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Molecular Model for the Mechanical Properties of Elastomers. 3. Networks Cross-Linked in a State of Strain

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ABSTRACT: A molecular model developed previously has been extended to a study of the elastic properties of elastomers cross-linked in a state of strain. The model allows a detailed analysis of both the network connectivity upon cross-linking and the mechanical properties upon tensile deformation. The nonaffine displacements of the network junctions during deformation is also fully taken into account. The results show that the permanent set and modulus values in the state of ease increase with an increase in the strain at which the cross-links are introduced. However, in contrast to the predictions of previous theories, these moduli and permanent set values level off at high cross-linking strains.

1. Introduction

In the first paper of this series,[1] we have introduced a new molecular model for the study of the factors controlling the deformation behavior of elastomeric networks. The main emphasis of the work was on the role of entanglements latent in the polymer prior to cross-linking. Our approach has been quite successful in predicting the dependence of mechanical properties on molecular weight of the starting polymer, cross-link functionality, and degree of advancement of the reaction. For simplicity, the study was restricted to the case of poly(dimethylsiloxane) networks formed through chemical end-linking of difunctional polymer chains with plurifunctional monomers.

That previous work is extended here to polymer networks cross-linked in a state of strain. Cross-link formation in stretched networks is of great technological importance since it is closely related to the the phenomenon of ageing in rubber materials. Another motivation for the present work is to be found in recent experimental

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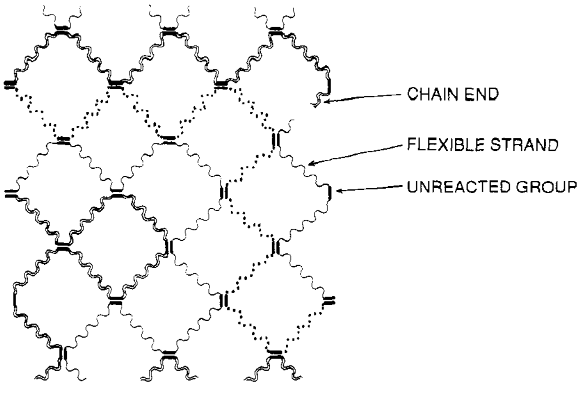

Figure 1. Model representation of the network of starting polymer chains prior to cross-linking.

studies by Ferry et al.[2-4] on stretched polybutadiene networks cross-linked with γ-radiation. These studies were aimed at isolating the effects of entanglements latent in the polymer prior to cross-linking.

Several theories have been developed for describing the elasticity of a polymer network cross-linked in a state of strain.[5-9] In all these approaches, however, the deformation is assumed to be affine and the cross-linking takes place in such a manner as to "form chains which are relaxed when the sample is at the length at which the cross-links were formed".[5] The purpose of the present work is to check the validity of those approaches with the help of a model, like the present, in which the state of stress of individual chains is explicitly taken into account when the cross-links are introduced.

2. Model

In our approach, the starting polymer is viewed as a linear macromolecule of flexible chain strands alternating with short reactive groups that constitute potential sites for cross-linking.[10] The flexible strands are assumed to be made of n statistical segments so that their end-to-end vector length at equilibrium equals $r = n^{1/2}$. We took, quite arbitrarily, $n = 14$. In the absence of strain, these macromolecules are in a random coil configuration and are modeled by a set of random walks on a lattice, as depicted in Figure 1. For simplicity, we choose a two-dimensional lattice with unit length equal to r, so that the end-to-end vectors of the flexible strands overlap the lattice bonds whereas the chain reactive groups fall on the lattice nodes. Details of the configuration of a flexible strand between two lattice nodes are omitted, and only end-to-end vectors (wiggling lines) are being considered. Broken chain strands between nodes account for the finite molecular weight of the macromolecules.

The first set of cross-links is introduced by making each reactive group react with its nearest neighbor with probability α. In the present case of no external strain (see Figure 1), nearest-neighbor groups are those located at the same lattice node. That partially cross-linked network is then stretched to a particular draw ratio, λ_0, and subsequently relaxed toward mechanical equilibrium. This is performed through a detailed relaxation of all the network junctions, i.e. reacted and unreacted groups, toward elastic equilibrium with their neighbors. That procedure is very computer-time consuming since it requires a large number of iterations over the whole network before *all* the groups have reached mechanical equilibrium. Therefore, in order to save computer time, only displacements of the groups along the tensile y axis are explicitly calculated. The groups thus effectively move along parallel tracks in the y direction. Besides a substantial reduction in the length of the calculations, the above simplification also greatly facilitates the search for nearest-

