THE MECHANICAL BEHAVIOR OF DOUBLE NETWORK ELASTOMERS

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ABSTRACT

It was found that at low residual strains, the modulus of double network rubbers can be less than that of an isotropic elastomer of equal crosslink density. At higher residual strains, the equilibrium modulus is higher for the double network. This aspect of the behavior of networks was investigated using two phenomenological descriptions of rubber elasticity, the Mooney–Rivlin (MR)[1] and the Roth, Martin, and Stiehler (RMS)[2] Equations. Calculations using either approach, which make use of the independent network hypothesis, were qualitatively in agreement with the experimental data.

The tensile strength of double networks based on natural rubber were found to be independent of the amount of residual strain. This is true even at higher residual strains, wherein the modulus is significantly amplified. This suggests that the conventional compromise between modulus and failure properties can be circumvented using double network rubbers. Their utilization can yield elastomers of better mechanical properties.

INTRODUCTION

Elastomers comprised of two networks, distinguished from one another by the strain present during their formation, have a long history.[3-8] Double networks are often formed inadvertently as a result of mechanical or thermal chain scission ("chemical stress relaxation")[3,9,10] or due to crystallization.[11-13] Most of the past work has been in using composite networks to interpret stress-relaxation in the presence of ageing [see, for example, Scalan and Watson,[5]] or to assess the contribution of trapped entanglements to the mechanical behavior of cured rubber.[14-23] Recently, the double network formalism has been used as a model to describe the deformation behavior of filled elastomers.[24]

It has been observed by various workers that the modulus of a double network rubber exceeds that of a conventional elastomer having the same total crosslink density.[25-28] This is an important result because the strength and other failure properties of conventional elastomers exhibit a maximum as a function of crosslink density.[29] At the usual crosslink densities of commercially viable rubbers, higher modulus entails reduced strength. To the extent that their failure properties (*e.g.*, strength and fatigue life) are the same as conventional elastomers, double network rubbers offer a route to obtaining superior mechanical properties, in that they may allow circumvention of the usual compromise between stiffness and strength.

EXPERIMENTAL

Natural rubber (SMR-L) was lightly milled to incorporate 2 phr dicumyl peroxide (Varox DCP-R, R. T. Vanderbilt Co., Inc.). Isotropic sheets were crosslinked by heating in a pressurized mold at 120°C for one hour. This crosslinking constituted the first network. The cured sheets were cut into strips (6.35 cm × 1.27 cm × 1.27 mm), onto which were placed fiducial marks to record the initial length (L_0). The second network was introduced by uniaxially extending the strips to various lengths (L_i) and reacting the remaining peroxide by heating in vacuum at 160°C for 1.5 hours. The permanent set (L_f/L_0) was measured for each sample 24 hours after the second curing (Table I). Samples from the initial sheet were crosslinked in the unstrained state simultaneously with the stretched samples, thus yielding controls of the same crosslink density.

Room temperature stress–strain data were obtained in tension by suspending weights from the samples and determining the distance between fiducial marks with a cathetometer.

TABLE I

SINGLE AND DOUBLE NETWORK L_0, L_i AND L_f VALUES

Sample[a]	L_0	L_i	L_f	L_i/L_o	Residual strain L_f/L_0	Modulus enhancement
A	25.6	25.6	25.6	1.00	1.00	1.00
B	25.6	40.0	37.0	1.56	1.45	0.85
C	25.6	59.9	50.5	2.34	1.97	0.85
D	25.6	77.6	58.8	3.03	2.30	0.73
E	25.6	104.0	76.9	4.06	3.00	1.11
F	25.6	126.0	91.3	4.92	3.57	1.49
G	25.6	150.0	100.0	5.86	3.91	1.68
H	25.6	176.0	110.0	6.88	4.30	1.84

[a] All samples have the same total crosslink density.

