

ORIENTATION EFFECTS IN RUBBER DOUBLE NETWORKS*

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INTRODUCTION

Orientation and crystallization are among the primary means for increasing the modulus and strength of materials comprised of flexible chain polymers. The attraction of employing orientation to enhance crystallization and mechanical properties is tempered by its non-equilibrium nature in flexible chain polymers. The configurational freedom of flexible chains facilitates processing; however, this flexibility also confers instability to the orientation so often an objective of the processing. Although rigid rod polymers spontaneously orient, a consequence of their lack of conformational freedom is an inherent lack of processibility. The attainment of thermodynamically stable orientation in a flexible chain polymer has obvious attraction.

The network formed when a rubber is crosslinked will have an equilibrium set of chain configurations. These configurations are usually associated with a macroscopic state of zero strain, since this corresponds to a condition of zero stress. When the rubber is cured while away from elastic equilibrium, however, configurations prevailing during crosslinking will shift the subsequent equilibrium state away from zero strain¹⁻⁸. For example, if a rubber is strained and then immediately quenched into the glassy state in order to suppress flow and relaxation, crosslinking of the oriented, but entangled, chains will create a pair of networks. The initial network is comprised of the entanglements responsible for the plateau modulus of uncured rubber, while the second network consists of the covalent crosslinks. This procedure has been employed by various investigators attempting to elucidate the contribution of trapped entanglement constraints to the mechanical behavior of crosslinked rubber⁹⁻¹⁷. These experiments have been interpreted as indicating that the modulus of an elastomer is significantly augmented by trapped entanglements. A putative "double network" is formed, possessed of dimensions and exhibiting a modulus which represent the competition between the physical and the chemical crosslinks. Actually, the existence of trapped entanglements *per se* is in dispute, with the mechanism of chain interaction alternately viewed as arising from spatial constraints on the domain of junction fluctuations, rather than actual knotlike entanglements¹⁸⁻²³.

The mechanical behavior of a rubber comprised of crosslinks formed under various conditions of strain can be described in terms of the additive contributions of each such independently acting network^{1,2,4,8}. Of course, the elastic response of a composite network can still then only be described as accurately as the rubber elasticity models used for single networks.

The consequence of network formation in a strained state on the isotropy of the resulting mechanical response has been an area of confusion. Early theories of double networks employed classical models for which the differential modulus is constant. This leads to the

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prediction that a double network will be mechanically isotropic, notwithstanding the residual strain (permanent set) it exhibits after the final crosslinking^{1,2,4}. The predictions of isotropy were seemingly confirmed by the observation of uniform swelling of double networks². Swollen networks, of course, generally exhibit phantomlike network behavior, with a nearly invariant differential modulus^{24,25}. Anisotropy in double networks arising specifically due to deviations from Gaussian statistics as network chains approach full extension has been discussed^{5,6}. Actually, double networks are inherently anisotropic; however, this anisotropy is only anticipated theoretically by models which predict a strain-dependent modulus.

This report describes preliminary efforts to utilize double networks as a means to alter the orientation and elastic behavior of elastomers based on natural rubber. Results concerning the influence of such a network structure on the mechanical and crystallization behaviors are presented.

EXPERIMENTAL

MATERIALS

Natural rubber (SMR-L) samples were mixed with various levels of dicumyl peroxide (Varox DCP-R, R. T. Vanderbilt Co., Inc.) on a two-roll mill. After the initial curing of the rubber sheets (while unstrained) to partially react the available peroxide, the sheet was divided prior to a second stage of crosslinking, the latter done in a vacuum oven. Double networks were prepared by carrying out this second crosslinking while the rubber was uniaxially extended. A strained state was maintained by holding the rubber between aluminum plates, which avoided stress concentration and problems with fracture. No strain crystallization was anticipated at the temperatures of this second stage crosslinking (150°C). The stretch ratio of the samples during curing, denoted by α_0 , was determined from fiducial marks. Sample dimensions prior to orientation were typically 12 cm \times 4 cm \times 1.5 mm.

To provide a control, a second portion of the initially-cured sheet was crosslinked a second time simultaneously with each double network; thus, samples consist of pairs of single (S-) and double (D-) networks of equivalent overall crosslink densities, the value of the latter deduced from the time and temperature of the curing. Note that the usual means

TABLE I
SINGLE AND DOUBLE NETWORK CHARACTERISTICS

Sample	$v_1^a \times 10^4$	$v_2^a \times 10^4$	α_0^b	α_r^c	α_{xtal}^c
S-1	2.8	4.4	1.0	1.0	3.3
D-1	2.8	4.4	4.0	2.1	2.8
S-2	1.0	3.3	1.0	1.0	3.1
D-2	1.0	3.3	4.0	2.1	2.2
S-3	1.0	7.2	1.0	1.0	3.1
D-3	1.0	7.2	4.0	2.7	1.9
S-4	1.0	4.1	1.0	1.0	na
D-4	1.0	4.1	3.0	2.4	na
S-5	1.0	4.1	1.0	1.0	na
D-5	1.0	4.1	5.0	3.5	na
S-6	1.0	4.1	1.0	1.0	na
D-6	1.0	4.1	7.0	4.4	na

^a Crosslink density determined from Flory-Rehner equation for single network swelling in toluene. v (mol/cm³) = $\rho/2M_c$, $\rho = 0.90$ g/cm³, $\chi = 0.39$. Double networks were assumed to have the same total crosslink density as the corresponding single network.

