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Constitutive modeling of Radiation effects on the Permanent Set in a silicone elastomer

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Abstract

When a networked polymeric composite under high stress is subjected to irradiation, the resulting chemical changes like chain scissioning and cross-link formation can lead to permanent set and altered elastic modulus. Using a commercial silicone elastomer as a specific example we show that a simple 2-stage Tobolsky model in conjunction with Fricker's stress-transfer function can quantitatively reproduce all experimental data as a function of radiation dosage and the static strain at which radiation is turned on, including permanent set, stress-strain response, and net cross-linking density.

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Filled elastomeric rubber materials are versatile components in numerous applications ranging from cushion, coating, adhesives, seismic isolation, thermal and electrical barriers and interconnects [1-3]. Such materials over long times can undergo chemical aging, which can alter and degrade many of its useful properties important to the application in question. Chemical aging signatures most profoundly affecting the elastic properties of the polymer include [4, 5]: (1) creation of new crosslinks; (2) breaking (scission) of covalent bonds; and (3) modification of the polymer-filler interface due to changes in cross-linking to the filler, as well as physico-chemical changes, e.g., involving removal of water, and so on. In applications, e.g., cushions, where the polymeric material is subjected to finite stress conditions for a long period of time, such chemical modifications can lead to a modified state of ease (*i.e.*, a state corresponding to zero stress) known as *permanent set*.

Given the slow nature of the above processes one often designs artificial aging experiments in which the polymeric material is subjected to harsher, but controlled environments than it experiences in reality. A relevant experiment in this regard is a recent one performed by Chinn et al. [6], in which a commercial, filled siloxane composite, DC-745 was subjected to states of finite tensile strain (λ_l) and exposed to controlled dosages (D) of γ-radiation from a Co-60 source. Following the irradiation, tensile tests were performed to measure the amount of permanent set and stress-strain response for each value of D and λ_l. In addition, NMR and swelling experiments were performed to measure the radiation-induced changes to the net cross-link density. These experiments revealed that: (1) exposure to ionizing γ-radiation primarily leads to radiative

cross-linking reactions; and (2) the net increase in cross-linking density is proportional to the radiation dosage D, but nearly independent of the strain state λ_1 at which the radiation is applied.

More than six decades ago, a simple, yet effective model for describing permanent set under conditions described above was given by Tobolsky and his collaborators [7, 8]. This model, an independent network hypothesis, surmises that the additional crosslinks introduced at strain $\lambda = \lambda_1$ can be treated as an additional independent network, whose state of ease is at strain λ_1. Mathematically this can be expressed by writing the total stress of the system as a sum of stress due to the original network and that due to the new network, as follows:

$$\sigma_{total} = \sigma(v_0, \lambda) + \sigma(v_1, \lambda'), \tag{1}$$

where λ denotes the system strain (the original zero stress corresponding to $\lambda = 1$), $\lambda' = \lambda/\lambda_1$, v_0 is the cross-linking density of the original network, and v_1 the new cross-linking density introduced (e.g., by radiation) at $\lambda = \lambda_1$. The function "σ" is the stress response function of the pristine material, for which one could potentially use one of several forms available in rubber elasticity theory [9], e.g., Neohookean, Mooney-Rivlin, Valanis-Lendel, Ogden, or more modern variants [10]. The efficacy of the Tobolsky model (eq. (1)) has been tested extensively in the literature, see, e.g., ref. [11-13].

Unfortunately, when eq. (1) in conjunction with a simple Neohookean materials model was used to interpret the permanent set data of ref. [6], the increase in cross-linking density was found to be very different from that measured in NMR and swelling

experiments, especially at higher radiation dosage. This failure of the Tobolsky model was attributed to the creation of elastically ineffective chains through the formation of crosslinks that close off loops [6].

