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Swelling of Rubber under Nonuniform Stresses and Internal Migration of Swelling Liquid When the Stresses Are Removed

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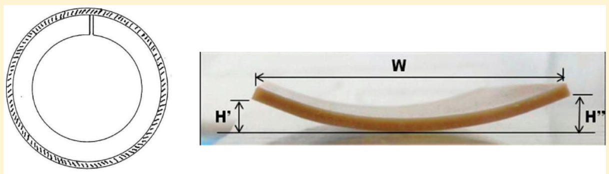
ABSTRACT: As shown by Treloar, the degree of swelling of a rubber sample is strongly affected by applied stress. His work suggests that the degree of swelling will vary from point to point in a sample, in accordance with the local stress field. Thus, when rubber sheets are bent, they are expected to swell more on the tension side and less on the compression side, and when the bending constraint is removed, recovery toward the initial flat state is expected to be only partial at first and then followed by a slow further recovery. These effects are explored here for natural rubber sheets swollen by dodecane. The measured "set" following release from bending is found to be in accord with simple swelling theory. The time dependence of later recovery is shown to be in agreement with the rate of diffusion of the swelling liquid. It is concluded that internal migration of compatible liquids will cause temporary delays in deformation kinetics and make a significant contribution to energy losses. Also, the bending experiment itself appears to provide a simple and generally applicable method for determining the internal diffusion coefficients of absorbed liquids.



Swelling and release of a bent rubber strip

1. INTRODUCTION

Lightly cross-linked rubber absorbs a surprisingly large amount of a compatible liquid. The ratio Q of the swollen volume to the unswollen volume may be as large as 5—the swollen volume being given approximately by the sum of the volumes of rubber and liquid. When a tensile stress (or, more generally, any system of stresses that tends to increase the volume) is applied, then the amount of liquid absorbed may be increased substantially. The present study is based on this effect. It was analyzed by Treloar[1,2] and shown to follow from rather general thermodynamic principles: the increase in entropy on mixing rubber and liquid molecules will favor swelling, but the stretching of molecular strands in the rubber network will limit it. The two terms are in balance at equilibrium, but the equilibrium can be shifted toward higher degrees of swelling by applying external stresses that themselves have a dilating tendency. If the applied stresses have a net compressive effect, then the equilibrium degree of swelling is reduced. It should be noted, however, that a uniform compression (a hydrostatic pressure) or a uniform dilatant stress (a negative pressure) will have virtually no effect on the degree of swelling because the rubber and liquid are both effectively incompressible in bulk.

It follows from Treloar's analysis that if a rubber sample is stretched unevenly, the degree of swelling will vary with position in accordance with the local stress field. Moreover, if the stresses change with time, the swelling liquid will migrate internally. However, this readjustment will be slowed by the finite rate of internal diffusion of the liquid. For simplicity, we consider here the changes that occur in the shape of a bent strip of rubber swollen in a slowly diffusing liquid and then having the bending stresses removed. Thus, the swelling liquid is absorbed initially to a greater degree in the outer (stretched) region than in the inner (compressed) region. Because the thickness of the rubber sheets used here is relatively small, swelling in the thickness direction and migration of solvent when the bending stresses are removed can be considered to take place under constrained conditions, with the length and width of the bent sheet remaining constant at the values attained in free swelling. Similar one-dimensional swelling processes have been examined by Southern and Thomas,[3] Alexander and Rabin,[4] and Kang and Huang,[5] with particular attention given to creasing of the free surface at high degrees of swelling caused by highly compressive stresses generated parallel to the free surface by the constraints. Treloar's assumption that the rubber network remains Gaussian in the stretched swollen state has been verified in one case[6] but shown to be incorrect when a phase transition occurs.[7] Valtier et al.,[8] in a detailed study of the process of absorption of a swelling liquid, observed higher rates of diffusion in regions where the material was stretched. However, stress gradients were not considered explicitly. In recent work by Suo and colleagues,[9,10] the dependence of the distribution of swelling liquid on stress gradients has been explored in detail, and the associated time dependence has been established. However, as far as we are aware, no previous work has dealt with release from applied stresses and recovery of shape of swollen samples.

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Measurements have now been made for sheets of lightly cross-linked natural rubber, swollen in a simple nonpolar liquid (dodecane) under a stress gradient caused by an imposed bending strain, and then released. First, the partial recovery that occurs when the bending constraint is removed is calculated from Treloar's theory of swelling of rubber under an imposed strain.[1,2] Then the protracted return toward the unstrained (straight) condition is compared with measured rates of diffusion of dodecane in natural rubber.[11] Reasonably good agreement is obtained in both cases. This suggests that a simple bending and recovery experiment is a useful method to examine the internal mobility of absorbed liquids. It should also be noted that internal migration of liquids could make a significant contribution to energy losses in rubber compounds subjected to varying stresses.