^b Initial and residual elongation, $\alpha = L/L_0$.

^c Extension at which strain-induced crystallinity becomes evident from the magnitude of the stress relaxation time.

to quantify crosslink density, *e.g.*, from swelling or equilibrium modulus, are inappropriate for double networks given the presumed role of the network structure itself on these quantities. A central assumption herein is that the chemistry of the peroxide crosslinking is independent of a rubber's state of strain. The various samples are listed in Table I, along with their respective residual extension ratios, defined by $\alpha_r = L/L_0$, where L is the length after final curing and re-equilibration and L_0 is the initial length, achieved for various second-stage cure conditions. Of course, for all single networks α_r is equal to unity.

MECHANICAL TESTING

Stress-strain testing was carried out with an Instron 4206 and Hewlett-Packard 9000 data acquisition computer. Stepwise stress-strain data were collected by extending samples at room temperature to a given strain, then allowing equilibration until the load decay did not exceed 5 g during a 15 min period. The deformation of the test specimens was measured using a Wallace optical (noncontacting) extensometer. This eliminates errors due to the constraint imposed by clamping the sample, as well as from any slippage in the grips. These errors contribute in opposite fashion to the measurements. Figure 1, which shows a comparison of strain measurements simultaneously obtained using the extensometer and based on grip separation, illustrates the consequence of slippage on the stress-strain curve.

WIDE-ANGLE X-RAY

Diffraction photographs were obtained using a Philips X-ray generator with Ni-filtered Cu $K\alpha$ radiation. Prior to exposure, the samples were strained and allowed to completely relax for a time period deduced from mechanical stress relaxation.

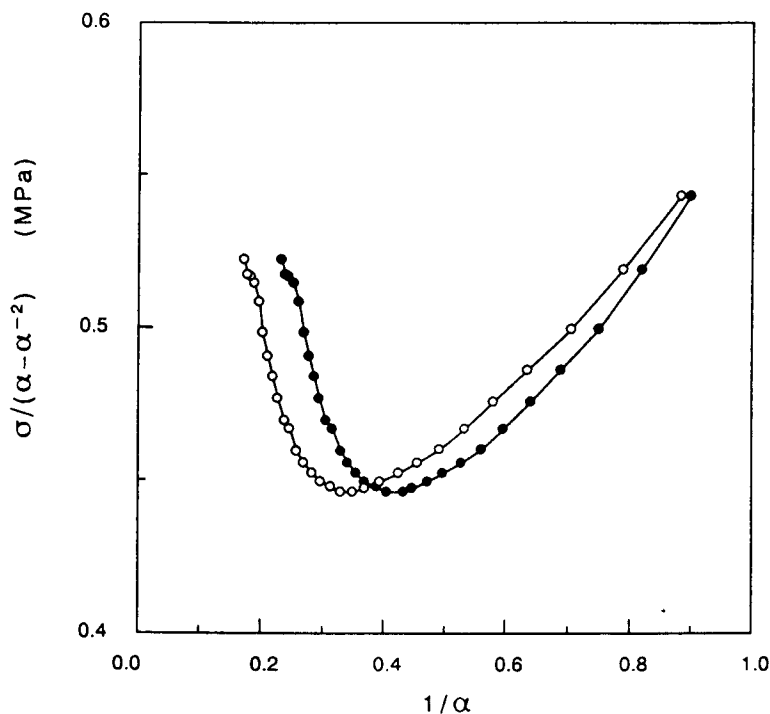


Fig. 1.—A comparison of the extension determined using a noncontacting optical extensometer (filled circles) with the strain deduced from grip separation (open circles). The data represent elastic equilibrium values for a crosslinked SMR-L specimen, whose initial dimensions (in cm) were $12 \times 4 \times 0.15$.

BIREFRINGENCE MEASUREMENTS

Optical birefringence measurements were used to characterize the equilibrium residual orientation in double-network samples. Strain-induced birefringence data were also obtained for both single- and double-network samples. A Model 801 Polarimeter (Vishay Intertechnology, Inc.) was used to obtain birefringence data. For low levels of retardation, the Senarmont method of goniometric compensation was used to determine birefringence. At higher levels of retardation, typically above 200 nm, a null-balance Babinet-Soleil compensator was used. In all cases, sample geometry was the same as that used for the mechanical tests.

DIFFERENTIAL SCANNING CALORIMETRY

Calorimetry measurements employed a Perkin-Elmer DSC-2 (liquid nitrogen cooling) and TADS acquisition computer. Thermal crystallization experiments were performed by allowing samples to crystallize in a homemade temperature chamber ($\pm 0.5^\circ$ variation). Samples were crystallized at -25°C for periods ranging from 1 h to several days. For DSC measurements, the samples were removed from the freezer, quenched in liquid nitrogen, then transferred to the DSC cell (the latter maintained at -110°C during sample loading). A scan rate of $20^\circ\text{C}/\text{min}$ was used over a temperature range from -110° to 50°C .

