FAILURE PROPERTIES OF NATURAL RUBBER DOUBLE NETWORKS

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ABSTRACT

When measured parallel to the curing deformation, double networks of natural rubber have a higher modulus than single networks of equal crosslink density. The difference is greater at higher strains. Despite the higher modulus, the mechanical fatigue lifetimes of double networks were found to be as much as a factor of ten higher than for conventionally crosslinked NR. The double network's tensile strength, on the other hand, was slightly lower. In contrast to these results, the modulus and tensile strength in the direction transverse to the curing strain are minimally affected by the presence of a composite network.

INTRODUCTION

"Double network rubber" refers to an elastomer that has been crosslinked twice, the second time while in a deformed state. Invariably, the deformation employed is simple tension, resulting in a rubber whose final length exceeds the length after the initial, isotropic cross-linking. The ratio of these two lengths, referred to as the residual strain, does not uniquely define a double network elastomer. A given residual strain can be achieved with different combinations of strain and crosslinking apportionment between the two networks.[1] Early studies were concerned with inadvertent double networks, produced by chain scission and reformation during the stretching of elastomers.[2-4] Double networks have also been used to assess the contribution of "trapped entanglements" to the elasticity of networks; in this situation entanglements alone comprise the first network.[5-7]

At least at high residual strains, the modulus of a double network rubber is greater than that of an isotropic elastomer having the same crosslink density.[1,8,9] When higher modulus is achieved in a conventional elastomer by increasing the crosslink density, poorer failure properties result.[1] This is not necessarily the case with double networks; for example, the tensile strength of natural rubber having a double network structure was found to be almost independent of residual strain, even at high residual strains.[1] This suggests that double networks may allow circumvention of the usual compromise between stiffness and strength. Failure performance can be maintained by keeping a constant crosslink density, while the modulus is enhanced through use of a double network.

Actually, the situation with double network rubbers may be even better. It is well known that the failure properties of natural rubber benefit significantly from strain crystallization. It has previously been shown that in natural rubber, the onset of strain crystallization transpires at lower strains for a double network than for a single network of equal crosslink density.[8] Potentially, such enhancement of strain crystallization can give rise to better failure properties in double network rubbers, notwithstanding their higher modulus.

EXPERIMENTAL

The rubber formulations are listed in Table I. Low temperature vulcanization was used to minimize degradation during the curing under tension necessary to produce double networks. Polysulfidic crosslinks must be avoided in the initial cure to prevent network rearrangement during the second curing. The compounds were mixed in a Brabender Prepcenter, with curatives added using a two-roll mill. Isotropic crosslinked films were prepared by heating at 70°C in a pressurized mold, followed by a second stage of crosslinking carried out in a vacuum oven at 80°C.

TABLE I

COMPOUND FORMULATIONS

	A	B	C
Natural rubber, SMR-L	100	100	—
Deproteinized NR, DPNR-CV	—	—	100
AgeRite Resin D[a]	1	0.5	1
ZnO	5	4	5
Stearic acid	2	1	2
Sulfur	1	0.5	1
Vanax A[b]	—	3.5	—
Morfax[c]	—	2.1	—
Altax[d]	0.5	—	0.5
Butyl Eight[e]	5	—	3
First curing	20 min @ 70°C	30 min @ 160°C	23 min @ 70°C
Second curing	120 min @ 80°C	—	180 min @ 80°C

[a] Polymerized 1,2-dihydro-2,2,4-trimethylquinoline.
[b] 4,4'-dithiodimorpholine.
[c] 4-morpholinyl-2-benzothiazole disulfide.
[d] Benzothiazyl disulfide.
[e] Activated dithiocarbamate.

During the second curing, specimens were deformed in order to yield a double network. For Compound A, tensile strips were cut from the once cured sheets, then held at an elongation of 340%. For Compound C, the initially cured sheets themselves were stretched 400% during the second cure, with samples subsequently cut from the central region of the sheets. Thus, the deformation geometries for A and C were approximately uniaxial and planar extension respectively. During each double network preparation, single network samples were simultaneously subjected to the same thermal history, but without any stretching. Assuming the crosslinking reactivity is independent of strain, the single and double networks should have identical crosslink densities. This assumption is reasonable, since the stress during crosslinking is low relative to the level necessary for bond distortion with consequent effect on chemical reactivity. An additional control sample, single networks of Compound "B" in Table I, was also prepared.