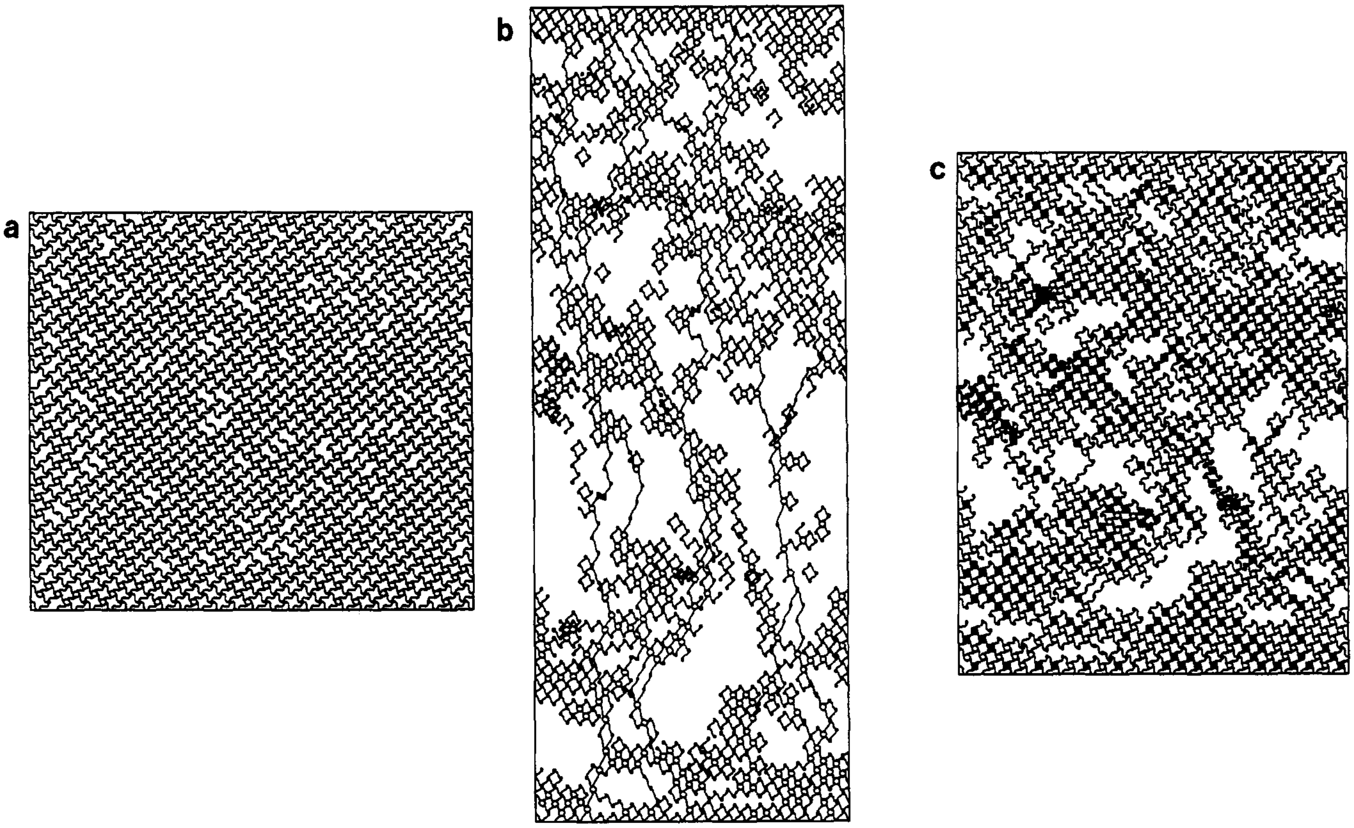

Figure 2. Computer-generated networks at various stages in the cross-linking process. The figure is for a density of first stage cross-links, $\alpha = 0.33$, and an initial molecular weight, $M = 19$ (in flexible strand units). The junction points are represented by the symbols ○ (first stage cross-links), ■ (second stage cross-links), and ■ (unreacted groups): (a) after first stage cross-linking. (b) after stretching to $\lambda_0 = 2$. (c) after second stage of cross-linking and relaxation toward the state of ease reached at $\lambda_s = 1.28$.

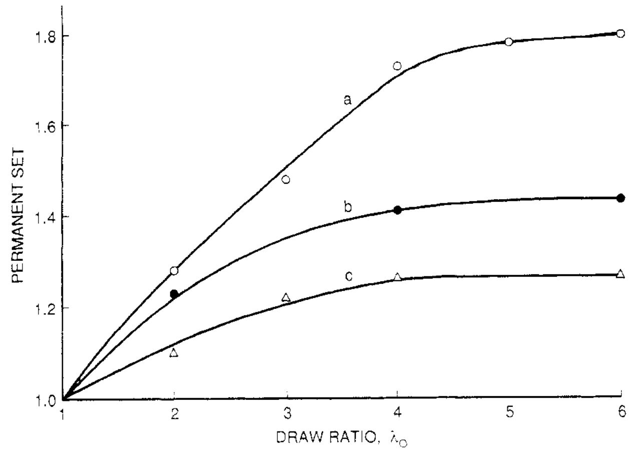

Figure 3. Dependence of permanent set λ_s on the stretch λ_0 in the state of ease: curve a, $M = 19$, $\alpha = 0.33$; curve b, M = 6, $\alpha = 0.5$; curve c, $M = 26$, $\alpha = 0.5$.