RESULTS

RESIDUAL STRAIN

The data presented in Table I show that a significant amount of residual strain (as high as 340% elongation) can be achieved in double-network samples. As seen in Figure 2, for samples with the same cure history there is an almost direct proportionality between the strain during crosslinking and the residual strain, at least when strains are expressed in terms of the strain function of rubber elasticity theory,

$$f(\alpha) = \alpha - \alpha^{-2}. \quad (1)$$

Such proportionality reflects the balance between the two networks, wherein α_r represents the state at which the elastic energy of two networks sums to zero^{1,2,4,8}. To the extent that the modulus is independent of strain, linearity in Figure 2 would be expected. A rubber accurately described by affine or phantom network models should exhibit direct proportionality between α_0 and α_r . When this condition exists, it follows that the double network's modulus will be isotropic. As mentioned above, isotropy of the swelling reported for double networks is a consequence of the more phantomlike behavior obtained by diluting the network segments^{24,25}. Generally, and in particular for dry networks, the nonlinearity in Figure 2 and concomitant anisotropy of the mechanical behavior are anticipated for double network rubbers.

STRESS-STRAIN BEHAVIOR

In uniaxial extension, elastic equilibrium stress-strain data commonly conform to the Mooney-Rivlin equation^{21,25,26}

$$\sigma = f(\alpha)(2C_1 + 2C_2\alpha^{-1}), \quad (2)$$

where the stress σ is defined as the equilibrium force divided by the initial cross-sectional area. This expression is obtained from an empirical representation of the strain energy by a power series in terms of the strain invariants²⁶. The constant C_1 is often taken to represent the actual crosslink concentration, whereby C_2 captures the deviation from simple phantom or affine network behavior. The deviation may arise from the effect of strain on the effectiveness of neighboring segments to confine the thermal motion of the crosslink junc-

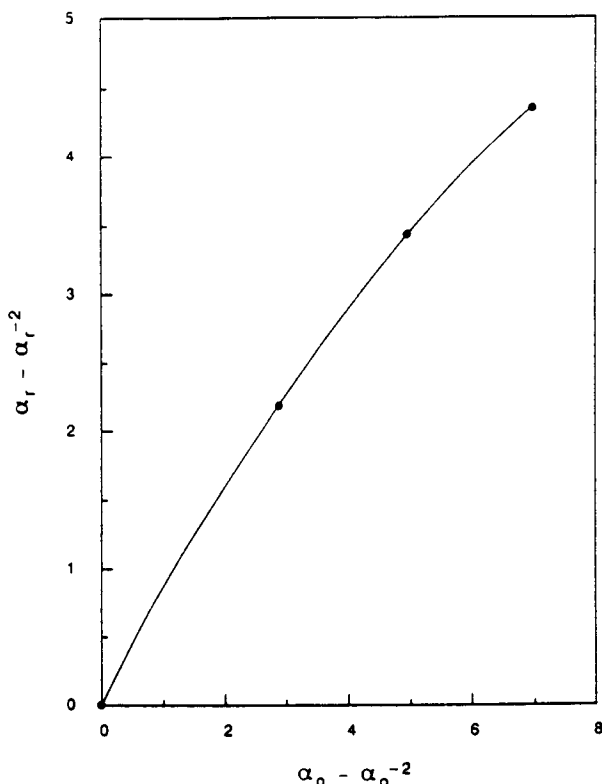


FIG. 2.—The dependence of residual strain on the strain during crosslinking for rubbers in which the respective concentration of crosslinks produced during the first and second crosslinking steps was maintained constant (see Table I). The strains herein are expressed in terms of the strain function of rubber elasticity theory.

tions¹⁸⁻²³. The inverse strain dependence in Equation (2) accounts for the amelioration by deformation of these constraints.

The equilibrium stress-strain isotherms for single and double networks (paired according to overall crosslink density, see Table I) are displayed in Figure 3. Each double-network sample shows a significantly higher modulus than the corresponding single network. This amplification parallels the magnitude of the residual strain in the double network.

The Mooney-Rivlin elastic constants obtained from the linear portions of the isotherms in Figure 3 are tabulated in Table II. In every case, the double network sample shows a larger C_1 and a smaller C_2 value than the corresponding single network. This concurs with an earlier comparison of single- and double-network rubbers, although the Mooney-Rivlin analysis therein was applied to nonequilibrium mechanical data⁵. The differences in single and double networks were attributed therein to non-Gaussian effects in the latter^{5,6}. A chain is "Gaussian" when its statistical end-to-end separation can be described by a Gaussian distribution function. If a double-network rubber has chain segments approaching the limit of their extensibility, then certainly the modulus of such a material would be amplified relative to rubbers that remain Gaussian while deformed. However, the residual strains herein are well below the level at which non-Gaussian effects are anticipated, hence the increased modulus of the double network is not in general a non-Gaussian effect.

