JOURNAL OF APPLIED POLYMER SCIENCE VOL. 11, PP. 245-249 (1967)

Characterization of Photolyzed Elastomers

C. D. MILLER, *Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680*

Synopsis

The extent of photolysis of the surface of an elastomer may be characterized semiquantitatively by utilizing the physical model of a two-ply stressed beam. A brief mathematical exposition is given. This permits a numerical estimate of the degree of chain scission and crosslinking occurring in the surface during photolysis.

Although elegant experimental procedures exist,[1,2] for characterizing chain scission and crosslinking reactions which occur homogeneously in an elastomer, these have limited utility in photolysis studies, since the attenuation of the incident light by the sample leads to a non-uniform rate of reaction through the sample, and the mechanical properties of the irradiated sample may become very complex.

It has been our purpose, therefore, to devise a mathematical model which might permit at least a semiquantitative estimation of the chain-scission and crosslinking reactions in a reinforced elastomer. For simplicity, a rather unsophisticated model has been chosen; some of the assumptions represent rather gross approximations. However, the accuracy with which the necessary physical quantities could be measured did not seem to justify a more elaborate model.

Elastomer ribbons were irradiated on one face while the samples were under tension. At the conclusion of the experiment, when the samples were released from tension, they showed more or less curvature, with the irradiated side convex and the dark side concave. The extent of curvature was also seen to be more or less related to the radiation dosage, the initial elongation, and the nature of the sample. It was immediately apparent that the irradiated surface showed permanent set and that, if the approximate depth of this "surface" could be determined, the model of a two-ply stressed beam might be applied to determine the extent of the permanent set. It is, of course, a drastic simplification to assume a finite boundary between photolyzed and unphotolyzed materials or to assume that the photolyzed layer is homogeneous throughout.

Consider the model under tension, shown in Figure 1. This system can be characterized by t_1 and t_2, the thickness of the top and bottom layers, respectively; E_1 and E_2, the modulus of elasticity of the top and bottom layers, respectively; and I_1 and I_2, the moment of inertia of the

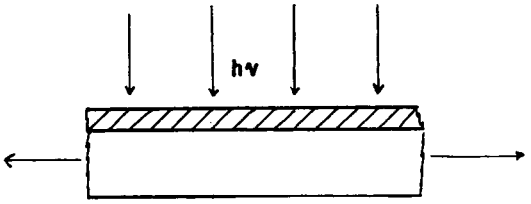

Fig. 1. Stressed sample irradiated.

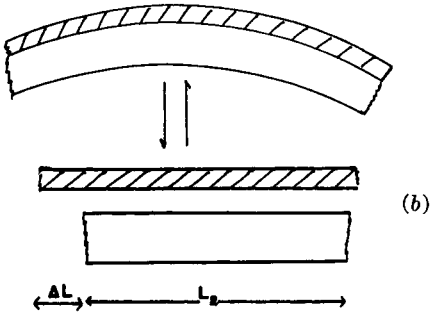

Fig. 2. Curvature induced by permanent set of irradiated surface; (*b*) plies shown as if separated.

top and bottom layers, respectively. Let E_0 denote the difference in unit length between the two layers if they were separated, such that (Fig. 2):

$$\Delta L = E_0 L \tag{1}$$

Axial forces T and bending moments M_1 and M_2 would be required to bring the two separated plies to match. Assume a common radius of curvature, ρ, and a common width, b.

$$M_1/E_1I_1 = M_2/E_2I_2 = 1/\rho \tag{2}$$

$$I_1 = bt_1^3/12 \tag{3a}$$

$$I_2 = bt_2^3/12 \tag{3b}$$

$$M_1 + M_2 = (T/2)(t_1 - t_2) \tag{4}$$

$$[(T/E_1bt_1) + (t_1/2\rho)] + [(T/E_2bt_2) + (t_2/2\rho)] = E_0 \tag{5}$$

Rearrangement of eq. (2) yields

$$(M_1 + M_2)/(E_1I_1 + E_2I_2) = 1/\rho \tag{2a}$$

On substituting eq. (2a) in eq. (4) we obtain

$$1/\rho = (T/2)(t_1 + t_2)/(E_1I_1 + E_2I_2) \tag{4a}$$

from which

$$T = (2/\rho)(E_1I_1 + E_2I_2)/(t_1 + t_2) \tag{4b}$$

Substituting eqs. (4b), (3a), and (3b) into eq. (5) yields

$$E_0 = \frac{2}{\rho}\left(\frac{E_1I_1 + E_2I_2}{t_1 + t_2}\right)\left(\frac{1}{E_1bt_1} + \frac{1}{E_2bt_2}\right) + \frac{t_1 + t_2}{2\rho}$$

and

$$E_0 = \left(\frac{E_1t_1^3 + E_2t_2^3}{6\rho(t_1 + t_2)}\right)\left(\frac{1}{E_1t_1} + \frac{1}{E_2t_2}\right) + \frac{t_1 + t_2}{2\rho} \tag{6}$$

Thus E_0 can be computed from the moduli, the thicknesses of the photolyzed and unphotolyzed layers, and the radius of curvature.

The elastic modulus of the lower layer was obtained from Instron data for unexposed samples. The modulus for the degraded layer was approximated from the corresponding value of the undegraded multiplied by the relative crosslink density of the two samples. This required an independent method for calculating crosslink density, and a differential swelling method was devised:

$$\frac{w_2 - w_1[t_2/(t_1 + t_2)]}{w_1[t_1/(t_1 + t_2)]} = \frac{\text{crosslink density in photolyzed layer}}{\text{original crosslink density}} \tag{7}$$

where t_1 and t_2 are as defined above, and w_1 is the weight of solvent imbibed per gram unexposed sample and w_2 is the weight of solvent imbibed per gram exposed sample.

