Radiation-induced mechanical property changes in filled rubber

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In a recent paper we exposed a filled elastomer to controlled radiation dosages and explored changes in its cross-link density and molecular weight distribution between network junctions [A. Maiti *et al.*, Phys. Rev. E **83**, 031802 (2011)]. Here we report mechanical response measurements when the material is exposed to radiation while being under finite nonzero strain. We observe interesting hysteretic behavior and material softening representative of the Mullins effect, and materials hardening due to radiation. The net magnitude of the elastic modulus depends upon the radiation dosage, strain level, and strain-cycling history of the material. Using the framework of Tobolsky's two-stage independent network theory we develop a model that can quantitatively interpret the observed elastic modulus and its radiation and strain dependence.

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I. INTRODUCTION

Filled and cross-linked elastomeric rubber and foam are versatile network materials with a multitude of applications ranging from artificial organs and biomedical devices to cushions, coatings, adhesives, interconnects, and seismic-isolation-, thermal-, and electrical barriers [1–3]. However, upon long-term or repeated exposure to external factors like mechanical stress, temperature fluctuations, or radiation [4], such materials can undergo chemical changes, including [5–7] (1) creation of new cross links, (2) breaking (scission) of covalent bonds, and (3) modification of the polymer-filler interface.

In a recent paper [8] we examined the effect of radiation on the molecular weight distribution (MWD) of a filled networked elastomer. However, one important aspect that was not analyzed was the stress-strain response of samples irradiated under a finite strain. Assuming that the cross-link density is affected by radiation only and not by strain, one expects (see Sec. IV) that the elastic modulus (1) should increase as a function of the radiation dosage, and (2) should increase as a function of the strain at which the rubber material is being irradiated. However, very recent mechanical measurements show that although trend (1) generally holds true in all cases, trend (2) has a strong dependence on the stress-strain history of the sample. In this paper we discuss these recent measurements, and develop a model for quantitative interpretation of the observed modulus as a function of radiation dosage and strain level.

II. MECHANICAL MEASUREMENTS

As in the previous work [8], all experiments were performed on the commercial silicone elastomer TR-55 from Dow Corning. Thin rectangular samples were stretched to specific strain levels and exposed to controlled dosages of γ radiation from a Co-60 source (1.4 MeV, ~0.1 Mrad/h dose rate) in a nonreactive nitrogen atmosphere. Seven different strain levels were studied, corresponding to stretch ratios $\lambda_1 = 1.20$, 1.47, 1.67, 1.84, 2.00, 2.33, and 2.67. Following exposure to controlled duration (and therefore dosages) of radiation, each sample was removed from the irradiation chamber, released from the λ_1 strain, and allowed to relax at ambient conditions for 24 h. The relaxed samples were then subjected to measurement of the new equilibrium length, called the recovered length λ_s. After several weeks of further equilibration, stress-strain analysis was carried out for five load-unload cycles at strains of up to 50% elongation. The stress-strain analysis was performed on rectangular specimens (width ~3 mm and thickness 0.6–0.9 mm) using an Instron 5565 dual-column electromechanical test system with an initial grip separation of ~20 mm and a stretching rate of 20 mm/min.

Figure 1 plots the measured recovered length (λ_s) as a function of radiation dosage D for the different values of λ_1. Error bars indicate sample-to-sample variation in cases where multisample measurements were performed. A subset of these results was already reported in Ref. [8]. These results can be quantitatively interpreted using Tobolsky's two-stage independent network model [9,10], as discussed in Sec. III.

Figure 2 plots a typical stress-strain response of such samples (only the loading curves are shown and the unloading curves hidden for clarity). The main feature is that there is strong dependence on the cycle number. In particular, in cycle 1 the response is much steeper, corresponding to a significantly higher elastic modulus, while the response becomes progressively softer in subsequent cycles, but with a much smaller dropoff than between cycle 1 and cycle 2. This type of softening has long been known to occur in filled rubber materials and is generally known as the Mullins effect [11]. At the end of cycle 1 a small permanent stretch (~2%) is also incurred, which is smaller than typical permanent sets reported in Fig. 1. It is important to note here that the recovered length in Fig. 1 was obtained *prior* to subjecting the samples to the stress-strain cycles as in Fig. 2.