A nonzero C_2 elastic constant implies a reduction in the differential modulus (defined as the ordinate in Figure 3). Consistent with this strain softening, a network with a residual strain is expected to be lower in modulus than a single network of equal crosslink density.

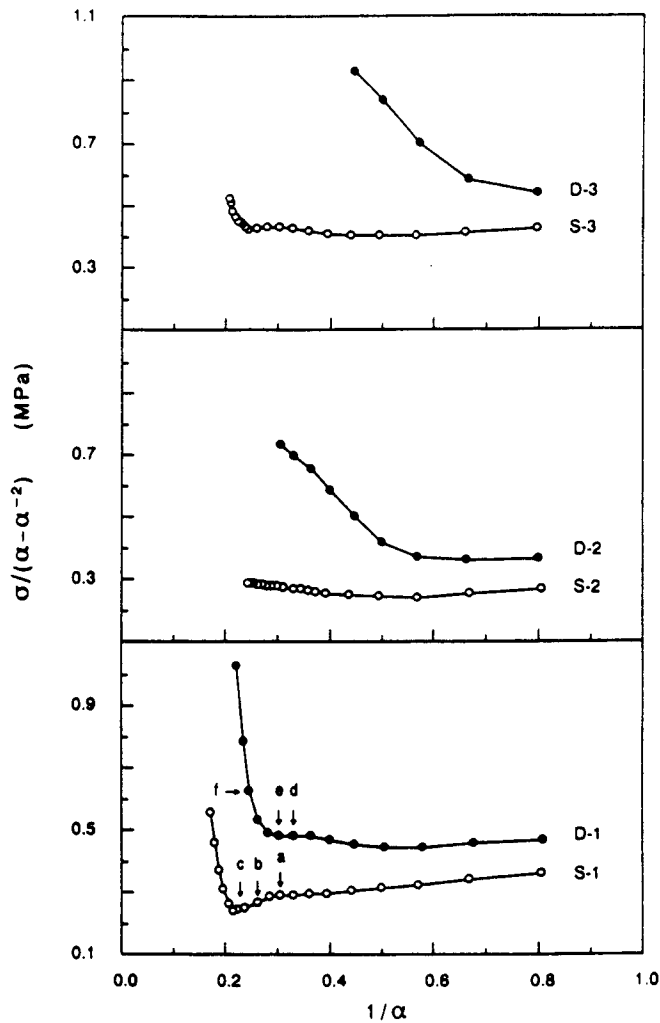


FIG. 3.—Stress-strain isotherms at 20°C for the single- and double-network samples listed in Table I. The double-network rubbers in all cases exhibit higher stresses than single-network samples having the same total crosslink density. The arrows for the data for S-1 and D-1 indicate the strains at which the x-ray diffraction photographs shown in Figure 7 were obtained.

Certainly, the observation of substantially higher moduli in double networks is unanticipated. It is noted that samples D-1 and D-2 had approximately the same level of residual strain (110%), but differed in their respective concentrations of first and second network crosslinks. Although the stresses at low strain are comparable for D-1 and D-2, at high elongations it is seen in Figure 3 that their behavior differs significantly. The strain at which the modulus markedly increases is lower for D-2, while its upturn has a lower slope. The set of chain configurations prevailing during second-stage crosslinking is different for D-1 and D-2. Although the balance of the elastic potentials results in equivalent residual strains, the rubbers evidently have consequential differences with respect to their distribution of chain trajectories and the spatial arrangement of crosslink sites. The details of these differences are presently unclear, but a further understanding will likely provide insights into the general problem of rubber elasticity.

TABLE II
MOONEY-RIVLIN CONSTANTS FOR NETWORKS

Sample	C_1	C_2
S-1	0.104	0.088
D-1	0.192	0.050
S-2	0.088	0.056
D-2	0.167	0.020
S-3	0.166	0.059
D-3	na	na

BIREFRINGENCE

The engaging feature of double-network rubbers is the stability of their orientation. Flexible chain molecules in the amorphous state above their glass transition temperature spontaneously assume a random configuration. By virtue of its network structure, however, a double network does not possess the unoriented isotropy conventionally associated with a rubber at equilibrium. Birefringence provides a direct means to characterize this orientation.

The birefringence measured at zero stress for double-network samples D-4, D-5, and D-6 (Table I) are displayed in Figure 4. These rubbers have the same crosslink densities (both in the first and the second networks), such that the different α_r values are due only to differences in α_0 . As expected, the inherent orientation, as reflected by the birefringence of the rubber, increases with an increasing level of residual strain. More interestingly, the level of birefringence is quite low, given the magnitude of α_r . Displayed in Figure 5 is the equilibrium birefringence measured at various elongations for a single network and for the corresponding double network rubber. The intercept for D-6 in Figure 5 is much less than the birefringence exhibited by either S-6 or D-6 at elongations well below the residual strain of the latter. Clearly there is no correspondence between levels of macroscopic and microscopic orientation, notwithstanding the correlation between birefringence and α_r seen in Figure 4.