2. THEORETICAL CONSIDERATIONS

2.1. Equations for the Amount of Swelling. The basic relation between the volume swelling ratio Q of a cross-linked rubber sample and the applied stress t was developed by Treloar:[1,2]

$$t_1 = (RT/V_1)[F(Q) + AL_1^2/Q] \qquad (1)$$

with similar relations for stresses t_2 and t_3 in the perpendicular directions. In eq 1, L_1 denotes the ratio of the length in the 1-direction in the swollen, stretched state relative to that in the unswollen, unstretched state and the function $F(Q)$ represents the entropy and heat of dilution of rubber by the swelling liquid as a function of the volume swelling ratio Q:

$$F(Q) = \ln[1 - (1/Q)] + 1/Q + X/Q^2 \qquad (2)$$

where X is the polymer/solvent interaction parameter.

The term A ($= \rho V_1/M_c$) in eq 1 characterizes the elastic resistance of the rubber molecular network to expansion, where ρ is the density of the swelling liquid, V_1 is its molar volume, and M_c is the average molecular weight of network strands. Note that highly swollen rubber is assumed to obey a simple Gaussian (one-term) elastic strain energy function, as found experimentally.[12]

We now consider two special cases: first, swelling in simple extension, when the sample is swollen with the length L_1 held constant while the other two dimensions are unconstrained, and, second, swelling in constrained extension when the length and width dimensions, L_1 and L_2, are held constant at the values set up in free swelling, so that additional swelling under stress occurs only in the L_3 direction, when L_3 is increased. These results are then employed to calculate recovery when the L_3 stress is removed.

2.2. Swelling in Simple Extension. In this case, no stress is applied in directions 2 and 3, $t_2 = t_3 = 0$, and hence $L_2 = L_3 = (Q/L_1)^{1/2}$. Thus, from eq 1, $F(Q) + AL_2^2/Q = 0$, and

$$F(Q) = -A/L_1 \qquad (3)$$

Equation 3 relates the swelling ratio Q to the applied strain L_1. For free swelling, when all the stresses are zero, the corresponding volume swelling ratio, denoted Q_0, is obtained in terms of the swollen length $L_{1,0}$ as $Q_0 = L_{1,0}^3$. Calculated values of the swelling ratio Q as a function of the applied strain L_1 are obtained from eq 3 and compared in Figure 1 with Treloar's measurements[1,2] of swelling of a natural rubber sample in heptane and benzene, using a representative value of X for the rubber/solvent system of 0.4, and a value of A of 0.019, chosen to give the best fit for swelling by

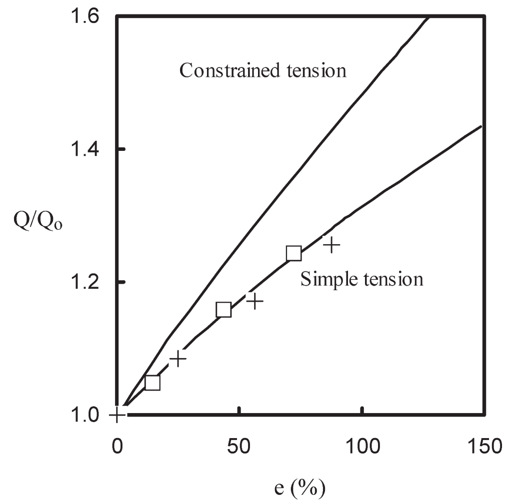

Figure 1. Increase in the volume swelling ratio Q, relative to the value Q_0 in the unstressed state, versus the imposed tensile strain e [$= (L_1 - L_{1,0})/L_{1,0}$]. Lower curve: calculated results for simple extension. Points taken from Treloar's data[1,2] for swelling with heptane (crosses) or benzene (squares). Upper curve: calculated results for constrained extension.

heptane. Plotted as the relative increase Q/Q_0 in the volume swelling ratio versus the imposed tensile strain e [$= (L_1 - L_{1,0})/L_{1,0}$], the results are seen to be similar for both solvents, even though the actual swelling ratios were quite different, and show an approximately linear dependence on tensile strain, the amount of swelling increasing by about 30% at an imposed strain of 100%. And, as shown by Treloar,[1,2] the experimental results are in remarkably good agreement with the theory.