Next, the Young's modulus (E) was extracted from the stress-strain *slope* at small deformation (corresponding to strain levels of 5% or less) for various cycles and various values of λ_1 and D. Figure 3 displays the results for E in cycles 1 and 5. We observe the following trends: (1) For all values of λ_1 the modulus increases as a function of D within each cycle. For $\lambda_1 = 1$ and cycle 1 this increase is nearly linear, as observed previously [8]. (2) For all values of λ_1 and D the modulus significantly decreases from cycle 1 to cycle 5, similar to the softening behavior seen in Fig. 2. The modulus softening is the largest for $\lambda_1 = 1$ and gets progressively smaller for

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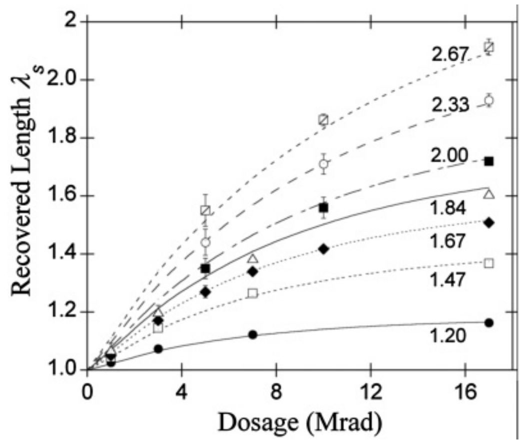

FIG. 1. Recovered length (λ_s) as a function of radiation dosage for different values of tensile stretch ratios (λ_1) at which the material is subjected to radiation. The symbols denote experimental measurements while the lines (solid, dashed, and dotted) are theoretical results using λ_1-independent f_{eff} (see Sec. III). The λ_1 values are indicated by each curve.

increasing values of λ_1. (3) As a function of λ_1 the modulus displays complex behavior that can be increasing, decreasing, or nonmonotonic depending upon the cycle and the radiation dosage D. In particular, in cycle 1 the modulus E shows an overall decreasing trend as a function of increasing λ_1, with the rate of decrease of $|\partial E/\partial\lambda_1|$ getting smaller with increasing λ_1 and increasing D. In cycle 5, on the other hand, E shows more complex behavior as a function of λ_1, decreasing at $D = 5$ Mrad, increasing at $D = 17$ Mrad, and nonmonotonic at intermediate values (10 Mrad). This behavior of E can be traced to a combination of (i) material softening due to the Mullins effect, and (ii) radiation hardening due to the creation of a net number of new cross links [8]. Below we analyze the above results within the framework of Tobolsky's two-stage network theory [9,10].

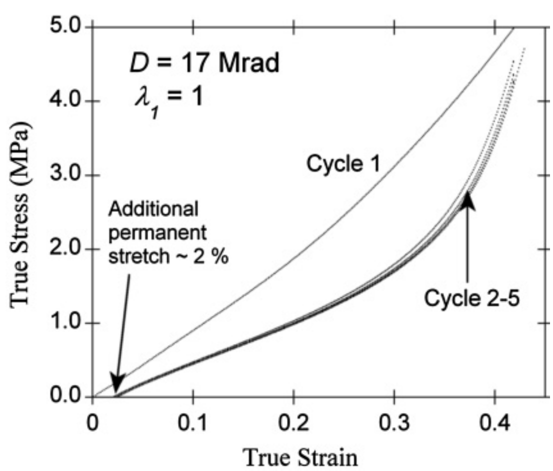

FIG. 2. Typical stress-strain response of a radiation-exposed TR-55 sample through the first five cycles. The data shown correspond to a sample that was exposed to 17 Mrad of radiation (under $\lambda_1 = 1$) and then stretched to a maximum of 50% of its original length during each cycle.