All mechanical results reported herein were taken at room temperature. The stress/strain data are at mechanical equilibrium, with two data points taken per day. Weights were suspended from the samples and the displacement of fiducial marks measured with a cathetometer. The force on a sample was alternately increased and decreased during the course of the experiment in order to verify reversibility of the data. Samples were maintained in a nitrogen atmosphere during these measurements.

Tensile strengths were measured with an Instron 4206 at 500 mm/min cross-head speed. To obtain a large number of results on Compound A, small rings (6.5 mm diameter) were used. This is a poor geometry for tensile strength measurements, given the variation in stress from the inner to the outer circumference. The strength determined using this ring geometry has been found to be lower by a factor of 3 to 4 than measurements made on dumbbells or strips. Only results for rings which failed away from the grip were used. For Compound C, test specimens were cut both parallel and perpendicular to the direction of stretching during curing. The sample dimensions conformed to ASTM D638 in these measurements.

Tensile fatigue testing (ASTM D4482–85) was carried out on Compound A using a Monsanto Fatigue to Failure Tester. The test specimens were cycled 1000 times prior to removal of the "set". The extension ratios were 1.61, 1.78, 2.01, and 2.36, with the minimum of the deformation cycle being zero stress.

RESULTS AND DISCUSSION

FAILURE PROPERTIES OF DOUBLE NETWORKS

Displayed in Figure 1 are equilibrium stress–strain data for Compound A comprised of respectively a single network and a double network with residual elongation equal to 200%. For the latter, the results in Figure 1 correspond to deformation parallel to the crosslinking strain. Although the two rubbers have equal crosslink densities, the double network has a significantly higher modulus. For example, at 10% strain the modulus of the double network is 1.6 MPa, versus a value of 1.0 MPa for A with a single network rubber. Such differences in modulus despite equal crosslink density have been reported previously,[8,9] although it is important to recognize that *higher* modulus occurs only for double networks with high residual strains.[1]

Also shown in Figure 1 are stress–strain measurements for a conventional, single network elastomer ("B" in Table I) having a 10% modulus equal to that of the double network rubber. In order to achieve the same modulus, the crosslink density of Compound B was made higher than for A. An interesting point is that at higher strains, the stresses for the double network are much higher than for single network of B; that is, double network formation is associated with a change in the shape of the stress–strain curve. This aspect of their behavior is brought out by analyzing the mechanical response in terms of the additive contributions of two independently acting networks.[1] Although strictly speaking the independent network assumption is not realistic — there is only one set of chains which simultaneously belong to "both" networks — calculations based on it yield results in good agreement with experiment.[1,10]

When higher modulus is attained in conventional elastomers by increasing the concentration of crosslinks, lower strength results. This is primarily due to lower hysteresis (*i.e.,* embrittlement). Since the network structure *per se* does directly affect hysteresis, it might be expected that double networks would have tensile strengths equivalent to single networks,
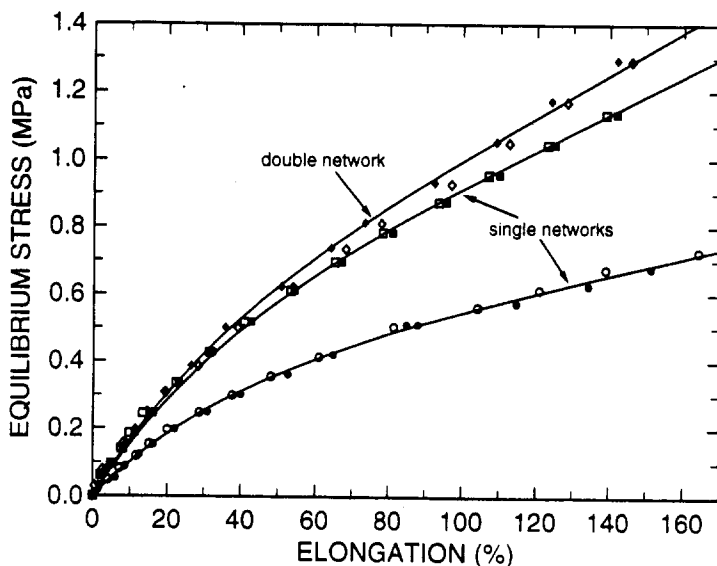