On releasing the strain, all of the stresses become zero but the swelling ratio remains at Q. Thus, all three length ratios become $L_R = Q^{1/3}$. Comparing this to the original length $L_{1,0}$ in the swollen stress-free state, the residual strain e_r after releasing the imposed strain is obtained as

$$e_r = (L_R - L_{1,0})/L_{1,0} = (Q^{1/3}/Q_0^{1/3}) - 1 \qquad (4)$$

The sample is now overswollen and the excess solvent would eventually be expelled from the surface, but this is generally a slow process and the sample will exhibit the residual strain e_r, or "set", for some time. Values of residual strain e_r from eq 4 are plotted in Figure 2 as a function of the imposed strain L_1, using the swelling ratios Q and Q_0 calculated from eqs 1 and 2 for the two rubber/solvent systems studied by Treloar. The residual strain is seen to be approximately proportional to the imposed strain for small strains, less than about 100%, and is about 10% of the imposed strain in both cases. This appears to be a useful guide to the amount of recovery when stresses applied to swollen samples are removed, and it can be inferred that a similar result would be obtained with other swelling liquids. However, the results for other modes of deformation are somewhat different, as described next.

2.3. Swelling in Constrained Extension. In this case, the stretched state is attained by stretching in the 1-direction a sheet that was initially swollen uniformly, while simultaneously holding the length $L_{2,0}$ in a perpendicular direction unchanged, at the initially swollen length. The stress t_3 in the third direction is assumed to be zero. Thus, the new dimensions are L_1 (imposed), $L_2 = Q_0^{1/3}$ (held constant), and $L_3 = Q/Q_0^{1/3}L_1$ (from the relation for the swollen volume: $Q = L_1L_2L_3$). From eq 1, on putting

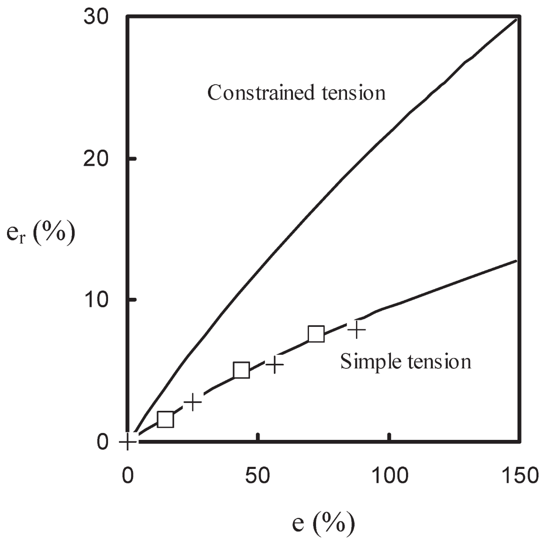

Figure 2. Residual strain e_r as a function of the imposed strain e. Lower curve: calculated from eq 4 for simple extension. Points taken from Treloar's data[1,2] for swelling with heptane (crosses) or benzene (squares). Upper curve: calculated from eq 6 for constrained extension.

$t_3 = 0$

$$F(Q) = -AL_3^2/Q = -AQ/(Q_0^{2/3}L_1^2) \qquad (5)$$

Swelling ratios predicted by eq 5 are compared with those in simple extension in Figure 1. They are seen to be considerably higher for a given imposed strain, but they still follow an approximately linear increase with applied strain.

When the applied strain L_1 is released, the stresses in both the L_1 and L_3 directions become zero, and the lengths L_{1R} and L_{3R} after release therefore become equal, while the length ratio L_{2R} remains unchanged.

Thus, the strain ratios become $L_{1R} = L_{3R} = (Q/L_{2R})^{1/2}$ and $L_{2R} = Q_0^{1/3}$.

Hence, $L_{1R}^2 = Q/Q_0^{1/3}$, and the residual strain e_r in this case is given by

$$e_r = (L_{1R} - L_{1,0})/L_{1,0} = [(Q/Q_0)^{1/2} - 1] \qquad (6)$$

where $L_{1,0}$ is the original swollen length in the 1-direction, $Q_0^{1/3}$. Calculated values of e_r are plotted in Figure 2 as a function of the imposed strain ratio e ($=L_1$). They are seen to be substantially higher than for samples swollen in simple extension.