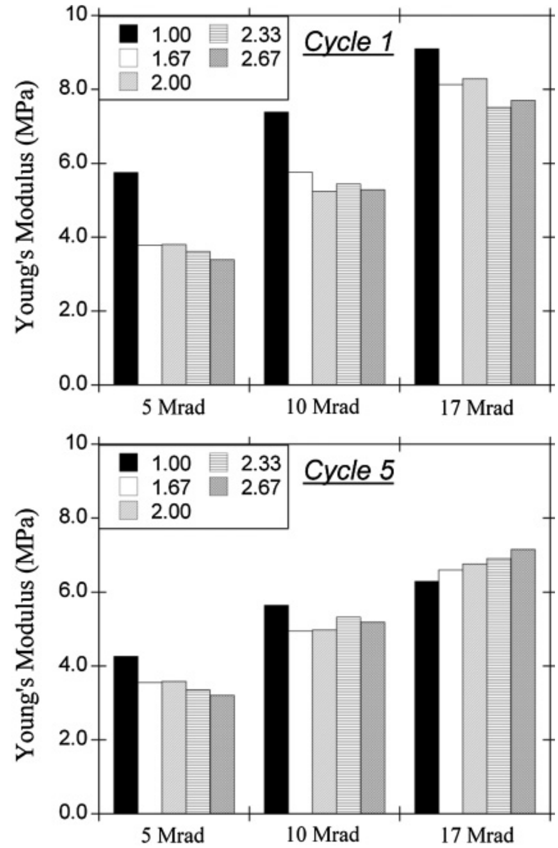

FIG. 3. Young's modulus obtained from the small-deformation slope of experimental stress-strain data for various values of λ_1, three different radiation levels, and two cycles (cycle 1 and cycle 5). Depending on the cycle and the radiation level the elastic modulus displays increasing, decreasing, and nonmonotonic behavior as a function of λ_1.

III. CONSTITUTIVE MODELING

To analyze the experimental data on recovered length λ_s (Fig. 1) and Young's modulus E (Fig. 3) we adopted the Neohookean stress response model [12] defined by the function $\sigma(\lambda) = G(\lambda^2 - 1/\lambda)$, where σ is the (true) stress under a uniaxial stretch ratio λ ($\lambda = 1$ corresponds to a state of no deformation), and G is the shear modulus that depends on the cross-link density in the material. Before deriving a general formula for the Young's modulus E (see Sec. IV) we note that for the special case $\lambda_1 = 1$ the Young's modulus is simply three times the shear modulus, i.e., $E = 3G$. Thus the near-linear increase of E with D for $\lambda_1 = 1$ in cycle 1 [see Fig. 3 (top)] can be expressed as $G = G_0(1 + C_0 D)$, where $G_0 \sim 1.5$ MPa is the shear modulus of the pristine material, D the radiation dosage in Mrad, and C_0 is a constant ~ 0.05 Mrad^{-1}. This change in modulus results from a net increase in the number of cross links in the system induced by radiation.

For the case $\lambda_1 > 1$ the radiation-induced cross links give rise to two independent networks: (1) the original one created in the unstrained state, a fraction of which gets modified during exposure to radiation, and (2) the new cross links created at strain state λ_1. At the length scale of our mesoscale junction model [8,13] all network junctions, original and radiation-induced, are assumed to be homogeneously distributed throughout the bulk elastomer. In the presence of these two networks the stress response function becomes

$$\sigma(\lambda) = G_0\left\{(1-f'_{\rm mod})\left(\lambda^2-\frac{1}{\lambda}\right)+f'_{xl}\left(\frac{\lambda^2}{\lambda_1^2}-\frac{\lambda_1}{\lambda}\right)\right\}. \tag{1}$$

In Eq. (1) $f'_{\rm mod}$ and f'_{xl} are, respectively, the amounts of pristine cross links that are modified and the amount of new cross links created by radiation, both expressed as a fraction of the pristine cross-link density [8], taking into account subtle feedback effects [14] that are present for $\lambda_1 > 1$. The net increase in cross-link density in cycle 1 as a function of the radiation dosage D can be expressed through the relation [8]:

$$\Delta f_{xl} = f'_{xl} - f'_{\rm mod} = C_0 D. \tag{2}$$

For the data in Fig. 1 the recovered length λ_s can be modeled by solving Eq. (1) for $\sigma(\lambda_s)=0$, which yields

$$\lambda_s = \left\{\frac{1+f_{\rm eff}\lambda_1}{1+f_{\rm eff}/\lambda_1^2}\right\}, \tag{3}$$

where $f_{\rm eff} = f'_{xl}/\left(1-f'_{\rm mod}\right)$. When Eq. (3) is inverted to solve for $f_{\rm eff}$ for all experimental value of λ_s in Fig. 1, one obtains the expression:

$$f_{\rm eff} = \frac{\lambda_1^2\left(\lambda_s^3-1\right)}{\left(\lambda_1^3-\lambda_s^3\right)} \quad (\text{for } \lambda_1 > 1). \tag{4}$$

When the experimental values of λ_s and λ_1 (from Fig. 1) are used in Eq. (4) we find that $f_{\rm eff}$ is a function of D only, and nearly independent of λ_1. The values of $f_{\rm eff}$ (averaged over λ_1) as a function of D is plotted in Fig. 4, with the behavior well described by the exponential fit (solid line):

$$f_{\rm eff} = \exp(\alpha_1 D - \alpha_2 D^2) - 1, \tag{5}$$

where constants $\alpha_1 \sim 0.165$ Mrad^{-1} and $\alpha_2 \sim 0.003$ Mrad^{-2}, respectively.