It is assumed that the photolysis has not materially altered the affinity of the polymer for the solvent, and that the degree of swelling is not changed by the tensile and compressive stresses in the exposed sample.

Therefore

$$E_1 \approx E_2\left\{\frac{w_2 - w_1[t_2/(t_1 + t_2)]}{w_1[t_1/(t_1 + t_2)]}\right\} \tag{8}$$

The thickness of the photolyzed layer is an arbitrary, even artificial, quantity. It was estimated by stretching the sample to approximately 50% beyond its original length and measuring the depth of the cracks so produced.

The radius of curvature was obtained by suspending the sample in a nonswelling solvent of appropriate density and measuring l and h (Fig. 3) with a travelling microscope. The radius of curvature of segment AB is

$$\rho = [(l^2/4) + h^2]/2h \tag{9}$$

A numerical value of E_0 can now be obtained. However, from eq. (1) it is seen that

$$E_0L = \Delta L = L_1 - L_2$$

where L_1, L_2 are the permanently set and the original length, respectively. With the addition of one more value, L_3, the extended length during irradiation, the per cent permanent set can be evaluated:

$$\%\ \text{Permanent set} = \{[(L_1/L_2) - 1]/[(L_3/L_2) - 1]\}100 \tag{10}$$

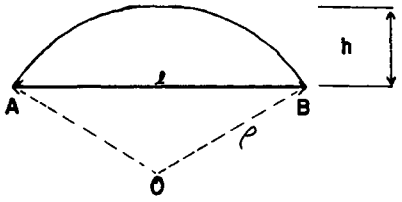

Fig. 3. Calculation of radius of curvature.

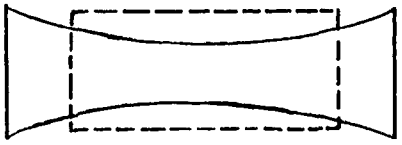

Fig. 4. Perpendicular compressive stress at large elongation.

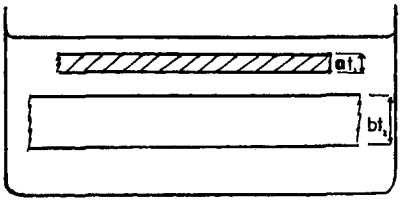

Fig. 5. Swelling of irradiated sample. Plies shown as if separated.

By equating tensile and compressive forces, and substituting eq. (10), the permanent set may be expressed as a relation between the relative concentrations of two independent crosslink networks, one at equilibrium at L_3 and one at equilibrium at L_2:

$$\% \text{ Permanent set} = \left\{\left[\frac{(L_3/L_2)^3 - 1}{(S_u/S_x)(L_3/L_2)^2 + 1} + 1\right]^{1/3} - 1\right\}\left\{\frac{100}{(L_3/L_2) - 1}\right\}$$

where S_u and S_x is the number of network chains per cubic centimeter at equilibrium in the unstretched and extended configurations, respectively.

The equations suggest that the sensitivity of the method could be improved by increasing the stressed length of the sample L_3. In practice, it was found (Fig. 4) that elongations in excess of 20% beyond the original length produced excessive compressive stress at right angles and permanent set produced compound curvature.

While gravimetric swelling measurements were being made, it was observed that the curvature of the samples in a swelling solvent was reversed; the photolyzed surface, at equilibrium, swelled less than the bulk of the material. This was in qualitative agreement with the gravimetric results; but a mechanical analysis utilizing a comparable stressed-beam calculation, required irradiation of a second sample at normal elongation (Fig. 5).

The same equations were used; values of E and t were, of course, those of the swollen plies.

Having then values of S_u/S_x in the photolyzed surface from the original curvature studies and $(S_u + S_x)/S_0$ in the same surface from the swelling measurements where S_0 is the original crosslink density, we may combine these:

$$S_u/S_x = A$$

$$s_u/S_0 = B/l + A$$

$$(S_0 - S_u)/S_0 = (A - B + l)/l + A$$

$$(S_u + S_x)/S_0 = B$$

We thus obtain an estimate of the magnitude of the chain-scission reaction.

This work was supported in part by the United States Air Force, Contract No. AF 33(616)-7310.

References

1. R. D. Andrews, A. V. Tobolsky, and E. E. Hanson, *J. Appl. Phys.*, **17**, 352 (1953).
2. A. V. Tobolsky, *J. Appl. Phys.*, **27** 673 (1956).

Résumé

Le degré d'avancement de la photolyse à la surface d'un élastomère peut être caractérisé semi-quantitativement en utilisant un modèl physique d'un faiseau appliqué à divers endroits. Un exposé mathématique bref est donné. Ceci permet une estimation numérique du degré de sission de chaînes et du pontage qui se passe au cours de la photolyse en surface.

Zusammenfassung

Das Photolyseausmass der Oberfläche eines Elastomeren kann halbquantitativ mit dem physikalischen Modell eines gespannten Zwei-Schichtenstabes charakterisiert werden. Eine kurze mathematische Darstellung wird gegeben. Damit ist eine numerische Bestimmung des Kettenspaltungs- und Vernetzungsgrades in der Oberfläche während der Photolyse möglich.

Received July 16, 1966
Prod. No. 1453