1.0	0.67	<.05	—	1.1	.055	.072
SBR10	1.0	1.0	.11	0.104	2.2	.114	.197
SBR10-S	1.0	0.67	<.11	—	2.2	.101	.108
SBR-E	0.5	1.0	0[b]	0.0933[b]	1.5	.032[c]	.113[c]
PIP	1.0	1.0	.04	0.113	1.4	.112	.168

[a] Per ml as determined from v_e using Eq. (8).

[b] All soluble material was extracted prior to testing.

[c] For $\lambda > 1.3$ only.

of time were obtained. The numerical relaxation data were used directly, with double logarithmic interpolation employed between data points.

RESULTS AND DISCUSSION

Equilibrium Response

Cross-link densities for the various rubbers are listed in Table I as calculated assuming no dangling ends[8]

$$\ln(l - \upsilon_e) + \upsilon_e + (V_p/RT)((\Delta\delta)\upsilon_e)^2 = -NV_s\upsilon_x(\upsilon_e^{1/3}) \qquad (8)$$

V_p and V_s are the polymer and solvent respective molar volumes. Also in Table I are the elastic constants C_1 and C_2 determined from the equilibrium stress-strain data. With two exceptions, the strain dependence of the equilibrium stresses for the networks conformed to the Mooney–Rivlin description [Eq. (5)] over the range of strains employed. The polyisoprene rubber at very high extension ratios exhibited a decreasing stress due to the onset of strain-induced crystallization. This orientational crystallization required elongations (>450%), however, in excess of those of interest herein. The behavior of the SBR-E material also deviated from the Mooney–Rivlin relation, but the divergence was only at the lowest extensions. The SBR-E was swollen during formation so that upon removal of the diluent the network chains assume a more compact configuration.[13] As a consequence, the initial stages of extension mimic the removal of compressive loading. The Mooney–Rivlin expression is not a valid constitutive equation due to its failure to account for behavior in all types of strain.[14,15] The initial nonadherence of the SBR-E to Eq. (5) reflects this effect. The values of C_1 and C_2 for the SBR-E at the higher strains are given in Table I.

From the measured values of the elastic constants, the strain dependence of the mechanical behavior of the various rubbers is seen to be a reflection of the network architecture. Networks with a low concentration of low functionality junctions (sample PIP) or in the presence of diluent (SBR05-S and SBR10-S), have the most strain-independent elastic modulus since, at the low crosslink concentrations employed herein, their junctions are relatively uninhibited even at low strain. Consequently, the greater configurational freedom in the stretch direction conferred by stretching does not influence the differential modulus as much as for networks with extensively constrained junctions. The latter have a large C_2/C_1 ratio only to the extent that the domain of the constraints can be reduced by elongation. Steric constraints due to entanglements become less confining on junction fluctuations as straining proceeds (thus SBR-05 and SBR-E have higher relative C_2 terms), unlike the constraint arising from a concentration of covalent linkages. The most nearly affine network, SBR-10, has an intermediate ratio of C_2/C_1 since constraints arising from its higher concentration of cross-links of higher functionality are less effectively ameliorated by deformation; thus, it exhibits a response that becomes less phantom-like at higher elongations. Deviations in the equilibrium modulus with strain are an indication, not of affine or of nonaffine motion, but rather a change in the degree of affineness of the mechanical response.

Relaxation Behavior

The nonlinearity of the elastic response of the rubbers indicates that the Boltzmann superposition principle [Eq. (1)] is inapplicable for these networks at the strains of interest. If time invariance is maintained, however, separability of time and strain will enable application of Eq. (3). 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 at various strains for the rubbers. The only deviation from apparent constancy in the form of $E(t)$ for any of the rubbers was measured for the PIP at very high elongations ($\lambda > 5$) due to the onset of orientational crystallization (which extends the decay of stress beyond that due to viscoelastic relaxation).

Mullins Softening

The stresses developing in the various networks during uniaxial extension and retraction were measured at various deformation rates, with representative results displayed in Figures 1 and 2. The magnitude of the strain softening, as reflected for example by the ratio of strain energy during extension to that during retraction (Table II), does not correlate with the magnitude of either C_2 or the ratio C_2/C_1. By utilization of Eq. (3) the magnitude expected for viscoelastically derived hysteresis can be calculated for comparison to the total energy dissipation.