The samples were kept under a nitrogen atmosphere during the measurements. The time to reach mechanical equilibrium was less than 24 hours. All moduli reported herein (measured in the direction of the crosslinking strain) are taken to be the ratio of stress to strain at an extension ratio of 1.1. The latter is defined relative to the state of ease; that is, the reference length is L_f rather than L_0.

Tensile strengths were measured at room temperature with an Instron 4206 interfaced to a Hewlett-Packard 9000 computer. A 50 mm/min cross-head speed was employed. To obtain a sufficient number of tests for statistical significance, rings (6.5 mm diameter) were used, although the variation in stress from the inner to the outer circumference makes this a less preferred geometry. Only results for samples which failed away from the grip were used.

RESULTS AND DISCUSSION

ELASTIC MODULUS—THEORETICAL

All analyses of double network behavior have relied on the independent network hypothesis.[3,4,6,30,31] This assumes that crosslinking produces a set of network chains whose (i) mechanical response is independent of other networks (even though, of course, segments of the actual chains "belong" to both networks), and (ii) equilibrium configuration corresponds to that existing during network formation. The residual strain (condition of zero stress) for the double network represents the state in which the tensile forces from the initial network, formed in the isotropic state, are balanced by the compressive forces from the second network, formed during elongation. The stress observed when the double network is deformed is the sum of the stresses from the component networks.

In the present paper two phenomenological descriptions are employed, the Mooney–Rivlin,[1,32]

$$\sigma = (C_1 + C_2/\lambda)(\lambda - \lambda^{-2}) \qquad \lambda \geq 1, \tag{1a}$$

$$\sigma = (C_1 + C_2)(\lambda - \lambda^{-2}) \qquad \lambda \leq 1, \tag{1b}$$

where C_1 and C_2 are constants, and the Roth, Martin, and Stiehler,[2]

$$\sigma = E(\lambda^{-1} - \lambda^{-2})\exp[k(\lambda - \lambda^{-1})], \tag{2}$$

where E and k are constants. In these equations σ is the engineering stress and λ is the stretch ratio. These expressions adequately describe experimental data in extension and compression,[32] and thus are sufficient for our purposes.

Displayed in Figure 1 are the calculated stress–strain isotherms for both the MR and RMS Equations, where $C_1 = 0.097$ and $C_2 = 0.079$ for Equation (1), and $E = 1.06$ and $k = 0.34$ for Equation (2). Also included in Figure 1 are measurements for the control (isotropic) sample. The values for the constants were chosen by fitting the initial slope of the experimental data, with the value of k based on typical values reported in the literature.[2,33] The two theoretical curves diverge at higher extensions and in compression. These differences have a significant effect on the moduli calculated for the double networks.

The double network can be regarded as a superposition of two networks independently contributing to the measured force

$$\sigma_D \equiv \frac{f_d}{A} = \frac{f_1}{A} + \frac{f_2}{A} = \frac{l_f}{l_0}\sigma_1 + \frac{l_f}{l_i}\sigma_2 \tag{3}$$

where f is the force and A the initial area ($A_D = A_1 = A_2$), and the subscripts D, 1 and 2 refer to the double, the initial, and the second network respectively. When the double network is in the state of ease, the force of the first and second networks sums to zero.

Displayed in Figure 2 as a function of residual strain (L_f/L_0) is the calculated modulus (at $L/L_f = 1.01$) of a double network, relative to an isotropic network with the same total crosslink density. For a single network, $L_0 = L_i = L_f$. For calculations using either Equation (1) or (2), it was assumed for that the second network of the double network had four times the number of crosslinks as the first network. This assumption, and the equivalence of the slopes of the stress–strain isotherms at equilibrium, establishes relative values for the C_1 and C_2 of the MR model and E of the RMS model for each independent network. Again, representative literature values[2,33] were used for k in Equation (2).