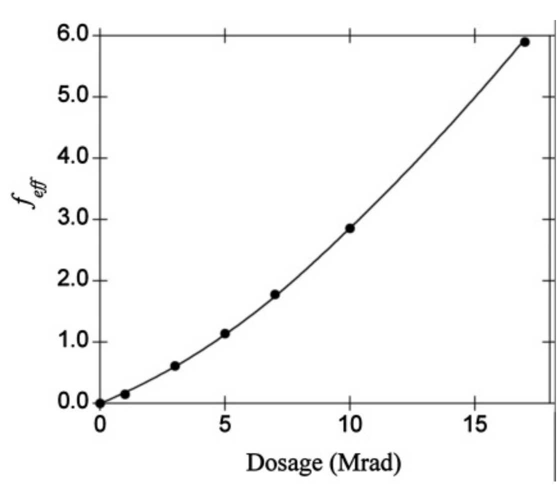

FIG. 4. The quantity $f_{\rm eff}$ (see text) as a function of radiation dosage D: The points correspond to (λ_1-averaged) values obtained by inserting experimental recovered lengths (λ_s) into Eq. (4), while the solid line corresponds to an exponential fit given by Eq. (5).

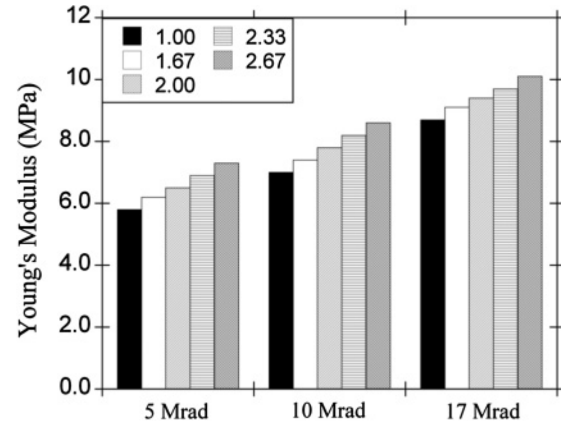

FIG. 5. Young's modulus (E) as predicted from Eq. (7) with a constant G_0 (=1.5 MPa) independent of stress-strain cycling.

IV. ANALYSIS OF YOUNG'S MODULUS (E)

The main motivation for the current paper was to analyze and understand the complex behavior of the Young's modulus E as seen experimentally (Fig. 3). The modulus E, defined as the small-deformation stress-strain slope about the altered equilibrium (λ_s) is given by

$$E = \lim_{\varepsilon\to 0}\frac{\sigma\left[\lambda_s(1+\varepsilon)\right]-\sigma(\lambda_s)}{\varepsilon} = \left(\frac{\partial\sigma}{\partial\lambda}\right)_{\lambda_s}\lambda_s, \tag{6}$$

where ε is the uniaxial deformation strain. Equations (1)–(3) and (6) yield (after some algebraic manipulation) the following expression for E:

$$E = G_0\frac{(1+C_0D)}{1+f_{\rm eff}}\left[\left(2\lambda_s^2+\frac{1}{\lambda_s}\right)+f_{\rm eff}\left(2\frac{\lambda_s^2}{\lambda_1^2}+\frac{\lambda_1}{\lambda_s}\right)\right]. \tag{7}$$

For $\lambda_1 = 1$ there is no permanent set, i.e., $\lambda_s = 1$ [as also follows from Eq. (3)], which substituted in Eq. (7) yields the relation $E = 3G_0(1 + C_0D) = 3G$, as mentioned in Sec. III. Assuming a constant $G_0 \sim 1.5$ MPa in Eq. (7) one obtains an increasing E as a function of increasing λ_1 as shown in Fig. 5, a behavior in clear disagreement with the experimental pattern of Fig. 3.

The behavior in Fig. 5 arises under the assumption that G_0 is constant and independent of the cycle number, λ_1, and D. This is equivalent to the assumption that the rubber network does not have any hysteresis effects, i.e., no Mullins effect. This assumption is clearly not correct for the experimental TR-55 samples as evidenced from the softening in Fig. 2 with strain cycling. In fact, Figs. 2 and 3 indicate two different stages at which the material softening takes place: (1) during the several-week-long annealing period following the λ_s measurements. This softening happens only for $\lambda_s > 1$, with the amount of softening increasing with increasing λ_s (and therefore increasing λ_1); (2) during the first stress-strain cycle following the annealing period. The amount of this softening decreases with increasing λ_1. The first type of softening leads to the behavior of E as seen in Fig. 3 (top), while the second type of softening causes the change from the behavior in Fig. 3 (top) to that in Fig. 3 (bottom). We elaborate on this point in the following discussion.