The possibility exists that scission events, promoted by the straining at elevated temperature during second network formation, might reduce the effective crosslink density of the first network. This would be consistent with low birefringence in double-network samples,

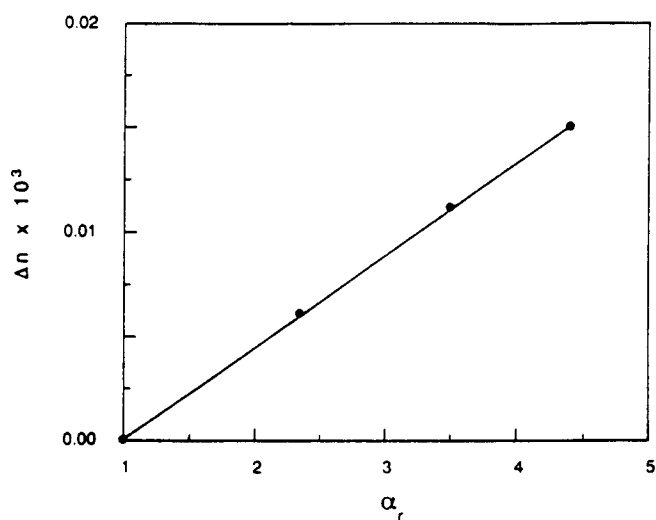


FIG. 4.—The birefringence measured for unstretched double-network samples of various values of α_r (see Table I).

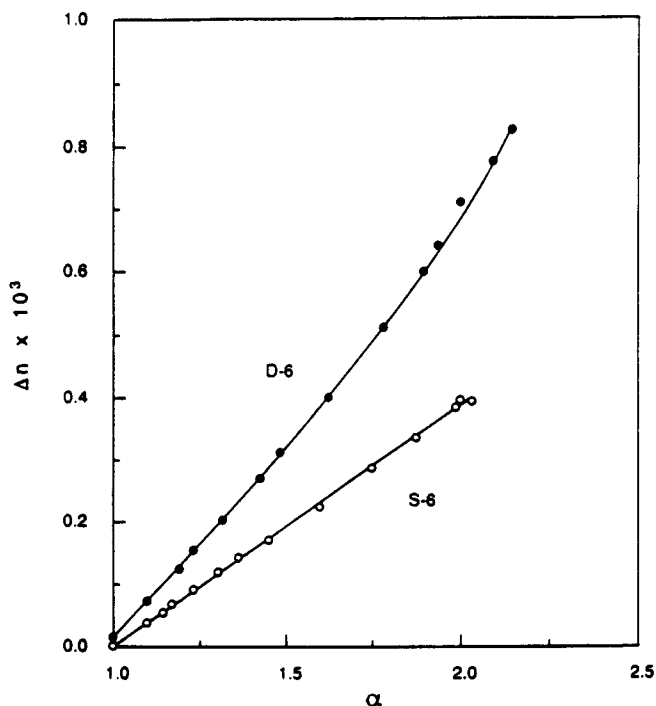


FIG. 5.—The relaxed birefringence of a single- and a double-network rubber at various elongations. This strain-induced birefringence greatly exceeds the inherent birefringence of the double networks. The respective stress-optical coefficients for single and double networks of equal crosslink density were roughly comparable.

but at odds with the substantially higher modulus of the double networks. The contribution of chain scission and reformation processes on stress relaxation and the permanent set of rubber has been discussed^{1,3,27-29}. The absence of a reduction in the slope in Figure 4 at higher α_0 , as well as some preliminary results obtained by utilizing room temperature gamma-ray crosslinking to form the second network, provided no indication that the low birefringence of thermally crosslinked double networks herein is related to chain scission.

Composite network models all predict that the elastic energy will be the summation of the independent contribution from each component network^{1,2,4,8}. It has been shown, however, that correlation effects between crosslink segments cause departures from additivity in the structure factor of composite network chains, particularly for length scales exceeding the length between crosslink junctions⁸. Nevertheless, diminution in the level of microscopic orientation is not seen to be a consequence of such correlation effects; this aspect of double-network behavior requires further examination.

ORIENTATIONAL CRYSTALLIZATION

The residual orientation of a double network is expected to facilitate strain-induced crystallization. It is tempting to seek evidence for such an effect in the stress-strain data of Figure 3; however, a tenuous connection exists between the shape of a Mooney-Rivlin curve and the occurrence of strain crystallization. Figure 6 shows equilibrium stress-strain data for a series of singly crosslinked NR networks plotted according to Equation (2). The stress-strain isotherms show a linear region at low strains followed by a gradual upturn in the modulus with increasing extension, in agreement with many previous results for natural rubber^{6,25,30-32}. At high extensions, these rubbers crystallize. For the intermediate crosslink densities in Figure 6, the modulus exhibits a negative deviation upon crystallization. This is a well-known instance of LeChatelier's principle, whereby crystallization effected by the