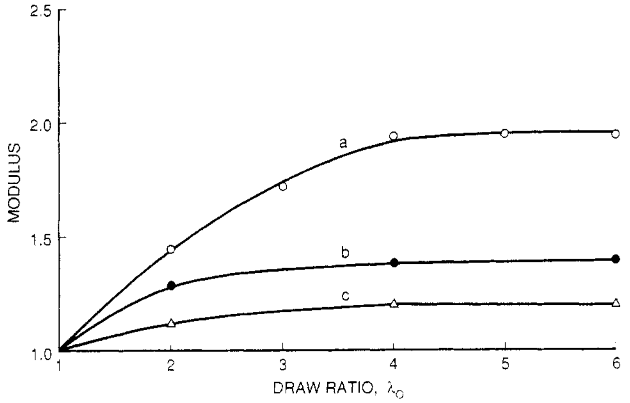

Figure 4. Dependence of the modulus on the stretch λ_0. The modulus values are measured at 50% strain and are in units of their value at $\lambda_0 \approx 1$. Notation is the same as that in Figure 3.

neighbor unreacted groups during the second stage of cross-linking.

In that second stage, the remaining unreacted groups are cross-linked starting from the pair of closest groups (along the y axis) until any additional cross-linking leads to an increase in the external stress by a few percent. In our simulations, that situation is obtained after 50% of the unreacted groups have cross-linked with their nearest neighbor. This is a very convenient feature of the model that allows us to isolate the effect of the draw ratio λ_0 on mechanical properties, keeping the total number of network junctions constant. Upon completion of the second stage of cross-linking, the external strain is released and the network allowed to relax to its new mechanical equilibrium configuration. Upon reaching the so-called "state of ease", the network is tested for its elastic properties by using the techniques developed in ref 1.

3. Results and Discussion

Figure 2a shows a typical network, as obtained from our model, after the first stage of cross-linking. First stage cross-links are represented by the symbol O whereas the symbol ■ denotes unreacted groups. Figure 2b shows the same network after stretching to $\lambda_0 = 2$. Note the quite nonaffine type of deformation and the particularly disorderly arrangement of the unreacted groups that have moved away from their regular pairwise distribution prior to deformation (Figure 2a). After introduction of the second set of cross-links between nearest neighbor unreacted groups, the network is relaxed toward its "state of ease", leading to the final structure depicted in Figure 2c. Figure 2c clearly demonstrates that the network structure is a true fingerprint of its cross-linking history. Thus, the network "remembers" the stretch λ_0 experienced during the second cross-linking stage through not returning to its original dimensions. That phenomenon is called "permanent set" and is responsible for the locking-in of residual orientation and stress in the network.

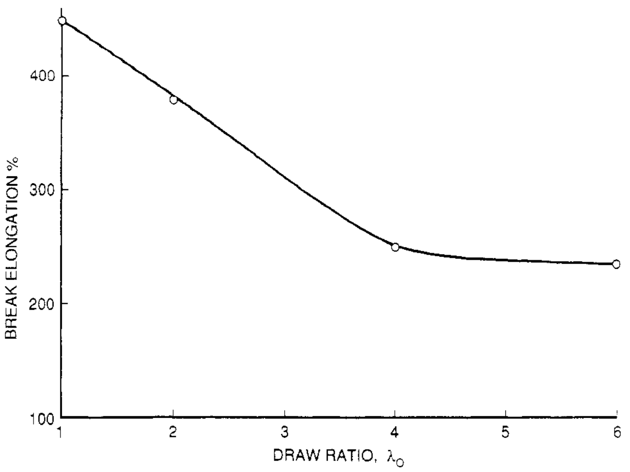

Figure 5. Dependence of elongation at break on the stretch λ_0. The figure is for $M = 19$ and $\alpha = 0.33$.