3. MIGRATION OF A SWELLING LIQUID (DODECANE) IN RUBBER

We consider here the changes that occur in the shape of a bent strip of rubber swollen in a slowly diffusing liquid (dodecane) when the bending stresses are removed. The strip is assumed to be long and wide compared to its thickness, so that the strain gradient lies in the thickness direction. It is first swollen homogeneously and then bent into a circular arc and allowed to reach equilibrium. The swelling liquid will now be absorbed to a greater degree in the outer (stretched) region than in the inner (compressed) region. Because the distance is small in the thickness direction, these changes in the degree of swelling can be considered to take place under constrained conditions, with the length and width directions remaining constant.

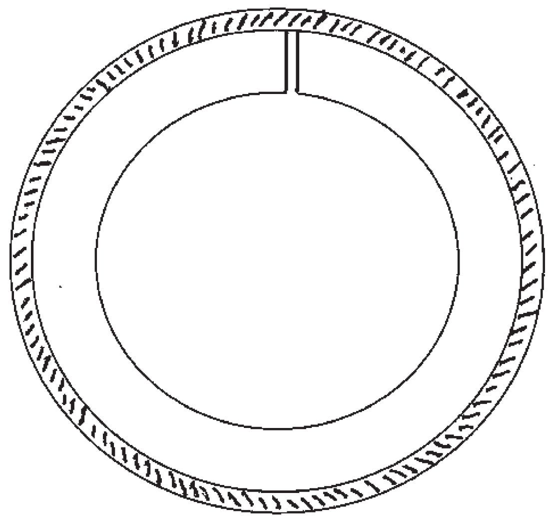

Figure 3. Sketch of experimental arrangement for swelling under constrained bending.

The mean radius of the bent strip is denoted R_0. On removing the constraint, the swollen strip returns to a less-bent shape, with a larger radius R, and then as the swelling liquid diffuses internally toward a homogeneous distribution, the strip slowly straightens.

The initial value of the ratio R_0/R gives the amount of "set" due to unequal swelling in the bent state and can be compared with the residual set e_r predicted by eq 6. The gradual increase in R as the strip straightens gives a measure of the rate of internal migration of the swelling liquid. Experimental details are given in the following section.

4. EXPERIMENTAL DETAILS

4.1. Measurement of Set and Recovery.

Strips were cut from molded sheets of soft vulcanized natural rubber with thicknesses of about 1 and 2 mm. The strip widths were generally about 25 mm, and the lengths were chosen so that a swollen strip could be accommodated within a plastic tube without being compressed in length (see Figure 3). The fully swollen state corresponded to a volume swelling ratio Q_0 of 3.6, similar to that reported previously for a lightly cross-linked sample of natural rubber, "mix A", in dodecane.[11] However, in studying recovery from swelling in the bent state, the degree of swelling was chosen to be less than the equilibrium value because initial observations indicated that some swelling liquid was exuded from the tension side of fully swollen sheets when the bent strip was released. Instead, samples were swollen to 70% and 90% of the equilibrium uptake of dodecane for the recovery experiments. No swelling liquid was seen to exude from these samples during the measurements of recovery.

Samples were swollen at a temperature of 50 °C to the chosen level and then bent by inserting them into a tube of suitable radius. They were then left to reach equilibrium at the same temperature, for a period about twice as long as the time required for swelling to the desired level. After removing the samples from the tube, they were allowed to recover in a heated chamber which contained pads moistened with dodecane to minimize evaporation during the slow recovery process. The mean radius of curvature R after release from the imposed bend was calculated from the average height H of the ends of the now partially bent strip above the horizontal plane on which the sample rested (see Figure 4) using the following relation obtained from the geometry of a circle:

$$R = L^2/8H + H/2 - T_s/2 \qquad (7)$$

where T_s is the thickness of the swollen sample. The radius R slowly increased with time as the sample straightened. Measurements were taken periodically to determine the time dependence of recovery.

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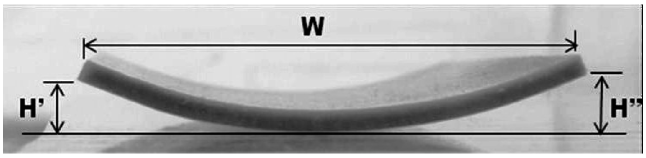

Figure 4. Photograph of swollen strip released from an imposed bend.