Using the time dependence of the stress relaxation taken from the experimentally measured relaxation functions, stress-strain

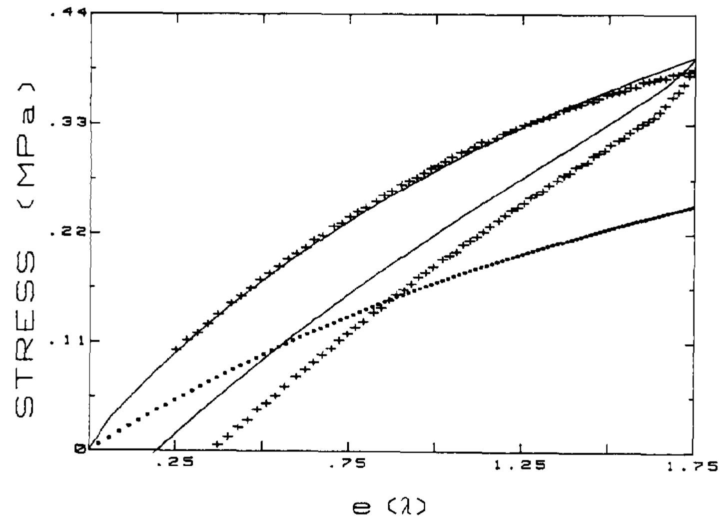

Fig. 1. The reversing stress-strain data measured at a nominal strain rate of 0.083 s^{-1} for the SBR05 (+ + +), along with the curve (——) calculated assuming reversible damping. Also shown are the corresponding elastic equilibrium stresses (●●●).

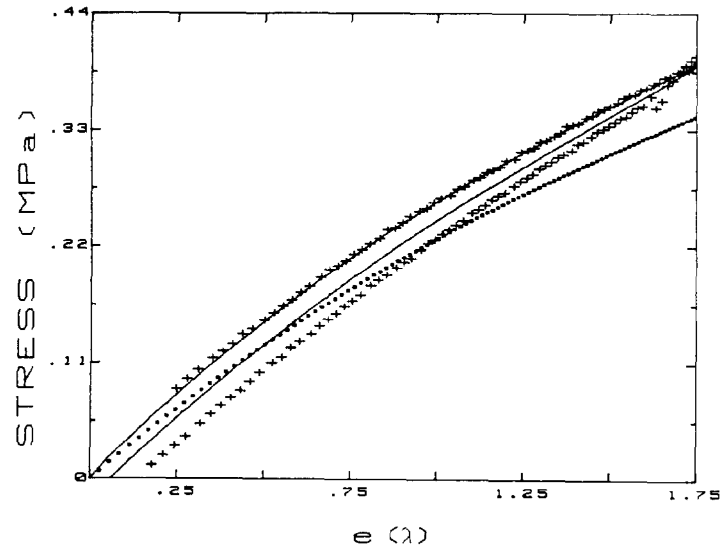

Fig. 2. The reversing stress-strain data measured at a nominal strain rate of 0.083 s^{-1} for the PIP (+ + +), along with the curve (——) calculated assuming reversible damping. Also shown are the corresponding elastic equilibrium stresses (●●●).

TABLE II
Tensile Retraction Hysteresis Results

					Hysteresis ratio (%)		
Sample	λ_{max}	$\dot{e}$ (s^{-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
	1.79	8.3×10^{-2}	0.165	1.56	21	10	11
	2.04	8.3×10^{-2}	0.183	1.56	23	15	8
	2.52	8.3×10^{-2}	0.467	1.56	26	14	12
	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
	2.05	8.3×10^{-2}	0.331	0.88	16	5	11
	2.54	8.3×10^{-2}	0.634	0.88	18	11	7
	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
	2.02	8.3×10^{-4}	0.172	0.63	23	7	16
PIP	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.

data were calculated for the various networks using Eq. (3). The scale factor for the $E(t)$ served as the sole fitting parameter and these values of $E(0)$ are given in Table II. For the damping function, $g(e)$, Eq. (6) was employed with the experimentally measured elastic constants. These computations are summarized in Table II, with representative results displayed in Figures 1 and 2. While the calculations are in good agreement with the experimental data during extension, the retraction stresses diverge significantly from the computed values. The discrepancy between the curves during retraction is a direct measure of the hysteresis in excess of apparent viscoelastic losses. The extent of this anomalous strain softening (i.e., the Mullins effect) is listed in Table II for all the networks. These results are expressed in terms of the hysteresis ratio, defined as the irrecoverable strain energy divided by the energy expended during extension.

These rubbers, whose elastic responses encompass a range of behavior, 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 is found to have no obvious dependence on the reversal strain.