FIG. 1. — The stress measured at mechanical equilibrium for Compound A having a single (circles) and double (diamonds) network, along with data for a single network of Compound B (squares). Filled and hollow symbols represent measurements on different test specimens. Note that the double network has a higher modulus at all strains than the single network of equal crosslink density. Although sample B has the same modulus at 10% strain, at higher elongations the stress from the double network is significantly higher. The experiments were terminated well before the breaking stress of the rubbers.

notwithstanding the former's higher modulus. An earlier study[1] found that the tensile strength of double networks was slightly lower than the strength of a single network, but the differences were less than the experimental error. Since tensile strength data exhibit substantial scatter, measurements were carried out herein on more than 600 specimens of Compound A, to determine if significant differences exist between the strength of double and single network rubbers of equal crosslink density. The elongation was parallel to the curing strain.

The results, displayed in Figure 2 in the form of two histograms, make evident that at equal crosslink density the double network has lower strength than the single network. There is a corresponding decrease in the ultimate elongation, suggesting that the reduced strength reflects the extensibility of the first network. Since the residual strain in this double network is 200%, network strands associated with the first curing process are significantly more extended than the nominal macroscopic deformation.

Since the measured tensile strengths have a broad distribution, there is significant overlap between the two data sets in Figure 2. These data were fit to the double exponential function

$$P(\sigma_b) = \frac{1}{2s} \, e^{-\left|\frac{\sigma_b - \bar{\sigma}}{s}\right|}, \tag{1}$$

where $P(\sigma_b)$ is the probability of measuring tensile strength σ_b, s is the standard deviation of the distribution, and $\bar{\sigma}$ is the arithmetic mean value. Although there is no fundamental basis for using this particular distribution function, empirically it has been found to accurately describe tensile strength data for elastomers.[11] Figure 2 gives no indication of any fundamental difference in the behavior of the double networks in comparison to the conventional rubber. Other than a reduced strength, the distributions have very similar shape. This suggests that negligible "damage" is introduced in the material during its crosslinking in a deformed state.

If two materials differ significantly both in their intrinsic resistance to fracture and in the nature of their pre-existing flaws, their relative failure performance could differ depending on the failure properties measured to make the assessment. With this in mind, fatigue ex-
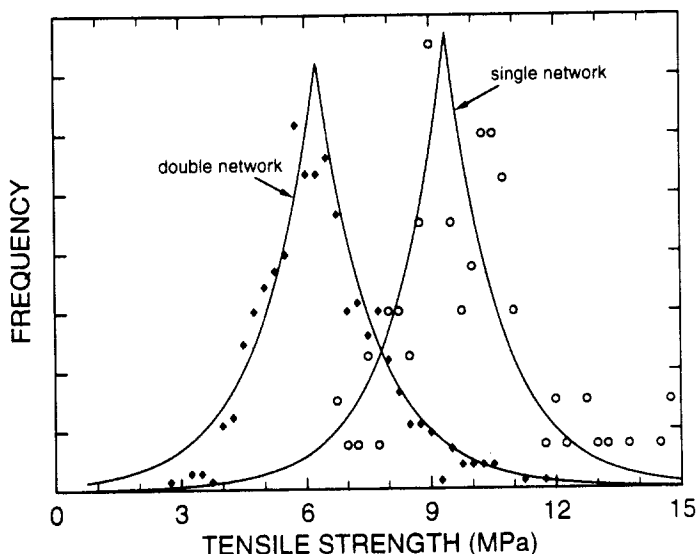

FIG. 2. — The distribution of micro-ring tensile strengths measured for a single (circles) and a double (diamonds) network (residual strain = 200%) from Compound A. Histograms were created by grouping the 600 individual measurements into ranges having a 0.5 MPa spread, with the solid curves representing fits of the data to Equation (1). The mean tensile strength of the single network exceeds that for the double network.

periments were carried out on Compound A. The results (Figure 3) show that when compared at equal strain energy, the double network has significantly longer fatigue lifetimes than the single network, at least for deformation along the direction of the curing strain. Notwithstanding its lower tensile strength, the double network rubber survives as many as ten times more cycles before failure. Since the modulus of the double networks is higher, this superiority would be even more substantial if the comparison in Figure 3 were made on the basis of equal strain.