In this Letter, we re-investigate the above problem by using a more generalized Tobolsky model that incorporates a subtle feedback effect of the new network on the original network when new crosslink creation is also accompanied with scissioning of some of the original crosslinks [14]. Mathematically this is expressed in terms of a stress transfer function $\psi_{transfer}$, which is the fraction of the new crosslinks that effectively become part of the original network through the feedback mechanism [15]. Thus, in the generalized Tobolsky model one replaces the crosslink densities ν_0 and ν_1 of eq. (1) by effective quantities:

$$\sigma_{total} = \sigma(\nu_{0,eff}, \lambda) + \sigma(\nu_{1,eff}, \lambda'),\qquad\qquad (1')$$

where,

$$\nu_{0,eff} = \nu_0 - \nu_{sci} + \psi_{transfer}\nu_1 ; \text{ and } \nu_{1,eff} = \nu_1 - \psi_{transfer}\nu_1 . \qquad (2)$$

In eq. (2) ν_{sci} is the density of original cross-links that undergo scissioning at strain λ_1. In the following we express chain scissioning and new crosslink formation as fractions of the original crosslink density, i.e., $\nu_{sci} = \xi_{sci}\nu_0$ and $\nu_1 = \xi_{xc}\nu_0$, which allows re-expressing eq. (2) as:

$$\nu_{0,eff} = \nu_0(1 - \xi_{sci} + \psi_{transfer}\xi_{xc}); \text{ and } \nu_{1,eff} = \nu_0(1 - \psi_{transfer})\xi_{xc} . \qquad (2')$$

4

As for $\psi_{transfer}$ we use a simple formula developed by Fricker [16] for a system of phantom chains:

$$\psi_{transfer} = \frac{\xi_{sci}}{1+\xi_{xc}} \quad , \tag{3}$$

which, by its very construction implies non-zero feedback only in the presence of chain scission, and has the following simple property:

$$v_{1,eff} = \xi_{xc} v_{0,eff} \quad . \tag{3'}$$

Accuracy of the Fricker's formula (eq. (3)) for elastomeric systems undergoing simultaneous chain scission and crosslinking has been verified through explicit molecular dynamics simulations on bead-spring models [14].

In order to compute permanent set and stress-strain response, one needs: (i) a materials model for the function "σ" of eq. (1'), and (ii) a model for ξ_{sci} and ξ_{xc} as a function of the radiation dosage D. For simplicity, we chose the first-order Mooney-Rivlin materials model [9]:

$$\sigma(v,\lambda) = v k_B T f(\lambda), \quad \text{where } f(\lambda) = (1+\beta/\lambda)(\lambda^2 - 1/\lambda)/(1+\beta) \tag{4}$$

In eq. (4), σ represents the "true" stress, k_B is the Boltzmann constant, and β is the ratio of the Mooney-Rivlin constants ($\beta = C_{01}/C_{10}$ in the standard notation of rubber elasticity literature [9]), which typically is in the range 0.3-1.0 for most elastomeric rubber materials. The product $v k_B T$ physically represents the shear modulus of the material

under zero strain. For the radiation model, we assume a simple linear dependence of chain scission and crosslinking on dosage D (within limits of $\xi_{sci} < 1$):

$$\xi_{sci} = k_{sci}D, \text{ and } \xi_{xc} = k_{xc}D. \tag{5}$$

In the rest of the paper we explore whether the simple theoretical model embodied in equations (1′)-(5) can be used to explain the permanent set and elastic response data of ref. [6] by exploiting just four fitting variables: ν_0, β, k_{sci}, and k_{xc}.

In Fig. 1 we compare the experimental recovered length and permanent set for different values of D and λ_l with computed values. To compute the recovered length λ_s, we numerically solve eq. (1′) for $\sigma_{total} = 0$. The permanent set P_s is simply defined by the ratio $(\lambda_s\text{-}1)/(\lambda_l\text{-}1)$. Note that when eqs. (3′) and (4) are substituted into eq. (1′), $\nu_{0,eff}$ becomes a multiplicative constant, thereby yielding the following simple equation for λ_s:

$$f(\lambda_s) + \xi_{xc} f(\lambda_s / \lambda_1) = 0, \tag{6}$$

which is independent of both ν_0 and (more interestingly) the amount of chain scissioning ξ_{sci} [17]. Thus, in order to compute λ_s, we only need values for parameters β and k_{xc}, for which we made the following choices: $\beta = 0.3$, and $k_{xc} = 0.010$ (kGray)$^{-1}$. As Fig. 1 indicates, the agreement between theory and experiment is excellent for all values, except a slight overestimation of the computed value at $D = 70$ kGray and $\lambda_l = 1.9$.