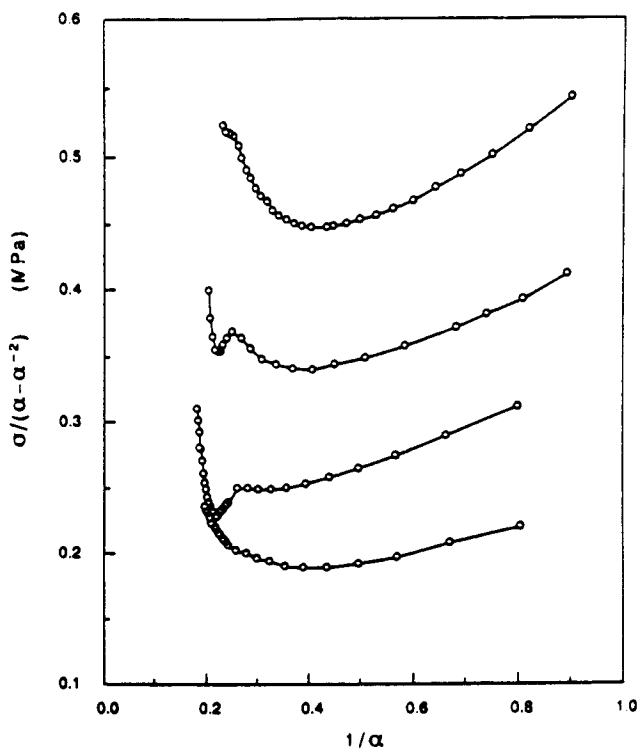


FIG. 6.—Stress-strain isotherms at 22°C for SMR-L gum rubbers crosslinked once in the unstrained state with varying levels of peroxide. All rubbers crystallize when stretched within the range shown here. This crystallization is made apparent by a downturn in the Mooney-Rivlin curve only for the rubbers of intermediate crosslink density.

application of stress will in turn reduce the stress³³⁻³⁶. As demonstrated by x-ray measurements, however, all these samples crystallized upon stretching, notwithstanding any absence of minima in Figure 6. Crystallites can restrict the flexibility of the network chains, acting as macroscopic crosslinks^{33,37}. This, along with any non-Gaussian effects and finite chain extensibility, may occasion the upturns in the moduli seen in Figure 6. Evidently, for samples with the extremes in crosslink density, this amplification of the stress obscures any minima in the stress-strain relationship. As a result, the onset of strain-induced crystallization can not be inferred from the shape of stress-strain isotherms^{37,38}.

X-ray diffraction photographs for S-1 and D-1 obtained at the strains indicated by arrows in Figure 3 are displayed in Figure 7. Certainly there is some ambiguity in determining from x-ray scattering the onset of strain-induced crystallization; however, the difference between the single and double network in this regard is significant. S-1 exhibits at 290% elongation x-ray evidence of crystallinity, while this becomes apparent for D-1 at about 220%.

In Figure 8 is shown for the various rubbers the dependence on strain of the time period required for equilibration of the stress after imposition of a step-increase in strain. Indicated by arrows are the strains at which evidence for crystallinity became apparent in x-ray diffraction photographs. It is observed that the increase in the time over which the stress decays, associated with the onset of crystallization, is a more sensitive measure of crystallization than x-ray measurements. By either measure, however, the onset of orientational crystallization transpires at lower strains for a double network as compared to the single network of equivalent crosslink density. It is not unexpected that the orientation produced with a double network promotes strain crystallinity. In Table I the extension at which strain-induced crystallization occurs, denoted as α_{xstal} , can be seen to be consistently lower in the double networks relative to single networks. This decrease varies from 50 to 120% strain