4.2. Minimizing the Effect of Gravity. A swollen strip, 110 mm long, was hung over a horizontal bar, and the difference d in height of the ends below the center of the strip was found to be 19 mm. The weight of the strip was 6.79 g, and its swollen width W and thickness T_s were 26 mm and 2.8 mm. Thus, the density of the swollen rubber was ~0.84 g/mL, and the force P of gravity, uniformly distributed along the length, was 67.2 mN. The equation for the displacement d of the ends of an elastic bar bent under a uniformly distributed force P is[13]

$$d = 5PL^3/384EI \tag{8}$$

where E is the modulus of elasticity and I is the moment of inertia of the cross section, given in the present case by $WT_s^3/12$. Thus, the modulus of the swollen rubber was obtained as 1.1 MPa. The droop d of test specimens of smaller length was then calculated, and a maximum acceptable length determined for which d would be negligibly small in comparison with the deflection due to "set". For example, the calculated droop for specimens with a swollen thickness of 2.9 mm is only about 0.5 mm when the length is 45 mm, and a similar value is calculated for a specimen with a swollen thickness of 1.6 mm and a length of 30 mm. Lengths of swollen strips used in the experiments were therefore chosen to be smaller than these values to minimize the effect of gravity.

4.3. Set Because of Other Causes. An unswollen sample was bent to a similar degree as the swollen samples and heated for a somewhat longer time to examine the amount of "set" that could arise from other causes. The set was found to be small, about 5%, and it did not change significantly after recovery periods of several hours. It was concluded that residual deformation as a result, for example, of chemical changes, might cause incomplete recovery but would not affect the observed time dependence.

5. EXPERIMENTAL RESULTS

Recovery of partially swollen strips from imposed bending is shown in Figures 5 and 6. R_0/R is the ratio of strains remaining in the released strip to the higher strains imposed by bending and is thus equivalent to the residual strain ratio, or set, e_r/e. For constrained extension, the value is therefore expected to be about 20% (see Figure 2). The experimental results in Figure 5 are much smaller than this because these samples were swollen to only about 70% of the fully swollen state, whereas in Figure 6, a sample swollen to 90% is seen to recover initially to about 20% of the imposed strain level, in reasonable agreement with the expected amount.

The dependence of the amount of recovery upon $(\text{time})^{1/2}$ in the initial stages of recovery, shown in Figures 5 and 6, is consistent with the mechanism of recovery being slow diffusion (migration) of swelling liquid toward a homogeneous distribution. Moreover, the slopes of the linear relations are in reasonable agreement with the diffusion coefficient determined directly from the initial rate of uptake of the same liquid by a thin rubber sheet, as discussed below. Measurements of weight uptake relative to the equilibrium amount are plotted in Figure 7 for a sheet of thickness T = 1.1 mm, bonded

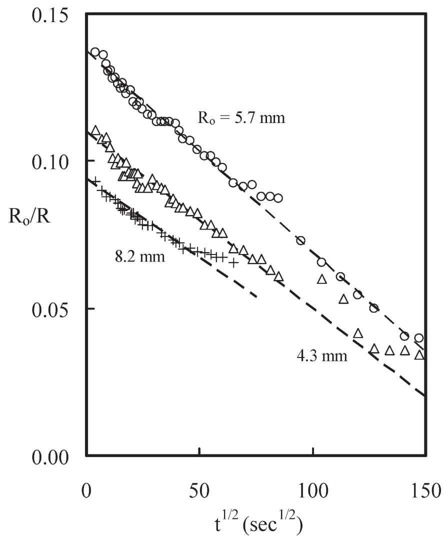

Figure 5. Increase in radius of curvature R with time t for strips subjected to imposed bends of various radii R_0. Swollen thickness T_s = 2.9 mm.

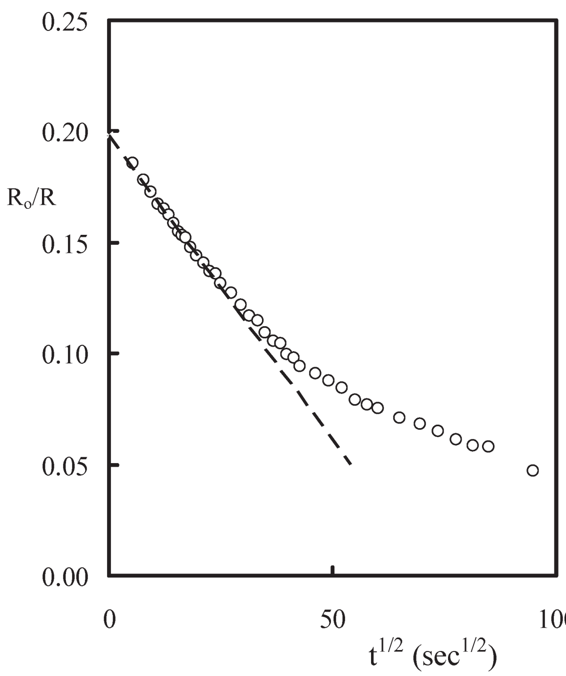

Figure 6. Increase in radius of curvature R with time t for a strip subjected to an imposed bend of radius R_0 = 4.3 mm. Swelling ratio Q = 4.0. Swollen thickness T_s = 1.6 mm.