The deformation in the fatigue experiments of Figure 3 was *fully relaxing*; that is, the minimum in the deformation cycle corresponded to zero stress. It is well known that under *nonrelaxing* conditions, NR and other strain crystallizing rubbers will exhibit markedly better fatigue performance in comparison to results obtained for fully relaxing deformations.[12-14] The superior performance of the double networks in Figure 3 may be a reflection of what is effectively a nonrelaxing condition. In this case, only the first-formed of the two networks comprising the material is under tension when the strain is minimum. This component of the composite network may stabilize the crystallinity induced at the front of growing flaws. Such crystalline material would inhibit the propagation of cracks, leading to longer fatigue lifetimes. An additional effect in NR double networks is that crystallization is induced at much lower strains than is the case for single networks having equal crosslink density.[8] This is consistent with the enhanced crystallization of natural rubber singly crosslinked while under stress.[15-17] The degree to which the longer mechanical fatigue life of double networks is due to strain induced crystallization, including any contribution from the presence of intrinsic strain in a double network at zero macroscopic stress, remains to be fully examined. Experiments on noncrystallizing rubbers would be instructive.

A second interesting aspect of Figure 3 is the larger scatter in the data for the double networks compared to the single networks. A large number of test specimens were required to obtain fatigue data at various strain energies. In order to minimize experimental error, for each strain measured in the fatigue experiment, test specimens were taken from separately prepared sheets. Thus, scatter in the measured fatigue lives reflects not only the imprecision of the measurement *per se*, but also irreproducibility in the preparation of double networks.
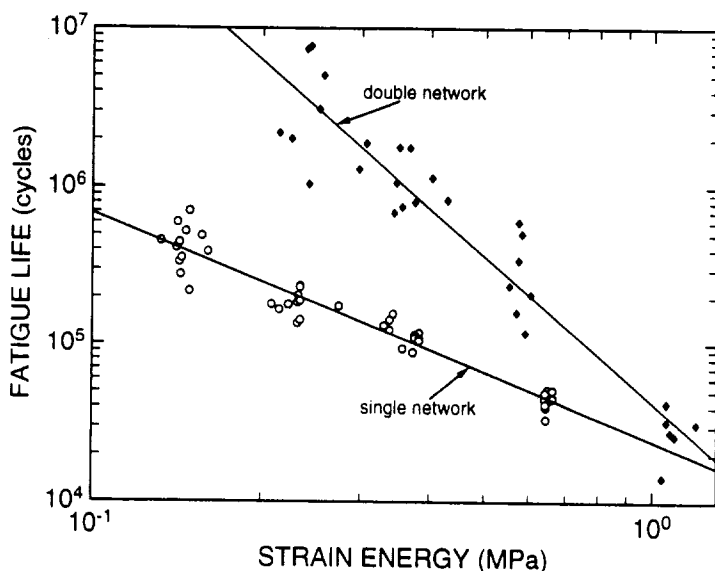

FIG. 3. — Mechanical fatigue lifetimes for Compound A having a single (circles) and a double (diamonds) network structure at elongations in the range of 60% to 140%. At each strain, test specimens from different cured sheets were used. The resulting subtle variations in the crosslink apportionment for the double network, contributes to the scatter in the measured fatigue lives.

Note that the data for the single networks has relatively small scatter. For these samples, variations in the first cure step are unimportant, since the second vulcanization depletes all the curative; the same final state of cure is attained. While it is true that the double networks also have the same final crosslink density, the apportionment of crosslinks between the first and second networks is sensitive to the details of the time and temperature of the first curing step. This crosslink apportionment has a significant effect on the properties of the double network. It has been previously demonstrated[1] that a double network is not uniquely defined by its residual strain. Both the crosslink apportionment and the strain during the second crosslinking are important. Double networks having the same residual strain, but attained through different crosslink apportionments and crosslinking strains, can exhibit markedly different mechanical properties. For this reason, the production of elastomers with double networks is inherently less precise than conventional rubber processes.

ANISOTROPY OF THE MECHANICAL PROPERTIES

The data in Figures 1–3 all refer to measurements made parallel to the direction of elongation during the second crosslinking; however, it is known that double network elastomers are inherently anisotropic. They are birefringent in the absence of stress[8] and have directionally dependent moduli.[9,18] Rubbers were made using the Formulation C in Table I, which differs from A primarily in the substitution of deproteinized natural rubber for SMR-L. In Figure 4, equilibrium stress–strain data are displayed for a single network of Compound C, along with two double networks. The latter were prepared by a second curing of stretched films, followed by cutting of individual test specimens in both the parallel and perpendicular directions. Thus, the deformation during the second network formation was pure shear.