To fit the other two parameters, i.e., the initial crosslink density ν_0 and the amount of radiation-induced chain scission governed by k_{sci}, we needed experimental data on stress-strain response, which was available for the specific radiation dose $D = 170$ kGray (see

Fig. 5 of ref. [6]). The crosslink density v_0 could be readily obtained from the elastic response of the pristine material (i.e. not exposed to radiation), which yields $v_0 k_B T =$ 135.4 psi. As for the chain scission parameter we chose $k_{sci}= 0.002$ (kGray)$^{-1}$, which provided an excellent fit to the low-strain ($\lambda < 20\%$) experimental data for all values of λ_I, as shown in Fig. 2. In particular, the observed stiffening of the material under irradiation through an increased elastic modulus is accurately reproduced in our model. It is to be noted, however, that the experimental stress-strain response for higher strains clearly deviate from the computed values. This stems from the well-known limitations of the simple first-order Mooney-Rivlin model employed here, and could be improved by using a more sophisticated materials model from the literature [9, 10].

Finally, we computed the net cross-link density $v_0 + v_{xc} - v_{sci} = v_0 (1 + \xi_{xc} - \xi_{sci})$ as a function of radiation dosage and compared with NMR and swelling data of ref. [6]. Fig. 3 displays such a comparison. We have also included values previously predicted from the measured permanent set data using a Neohookean materials model (see Fig. 11 of ref. [6]). Our computed cross-link density is in excellent agreement with the NMR and swelling data, clearly showing that the generalized Tobolsky model achieves remarkable consistency among all data, *i.e.*, permanent set, stress-strain response, as well as measured cross-link density as a function of radiation dosage.

In summary, with the commercial elastomer DC-745 as a concrete example, we have demonstrated the usefulness of a generalized 2-stage Tobolsky model in conjunction with the Fricker's stress transfer function in interpreting radiation-induced chemical aging as manifested in permanent set and changes in stress-strain response. Even a simple

materials model like first-order Mooney-Rivlin with very few parameters is able to quantitatively reproduce uniaxial tensile data over a wide range of experimental conditions, firmly establishing the strong predictive power of such an approach. Our model predicts that permanent set is independent of the amount of chain scission, while elastic response depends on both chain scission and new crosslinks created by the irradiation. Currently we are performing similar measurements on a number of elastomeric and foam systems, and adopting a finite-elements approach [18] in order to simulate more realistic geometries, stress patterns, and the effect of filler distribution morphology as well as the nature of the filler-polymer interface.

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15. The concept of stress transfer function was first introduced by Flory, where he derived an expression for $\psi_{transfer}$ for a system of Gaussian chains. See, P. J. Flory, *Trans. Faraday Soc.* **56**, 722 (1960). We use a much simpler form due to Fricker [16].

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17. The special case $\beta = 0$ corresponds to the Neohookean model. For this case one can solve eq. (6) analytically and obtain a closed-form analytical solution for the recovered length: $\lambda_s = \left\{ \dfrac{1 + \xi_{xc}\lambda_1}{1 + \xi_{xc}/\lambda_1{}^2} \right\}^{1/3}$.

18. See articles in: *Constitutive Models for Rubber V, Proceedings of the 5th European Conference*, A. Boukamel, L. Laiarinandrasana, and S. Meo (eds), CRC Press (2007).

Figure captions:

Fig. 1. Experimental (from ref. [6]) and computed recovered length (λ_s) and permanent set P_s ($=(\lambda_s-1)/(\lambda_l-1)$) for various values of λ_l and radiation dosage D. (Top left) Experimental λ_s; (top right) computed λ_s; (bottom left) experimental P_s; (bottom right) computed P_s. Parameters used: $\beta = 0.3$, $k_{xc} = 0.010$ (kGray)$^{-1}$.

Fig. 2. Stress-strain response data at a radiation dosage of $D = 170$ kGray. Response of the pristine material is included as well. (Left) Experimental (from ref. [6]) data; (Right) computed values. Parameters used: $\beta = 0.3$, $k_{xc} = 0.010$ (kGray)$^{-1}$; $k_{sci} = 0.002$ (kGray)$^{-1}$; $\nu_0 k_B T = 135.4$ psi. In both plots the y-axis represents the engineering stress, *i.e.*, $\sigma_e = \sigma/\lambda$, and all curves are shifted along the negative x-axis by $\varepsilon_s = \lambda_s - 1$ (so that they start from the origin).