The observation of comparable Mullins softening in all the networks clearly confutes the assertion that the Mullins effect is due to nonaffine junction motion.[1–4] The most nearly affine of these rubbers, the SBR10, displays about the same relative Mullins softening as does the SBR05-S, which due to its lower cross-link density and the presence of diluent behaves much more like a phantom network. It is evident that Mullins softening is 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 other relaxation mechanisms are operative and it is these relaxation processes which underlie 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.[6] The motion of a highly entangled polymer chain is inhibited by restrictions imposed by other chains. The group of chain conformations consistent with these topological constraints defines a so-called primitive path; a primitive chain then represents the real chain without its small-scale fluctuations.[11] In an uncross-linked polymer melt, relaxation after the application of a large strain will proceed via several processes. Upon deformation the segments of a chain are initially stretched or compressed along their primitive path depending on their local orientation. Although these local imbalances are rapidly adjusted, they cause an initial variation in force along the chain. This equilibration is followed by the rapid retraction of the primitive chain back to its original contour length. The longer time relaxation process consists of disengagement (primarily by reptation for linear chains) from the deformed "tube" of constraints. Only this slower process, however, is usually measured and thus included in the linear viscoelastic relaxation spectrum.[6,11] 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. Although this decrease in modulus is occasioned by a different physical effect than for rubber networks, it is similarly accounted for in the constitutive equation by introduction of a damping function. It has been suggested that in polymeric fluids the mechanism underlying the attenuation of the damping function with increasing strain is not reversible; that is, when the strain is reversed, the damping function does not increase back to unity.[6,16] Irreversibility in the damping function reduces the magnitude of the retraction stresses 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.[6,17] This contraction allows the chain ends to assume a more random conformation. The loss of microscopic deformation effects a loss of 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.[6,17] 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 $g(e)$ assumes the minimum value it had attained during the extension portion of the strain history.[16] 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 between networks and polymeric liquids in the nature of the phenomena represented by the damping function. Nevertheless, the Mullins effect in rubber has 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 relax by fluctuation in their contour length. Prior to this, however, retraction of their primitive path contour lengths will transpire, in addition to the rapid equilibration of the local segment density. Due to the virtual instantaneous nature of this latter process and to rapidity of the contraction of the primitive path, these dissipative processes are usually omitted from linear relaxation behavior as characterized by a linear relaxation modulus. A consequence of this omission is the failure of Eq. (3) to describe the stresses measured during tensile retraction of rubber (i.e., the Mullins effect).

The introduction of irreversibility into the damping function was adopted to calculate tensile retraction curves for the rubbery networks. It was assumed that, while the damping function during extension is given by Eq. (6), after reversal of the strain

$$g(e) = (1 + (C_2/C_1)\lambda_{\max}) \tag{9}$$

TABLE III
Reversible and Irreversible Damping

Sample	λ_{max}	$\dot{e}$ (s^{-1})	Recoverable strain energy (MJ/m^3) Measured	Eq. (6)	Eq. (9)
SBR05	1.54	8.3×10^{-2}	.077	.082	.073
	1.79	8.3×10^{-2}	.130	.149	.128
	2.04	8.3×10^{-2}	.205	.227	.191
	2.52	8.3×10^{-2}	.344	.402	.327
	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
	2.05	8.3×10^{-2}	.279	.314	.273
	2.54	8.3×10^{-2}	.519	.562	.478
	2.03	8.3×10^{-4}	.246	.266	.236
SBR10-S	2.04	8.3×10^{-2}	.174	.184	.166
PIP	1.54	8.3×10^{-2}	.075	.087	.080
	1.80	8.3×10^{-2}	.138	.165	.149
	2.04	8.3×10^{-2}	.241	.250	.223
	2.54	8.3×10^{-2}	.413	.459	.402

where λ_{max} is the extension ratio at reversal. This expression represents an extension of Wagner's constitutive equation for polymeric liquids.[16] The resulting recoverable strain energy calculated for the networks is displayed in Table III for various λ_{max}. The assumption of an irreversible damping function significantly improves the agreement between the experimental and calculated retraction results. Nevertheless the description of the experimental behavior for all samples under all deformation conditions is not quantitative. Introduction of an appropriate empirical measure of irreversibility could no doubt provide further improvement in the agreement of calculations with experimental data; however, no additional insights into the underlying physics would be provided thereby.

Actually a fundamental difficulty exists with the form of irreversibility given in Eq. (9). Unlike in polymeric liquids, sufficiently slow deformation of networks is fully reversible, at least in the absence of chain rupture. Network chains and their junctions cannot irreversibly change their relative positions. The connectivity of the network requires complete strain recovery ultimately. A consequence of this is that the irreversibility of the damping function for a cross-linked material must exhibit some time dependence.

SUMMARY

The Mullins effect refers to the dissipation in cross-linked 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 configurations contribute to the relaxation of the stress, but at a sufficiently rapid rate that it is omitted from the 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 appears to be independent of the extent to which the junctions of the network are affinely displaced at elastic equilibrium. Networks of widely varying structure were found to exhibit comparable degrees of Mullins softening.

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