Figure 2 has two striking features. First, at low residual strains, the calculated modulus of the double network is lower than the single network of equal crosslink density. This prediction has, in fact, been observed experimentally,[4] but attributed to scission of bonds in the original network. In the present experiments, the use of carbon–carbon network junctions is expected to minimize changes in the first network during the second crosslinking.[34]

Secondly, as the residual strain increases, the degree of modulus enhancement (that is, modulus of the double network divided by modulus of the corresponding single network) is

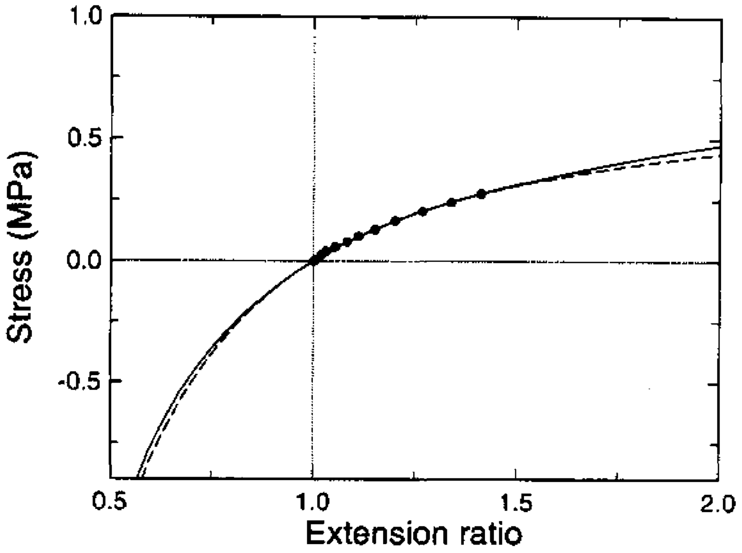

FIG. 1.—Stress-strain isotherms for the Mooney-Rivlin Equation (solid) with $C_1 = 0.097$ and $C_2 = 0.079$, and the Roth, Martin, and Stiehler Equation (dashed) with $E = 1.06$ and $k = 0.34$. Also shown is mechanical equilibrium data obtained for Sample A, Table I.

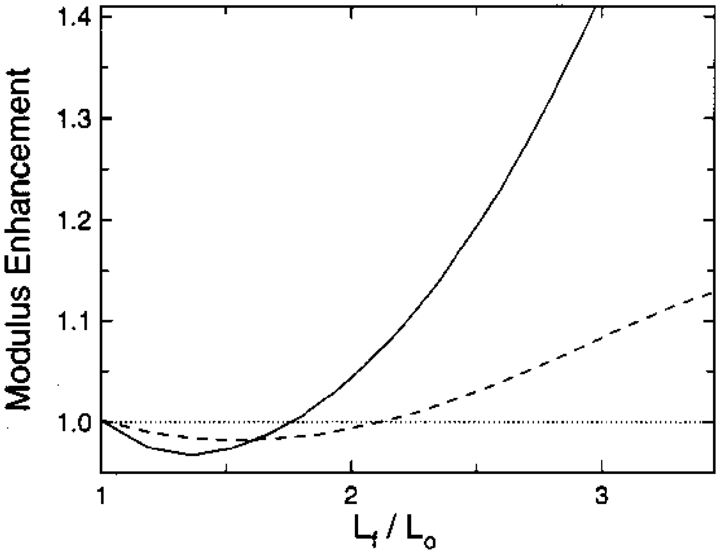

FIG. 2.—The ratio of modulus of the double network to that of the single network of equal crosslink density, calculated using Equation (1) (solid) and Equation (2) (dashed), for various residual strains. Parameters used were: first network—C_1 = 0.019, C_2 = 0.019, E = 0.22, k = 0.34; second network—C_1 = 0.076, C_2 = 0.060, E = 0.83, k = 0.42. Both equations predict that at low residual strains the double network has a lower modulus, while the situation reverses at higher residual strains.

found to be larger for the MR model than for the RMS model, notwithstanding the equivalence of their respective extension data, at least over the experimentally accessible region (Figure 1). This difference in the calculated degrees of modulus enhancement is due to the difference between Equations (1) and (2) for compression. As the second network is formed at higher strains (yielding higher residual strains), it moves further into compression as the double network relaxes to the state of ease.