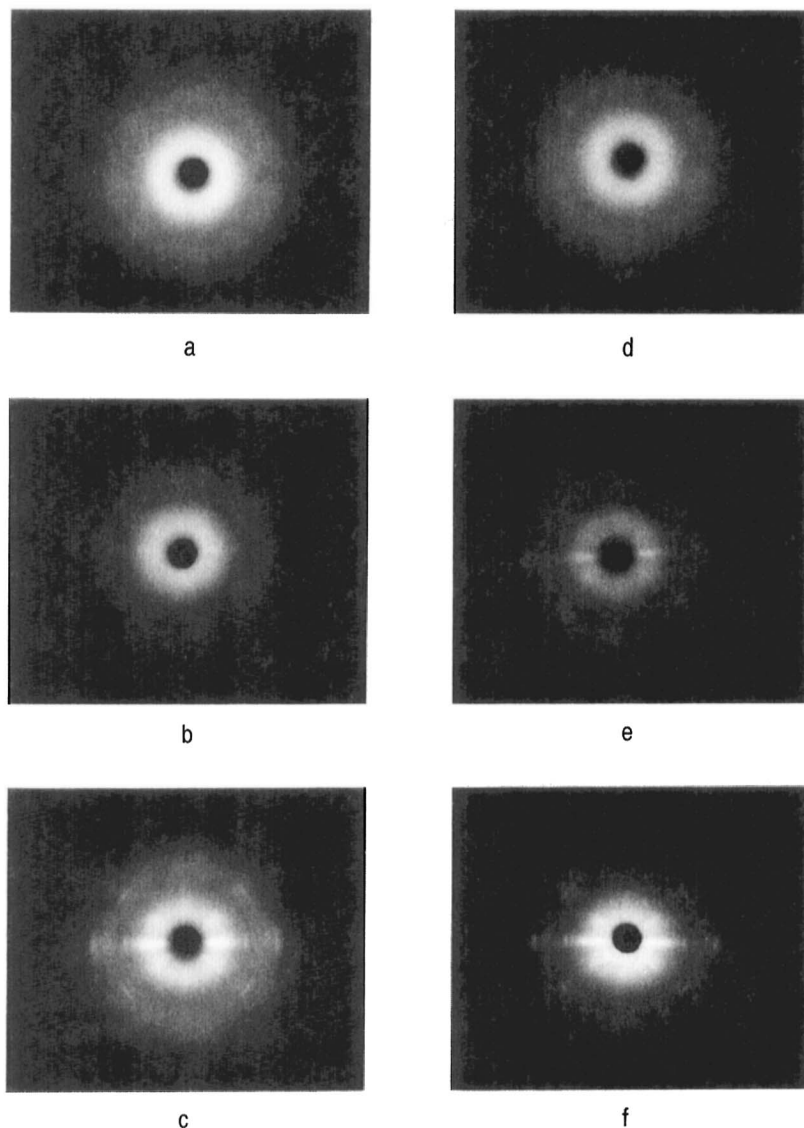


FIG. 7.—Wide-angle x-ray diffraction photographs of Sample S-1 at (a), 229%; (b), 281%; and (c), 300%; and D-1 at (d), 204%; (e), 229%; and (f), 279% elongation. The arrows in Figure 4 correspond to these strains.

in rough correspondence to the distribution in crosslink densities between the primary and secondary networks. Certainly, the enhancement in strain crystallizability of the double networks is substantially greater than would be predicted from the low levels of birefringence they exhibit while unstrained (Figures 4 and 5).

THERMAL CRYSTALLIZATION

Manifestations of orientation are not usually limited to crystallization under stress. It is expected that orientation will enhance nucleation rates, and thereby effect more rapid thermal crystallization^{39,41}. Moreover, since the thermodynamic stability of the crystalline phase relative to the liquid state pertains⁴²⁻⁴⁵, the melting point of the double networks is expected to be higher given the inherent orientation of their liquid state. Of course, crosslinking *per*

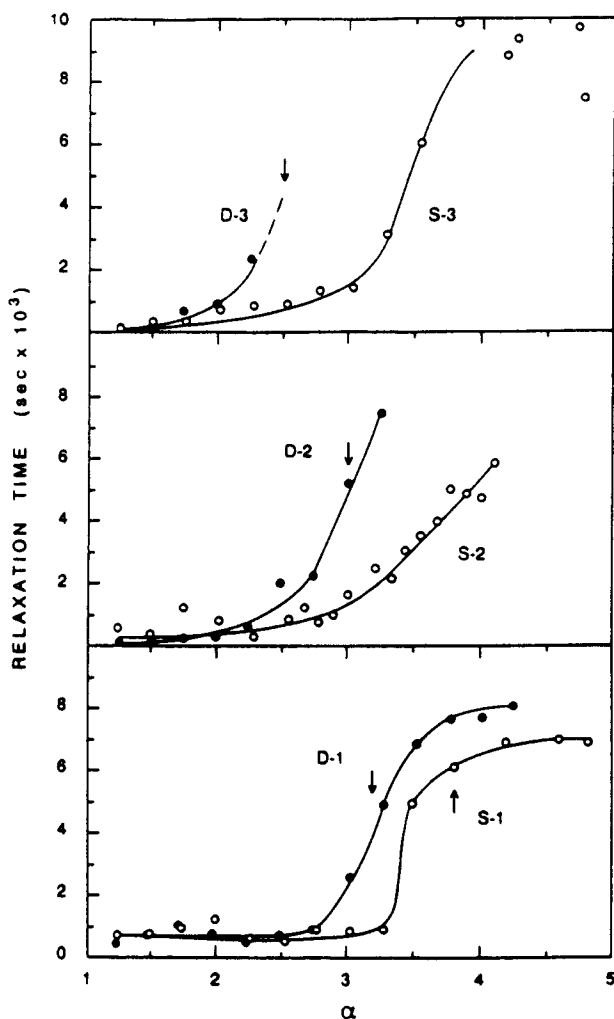


FIG. 8.—The time period required for complete relaxation of the stress for samples at various strains. The increase at high strain provides a sensitive measure of the onset of orientation-induced crystallization. Indicated by the arrows is the strain at which crystallinity could clearly be perceived from x-ray diffraction measurements. By either measure, the induction of crystallization is seen to transpire at significantly lower strains in the double networks than in single networks of equivalent crosslink concentration.

se will inhibit crystallization (both the extent and thermodynamic stability of), as has been shown for polybutadiene⁴⁶, polyethylene⁴⁷, polytetrahydrofuran⁴⁸, and natural rubber⁴⁹.