Due to differences in the exact thermal history during the second crosslinking, double networks of Compound C, while nominally identical, exhibited different residual strains (= 183% and 175%) and different mechanical properties (Figure 4). Nevertheless, consistent with the data in Figure 1, the modulus in the direction parallel to the cure extension is always higher than the (isotropic) modulus of the single network rubber having equal cross-
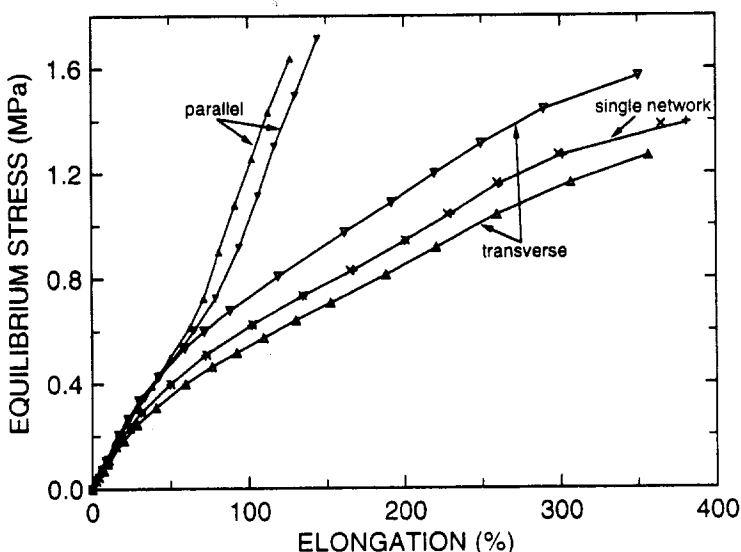

FIG. 4. — Mechanical equilibrium results for Compound C having a single (+++, ×××) and a double network (△△△ for I and ▽▽▽ for II in Table II). The latter differed in their crosslink apportionment and residual strain, giving rise to the differences in stress–strain behavior. The solid symbols refer to data measured parallel to the strain during crosslinking, while the hollow symbols corresponds to measurements transverse to the crosslink extension.

TABLE II

COMPOUND C

	Residual elongation	Tensile strength (MPa)
Single network	0%	24.2 ± 4.3
Double network I (parallel)	183%	9.0 ± 3.4
Double network I (transverse)	183%	20.2 ± 2.9
Double network II (parallel)	175%	14.7 ± 3.4
Double network II (transverse)	175%	21.2 ± 2.9

link density. This dependence of the parallel mechanical properties on the details of double network preparation is predicted by models assuming independently acting networks.[1] The modulus transverse to this direction is seen in Figure 4 to be significantly lower, and can even be less than that of the single network.

In Table II are listed the tensile strengths measured for the Compound C networks. The smaller values for the double networks in the parallel direction are consistent with the data in Figure 2, which were obtained with a ring geometry. Presumably ring specimens fail at their weakest point, which from Table II is evidently realized in the parallel direction. The most interesting result in Table II is the finding that double networks" tensile strength perpendicular to the curing strain is roughly equal to the single network's tensile strength.

SUMMARY

High residual strains are achieved in double network elastomers by having a large proportion of the crosslinking take place during the second cure, and by carrying out the latter at high strains. In the direction parallel to the cure strain, double networks with high residual strains exhibit a low strain modulus that is higher (by 60% herein) than single networks of equal crosslink density. At higher strains, the relative stiffness of the double network rubber is even greater. This elevation of modulus is accompanied by a modest decrease in tensile strength measured in the parallel direction. However, at least for natural rubber double networks, the fatigue lifetime for relaxing deformation is substantially higher. In the direction transverse to the cure strain, both the modulus and strength of a double network is much closer to that of the single network.

Although for the laboratory studies described herein deformations during curing were limited to elongation, obviously other, and more complicated, geometries can be used. In addition, the benefits of nonrelaxing crack growth conditions extend to other deformation modes, such as compression and shear.[12] Since double networks can be implemented with only modest alteration of existing processing techniques, their utility extends to any application where stiffness and strength are relevant. Particularly when advantage can be taken of anisotropy of the mechanical properties, double network rubbers offer the potential for improved performance.

ACKNOWLEDGEMENTS

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