to a thin aluminum plate. (This procedure was employed by Southern and Thomas[11] to eliminate the confusing effect of an increase in uptake area as an unrestrained sheet swells.) The results are plotted against $t^{1/2}$, where t is the time of immersion in the liquid, reduced by a factor of $2T$ to give the swelling rate for sheets capable of absorbing liquid from both sides. The diffusion coefficient D is then given in terms of the initial slope S by[14]

$$D = (\pi/16)S^2 = 37 \times 10^{-12}\ \text{m}^2/\text{s}$$

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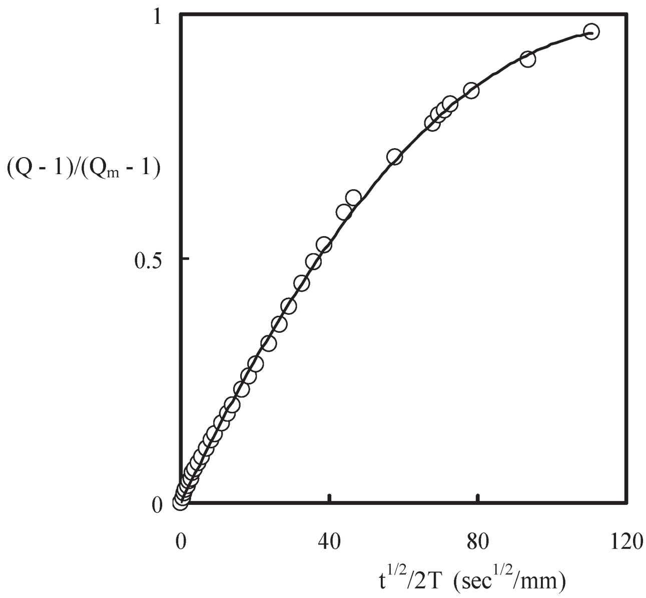

Figure 7. Swelling of a bonded sheet. Thickness T = 2 mm.

Table 1. Comparison of Half-Times for Diffusion and Recovery from Bending

thickness T (mm)	$t_{1/2}$ (s × 10^3)	$t_{1/2}/T^2$ (s/m^2 × 10^9)
swelling of sheet (effective thickness = $2T$)		
2.0	23.7	1.45
recovery from bending		
1.1	1.27	1.05
2.0	8.0	2.0
2.0	9.6	2.4
2.0	7.6	1.9

An alternative way of determining D uses the time $t_{1/2}$ to reach 50% of the final amount absorbed:[15]

$$D = 0.0492(2T)^2/t_{1/2} = 34 \times 10^{-12}\ \mathrm{m^2/s}$$

These values are consistent with that reported by Southern and Thomas[11] for diffusion of dodecane into natural rubber at a somewhat lower temperature, 25 °C: $D = 22 \times 10^{-12}$ m^2/s.

Rates of recovery can also be expressed in terms of the time $t_{1/2}$ at which the radius R of the bent strip has increased to twice its initial value after release from the imposed bend, i.e., when $R_0/R = 0.5$. Values obtained from Figures 5 and 6 are given in Table 1 for comparison with the half-time for uptake of swelling liquid by a sheet of comparable thickness. They are seen to be comparable in magnitude, supporting the hypothesis that the slow recovery process is indeed a reflection of internal migration of absorbed liquid.

6. CONCLUSIONS

When a rubber sample is swollen in the strained state, either in simple extension or in constrained extension, the amount of immediate recovery of shape when the applied stresses are removed can be estimated by applying Treloar's theory of swelling of rubber under strain. Recovery from an imposed bend is found to be in reasonable agreement with these predictions when bending is regarded as a form of constrained extension. Further recovery toward the unstrained state has been shown to follow the characteristic time dependence for diffusion of compatible liquids into rubbery solids, and the rates of recovery are similar to those for absorption of the liquid used, dodecane. Thus, recovery from an imposed bend appears to provide a simple method for studying internal migration of absorbed liquids under gradients of stress.

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