Single- and double-network pairs were annealed unstressed at -25°C for varying time periods, with the samples subsequently analyzed calorimetrically. The melting point of all samples, with either a single or double network, was found to be $1.0 \pm 1.0^{\circ}\text{C}$. No evidence was obtained of any augmentation in the thermodynamic stability of the crystalline phase by virtue of the orientation of the double networks.

The measured heats of fusion are displayed in Figure 9. The double-network rubbers crystallized no faster, and perhaps actually slower, than single networks of equivalent crosslink density. This is surprising in view of the presumed effect of orientation on crystallization rate, as well as the room-temperature crystallization enhancements described above (Table I and Figure 8). Crystallization at roughly 45° above the glass transition and only 25° below the melting point is expected to be controlled more by the incidence of

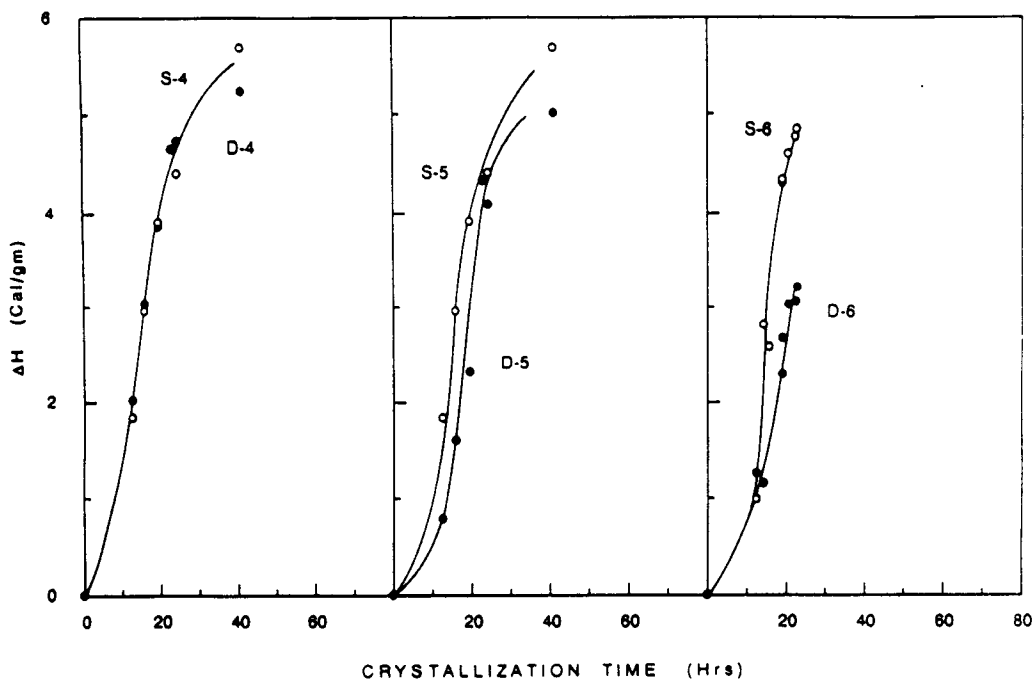


Fig. 9.—Calorimetry measurements of the heat of fusion for single and corresponding double networks annealed in the unstressed state for various time periods at -25°C . The data suggest an absence of measurably higher crystallization rates in double networks despite their inherent orientation.

nucleation than by crystal growth rates. The apparent induction period prior to crystallization seen in Figure 8 is consistent with this expectation.

It is viewed as an anomaly that the thermal crystallization of single- and double-network samples was found to be very comparable. Crosslinking in a strained state has been shown in both natural rubber⁵⁰⁻⁵² and polyethylene⁵³ to markedly influence crystallization behavior. Additional experiments at various crystallization temperatures are clearly needed to ascertain the contribution of a double network structure to unstressed crystallization.

SUMMARY

The utilization of network structure to impart stable orientation to a rubbery material has been largely unexploited to date. It is demonstrated that the presence of a double network will amplify both the modulus and strain crystallizability of an elastomer, presumably without the disadvantages encountered in achieving these through simple increases in crosslink density.

The high residual strains obtained *via* double-network formation are accompanied by surprisingly low levels of birefringence. The extent of molecular orientation necessary to engender high residual strain is evidently quite low, at least in so far as the former is reflected in a bulk macroscopic measurement such as birefringence. This low equilibrium birefringence, along with the absence of any measurable thermal crystallization effects, indicate that double networks are actually not highly oriented. As seen from their higher moduli and higher strain optical coefficients relative to single networks, and from their enhanced strain crystallizability, double networks are evidently very orientable. Investigation of this aspect of the behavior of double networks would likely prove fruitful, not only concerning these materials, but also with regard to obtaining a broader understanding of rubber elasticity.

While the enhancement of strain-induced crystallization might suggest that rubbers with double networks will exhibit superior failure properties, this remains to be demonstrated. The crystallization results described herein clearly raise more questions than can presently be answered concerning the behavior of rubbers with double networks.

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