Our results for the dependence of the permanent set on stretch λ_0 are presented in Figure 3. The permanent set is measured by the residual draw ratio λ_s in the state of ease. The figure is for different values of the initial molecular weight M (in flexible strands units) of the polymer and the density of first stage cross-links α. The latter is given by the ratio of the number of cross-links to the total number of nodes in the original network. Inspection of the figure shows that, at constant λ_0, low molecular weights and small values of α increase the amount of permanent set λ_s. This is because both situations contribute to a more nonaffine type of deformation before the second set of cross-links is introduced and, therefore, to more pronounced memory effects. There is, however, a limit to the extent of nonaffine deformation available in a given network due to the presence of a primary set of cross-links. This is clearly illustrated by the leveling off of the permanent set values at high stretch, $\lambda_0 > 4$. These observations are in contrast to those of previous theories[5-8] that predict a continuous increase of λ_s with λ_0. Note also that, by the very fact that they neglect stress distribution effects, these earlier approaches are incapable of estimating the importance of the initial molecular weight so that a quantitative comparison with our model results appears unfeasible.

The calculated dependence of the modulus on the stretch λ_0 is studied in Figure 4. Our modulus values have been measured at 50% strain. The figure is very similar to Figure 3 for the dependence of the permanent set on the stretch. This therefore indicates that the increase in the modulus with λ_0 (Figure 4) is due to the larger degree of residual orientation and extension present in the state of ease. That interpretation is consistent with our results in Figure 5 which show a sharp drop in elongation at break with an increase in λ_0. Note also that our modulus curves in Figure 4 level off at high λ_0 values, again in contrast to the predictions of refs 5–7.

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(10) A typical example would be linear block copolymers made of soft polyether chains alternating with polyurea hard segments. The latter form hydrogen bonds between themselves and thus act as potential physical cross-linking sites.

Characterization of the Free-Radical Homopolymerization of *N*-Methylmaleimide†

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ABSTRACT: A hydrogen atom bombardment technique was employed at room temperature to initiate the free-radical homopolymerization of *N*-methylmaleimide (MMI), which can be considered a model compound for prepolymer resins containing the maleimide functional group. Several different radical species were observed and identified by electron spin resonance (ESR). The initial radical, which produced a spectrum having four major resonance lines, was formed by the addition of atomic hydrogen to the C–C double bond. This initial radical, which was too reactive to be observed in pure MMI, was stable for a few minutes in a photopolymerized MMI matrix containing trace amounts of MMI. The second radical species, which produced a three-line ESR spectrum, was identified as the propagating radical associated with the homopolymerization. At later stages of the polymerization reaction this propagating radical was replaced by a third radical species whose ESR spectrum consisted primarily of two intense lines near the center of the spectrum and two weaker extrema lines. This species is assigned to a vinyl radical and/or an internal backbone radical centered on a tertiary carbon.

Introduction

Bis(maleimide) resins form a class of thermosetting polymers that are used as high-temperature matrices in high-performance composites. The mechanical properties of these materials depend on their network structures, which are controlled by the cure chemistry of the maleimide functional group. In several previous investigations electron spin resonance (ESR) spectroscopy has been used to examine the free-radical chemistry of the maleimide group. These studies have included the neat polycrystalline maleimides[1–5] as well as their solutions.[6–10] Typically, the free radicals have been generated by using UV irradiation or X- or γ-irradiation. Solution studies offer the advantage of spectral resolution (i.e., narrow ESR lines), but they also have the following disadvantages: (1) the radicals are less stable in solution than they are in the solid state, (2) the solvent can complicate the results by participating in the free-radical chemistry being investigated, and (3) the results cannot necessarily be extrapolated to the neat system. On the other hand, studies of polycrystalline systems have the disadvantage that the ESR lines are broadened because of hyperfine and *g* anisotropy, making identification of the radicals by way of their resolved hyperfine structures difficult. With high-energy irradiation the situation is further complicated by the frequent superposition of spectra from several different radical species.[1,10]

Free radicals can also be generated thermally, both with and without the presence of added initiators. We have used this approach to induce free-radical homopolymerization in bis(maleimide)s and maleimide compounds.[11] In this study, both the types and the concentrations of free radicals associated with the cure process were monitored. While many radical species of interest were identified, this method of radical generation had some of the disadvantages of the irradiation methods referred to above. In particular, the observed ESR spectrum was often a superposition of three or more broad spectral components, which made it difficult to analyze the spectra.

In our present work on bis(maleimide) curing reactions, we have been able to simplify the ESR spectral analyses by using another technique, viz., hydrogen atom bombardment, to generate radicals in the model compound *N*-methylmaleimide (MMI) and in the related thermally and photochemically cured homopolymers. This technique has already been shown to be more selective than either X- or γ-irradiation for producing radicals in many organic materials, several of which have contained functional groups similar to those in MMI.[10,12–14] For example, it has been observed[12] that the hydrogen atoms preferentially add to certain C–C double bonds, that they are somewhat less likely to induce C–H bond scission by hydrogen-atom abstraction (with C–H bond scission in methyl groups being particularly unlikely), and that C–C

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