Fig. 3. Net crosslink density (expressed as a fraction of the initial crosslink density ν_0) as a function of radiation dosage.
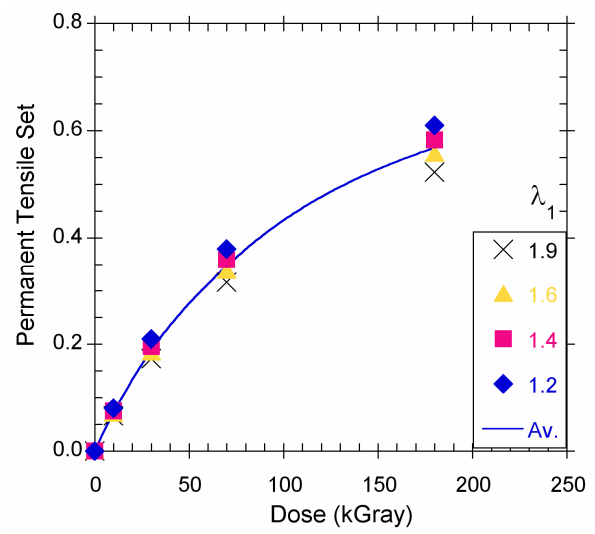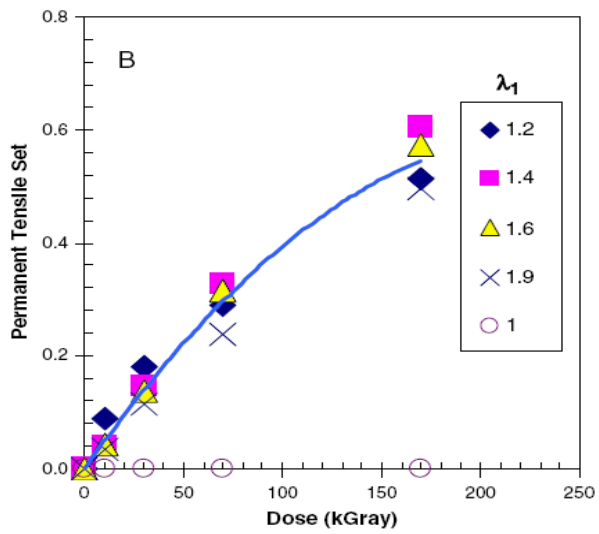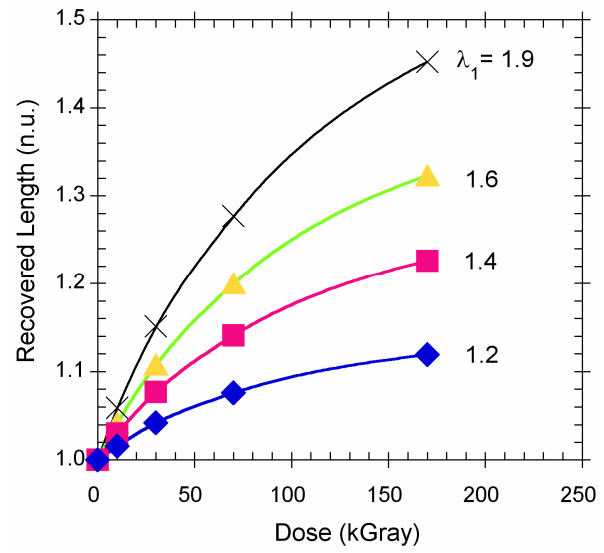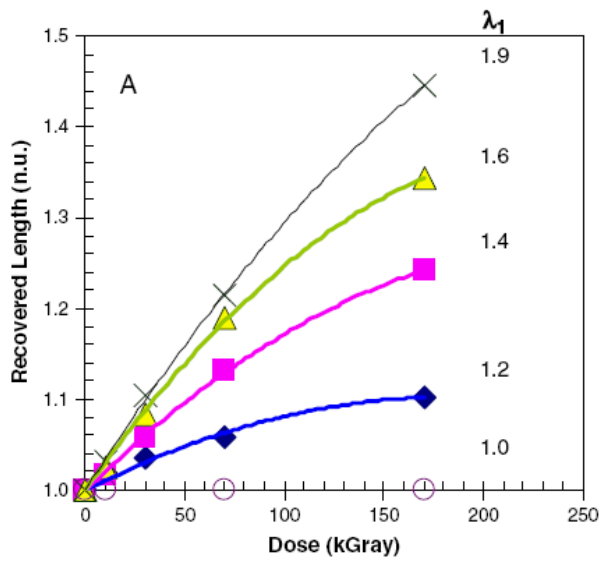
Figure 1

Figure 2

Figure 3