The *total* crosslink density is factored out by ratioing all moduli by the modulus of the single network of equivalent crosslink density. Hence, by choosing a fixed distribution of crosslinks between the two networks (80% in the second), the length at which the second crosslinking occurs, L_i, is the independent variable for the double networks in Figure 2. If the same L_i values are used, but the distribution between networks is altered, the modulus enhancement can change. In fact, if the crosslinking of the second network is decreased to less than 50% of the total, the RMS model predicts no modulus increase for double networks versus single networks, irrespective of L_i. The MR model, on the other hand, still predicts higher moduli in the double networks, at least at high residual strains.

Displayed in Figure 3 is the stress–strain data (23°C) measured for natural rubber double networks formed at various lengths L_i, with a constant crosslink density (both total and the ratio between the two composite networks). The values of L_0, L_i, and L_f are listed in Table I. Also included in Figure 3 is the curve for a (conventional) single network with the same total crosslink density. As illustrated in Figure 4, the moduli of the double networks are less than that of the single network for residual strains less than 170% (*i.e.*, $L_f/L_0 < 2.7$). At higher residual strains, the double networks exhibit modulus enhancement over the single networks. These results are consistent with the calculations shown in Figure 2.

While the modulus data in Figures 3 and 4 refer to the direction parallel to the elongation during crosslinking, a few measurements were obtained in the perpendicular direction. At low residual strains no significant differences were observed. At high residual strains, the transverse modulus was less than the modulus in the direction of the original crosslinking strain. This agrees with previous results.[25]

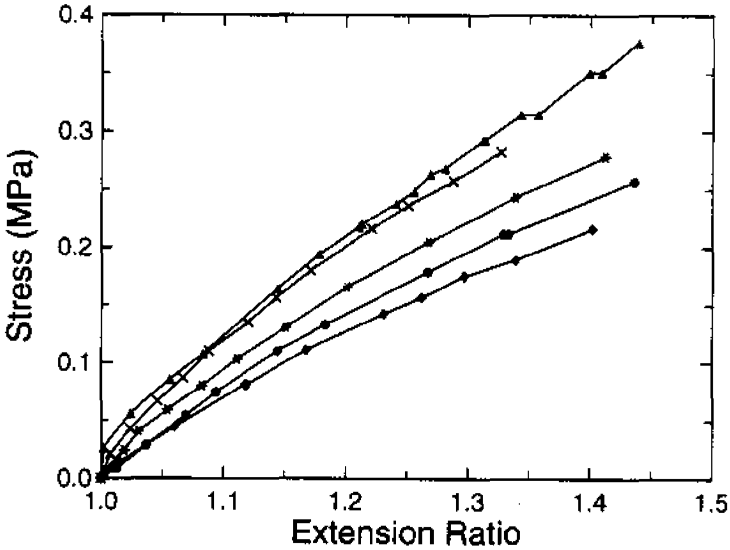

FIG. 3.—The stress–strain curves measured at 23°C for Table I, Samples: A(∗), B(●), D(♦), F(×), H(▲). The double networks exhibit higher stresses than the single network (A) of equal crosslink density for residual strains larger than $L_f/L_0 > 2.7$.

Notwithstanding the difference in modulus effected by the double network structure, the tensile strength of the NR elastomers was found to be invariant to residual strain (Figure 5). While higher modulus, conventionally obtained by higher crosslink density, is expected to result in a reduction in failure properties (*e.g.* tensile strength),[29] with double network rubbers modulus enhancement can evidently be achieved without loss of strength.