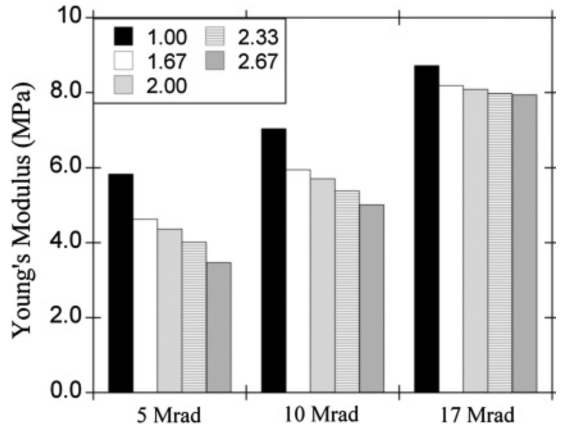

FIG. 6. Young's modulus (E) in cycle 1 as predicted from Eq. (7) by rescaling the pristine shear modulus G_0 (=1.5 MPa) with a multiplicative factor $[1-\alpha(\lambda_s-1)]$. This factor represents a simple model that illustrates the effect of λ_s and radiation dosage D on the cycle 1 response. See text.

Although the Mullins effect has been known for several decades, the underlying microscopic driving force is still unclear [15]. Suggestions range from the cleavage of chemical bonds between rubber and filler, slipping and disentanglement of chains, rupture of filler clusters, and so on. The true mechanism notwithstanding, it is clear that any of these processes will lead to a decrease in the overall cross-link density. In addition, the propensity for each of these processes is expected to (1) increase with the stress level the material is subjected to, and (2) decrease with increasing radiation dosage. The latter creates additional cross links that reduce the average stress levels per cross link for a given strain level. As a simple model illustrating these two effects on the cycle 1 response we have explored the behavior of E when the pristine shear modulus G_0 in Eq. (7) is rescaled by a multiplicative factor, i.e.,

$$G_0 \rightarrow G_0[1-\alpha(\lambda_s-1)], \tag{8}$$

where α is a decreasing function of the radiation dosage D. Figure 6 plots the resulting values of E for the parameter values of $\alpha = 0.95$, 0.48, and 0.19 for $D = 5$, 10, and 17 Mrad, respectively. This behavior is quantitatively consistent with Fig. 3 (top).

Finally, the behavior of E in cycle 5 [Fig. 3 (bottom)] can be interpreted as follows. With repeated cycling further loss in cross links continues to occur until all the loose links (weak chemical bonds to fillers or physical entanglements) are removed from the system. For larger values of λ_1 (and resulting larger λ_s) a larger fraction of these links are removed during the several-week-long annealing period (i.e., before the first stress-strain cycle), which is consistent with a higher degree of softening and a decreasing E with increasing λ_1 in cycle 1. As a consequence, any additional softening in subsequent cycles is higher for smaller values of λ_1. This effect, in conjunction with a decreasing $|\partial E/\partial\lambda_1|$ with increasing D in cycle 1 [see Fig. 3 (top) or Fig. 6] leads to less negative values of $\partial E/\partial\lambda_1$ in cycle 5 (as compared to cycle 1), which can even become positive for large D [as seen in Fig. 3 (bottom)] for $D = 17$ Mrad).

V. SUMMARY

In summary, as a follow-up to our recent work we have carried out mechanical stress-strain measurements on an elastomeric rubber material subjected to controlled radiation dosages under finite strain. Interesting trends in the measured Young's modulus is observed as a function of radiation dosage and the strain at which the radiation exposure is performed. More specifically, at lower radiation dosages and earlier stress-strain cycles the modulus is found to decrease with increasing strain of exposure, while the trend gets reversed at higher dosages and later cycles. We show that this behavior arises due to the interplay of two opposing effects, i.e., materials *softening* due to the Mullins effect and radiation *hardening* due to the creation of new cross links. Using the framework of Tobolsky's two-stage independent network theory we develop a phenomenological model that can quantitatively interpret the experimentally observed modulus as a function of radiation dosage and strain history. For future work it might be interesting to analyze stress-strain behavior in a direction orthogonal to the strain under which the radiation is applied.

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