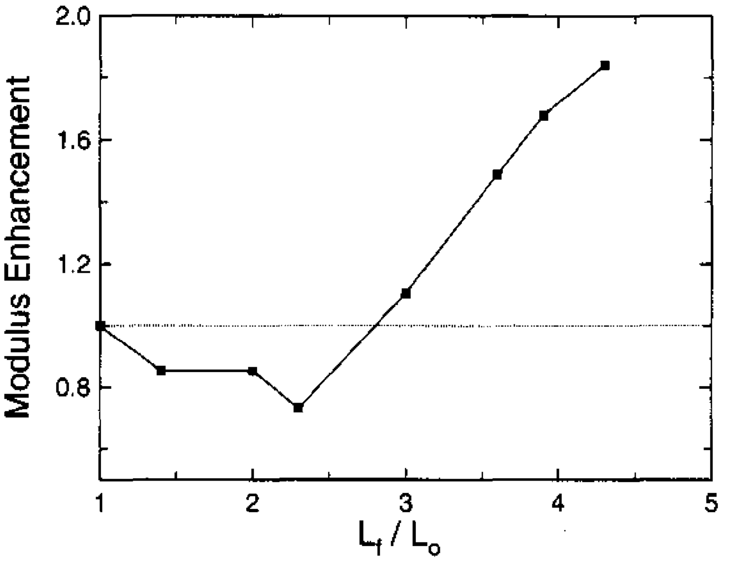

FIG. 4.—The ratio of double network modulus to that of the corresponding single network for various residual strains. The data is taken from Figure 3 at $L/L_f = 1.1$. The trend in the experimental data is qualitatively as predicted by models based on either Equation (1) or (2).

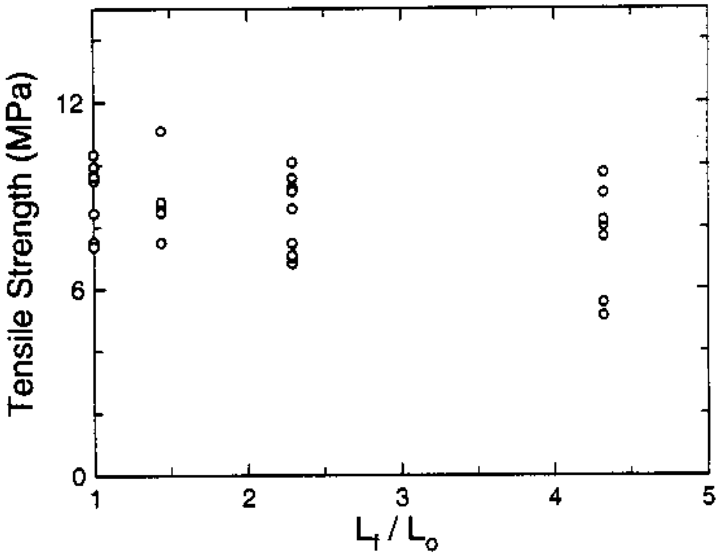

FIG. 5.—The tensile strength measured for four of the natural rubber networks listed in Table I.

SUMMARY

The present study focussed on the modulus at mechanical equilibrium obtained when an elastomer is crosslinked a second time while stretched. Contrary to previous literature, it is found that at fixed total crosslink density, the modulus of a double network can be less or greater than that of a conventional, isotropic rubber. The experimental results are in accord with calculations assuming independently acting networks and employing either of two phenomenological rubber elasticity models.

The utilization of double networks is demonstrated to be a viable route to obtaining better mechanical properties, in particular, higher modulus without loss of strength. In the present work the strain during the second curing step was varied, while the crosslink distribution between networks remained fixed. Double networks having the same total crosslink density and residual strain can be obtained by varying both L_f and the crosslink apportionment. Such elastomers exhibit different behavior; that is, the residual strain does not uniquely define the double network material. This aspect of double networks is currently under investigation. We are also exploring the manner in which enhancement of strain-induced crystallization in double network rubbers[27] affects the failure properties.

ACKNOWLEDGEMENTS

This work was supported by the Office of Naval Research.

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[*Paper No. VII, presented at the Spring ACS Rubber Division Meeting (Chicago), April 19–22, 1994.*]