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An explicit polymer and node network model to compute micromechanical properties of silica-filled polydimethylsiloxane

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Abstract

Two important aspects of filled polymer systems that can influence elasticity are the random position of filler particles and the nonuniformity of polymer chain lengths that form the chain/particle network. Historically, most network elasticity models have been based on idealized assumptions of uniform chain length constrained to highly symmetric orientations. We present a novel, three-dimensional explicit polymer and node network model (EPnet) that includes both randomly distributed filler particles (nodes) and polymer lengths taken from a Gaussian distribution. The molecular level polymer forces that produce elasticity are assumed to operate between pairs of connected network nodes. The numerical model is amenable to any molecular force that depends on the distance between two nodes, however, for this paper, we assume that the polymer chain segments that connect the filler particles obey a simple two-force model, i.e. a constant force required to stretch a single polymer chain and a force arising from the binding energy between a polymer chain and a filler particle surface. Free ends, i.e. polymer segments connected to only one particle, do not contribute to the elasticity. With these assumptions, the model contains intrinsic mechanisms that appear to predict the phenomena of yield stress, tensile failure, permanent set and stress hysteresis. The model is applied to a mesoscale volume element ($\sim 1\ \mu\text{m}^3$) of silica-filled polydimethylsiloxane to study the micromechanical stress in response to various strains, e.g. tensile, compressive, shear and swell. Model predictions are in quantitative agreement with tensile stress/strain experiments.

Keywords: Polymer physics; Node network; Polydimethylsiloxane

1. Introduction

Most network elasticity models are based on the change in entropy of a network chain that occurs in response to an applied strain. Analytic expressions for the stress are obtained starting with thermodynamic considerations [1–3]. The Helmholtz free energy, F, may be written as

$$F = E - TS, \tag{1}$$

where E is the internal energy, T is the absolute temperature and S is the entropy. Both the temperature and volume are assumed to be constant. The tensile force, f, is obtained by differentiating with respect to the length, L, and assuming that the internal energy does not change as the sample is extended.

$$f = \frac{\partial F}{\partial L} = -T\frac{\partial S}{\partial L}. \tag{2}$$

To obtain analytic solutions for the stress, requires a tractable expression for the entropy derivative which leads to a number of idealized assumptions about the network. All of the chains must have the same length and, for most models [4–9], they must be constrained to highly symmetric orientations, i.e. along the Cartesian axes or diagonals. The solutions are valid only if the strain is imposed along an axis of symmetry. As applied to systems of silica-filled polydimethylsiloxane (PDMS), these models may be criticized for a number of reasons. The chain lengths between filler particles or crosslinks are obviously not all of the same length and, because the filler particles are dispersed randomly throughout the volume, there are no axes of symmetry, a priori. Also, these models contain no physical mechanisms that provide quantitative predictions of permanent set or stress hysteresis. A notable exception to these approaches is that due to Kilian et al. [10]. They proposed an analytic theory for the elasticity of carbon black rubbers that explicitly included a number of distributions of connecting chain lengths. The elastic force was assumed to

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be the volume weighted average of the usual rubber elastic force and a force arising from the interaction of filler particles with themselves and the rubber matrix. Reichert et al. [11] has proposed a double network model, one parallel to the strain axis and one perpendicular, based on the observation in carbon black rubber that the local deformation is not homogeneous. The total stress is assumed to be the average of the two networks, weighted by the volume fraction of the filler particles. Wu and van der Giessen [12,13] extended Treloar's non-Gaussian model for a crosslinked rubber network to include random chain orientations. The analytic expression that they derived for the stress assumed a constant chain length and the usual rubber elastic force for a chain due to changes in conformational entropy. Termonia applied a two-dimensional lattice model to study the elasticity of spider silk [14]. Silk is known to be comprised of amorphous polymer chains and small crystallites that presumably form a network, making it functionally similar to a filled polymer. Termonia's model included four tensile moduli: chain–chain hydrogen bonding, single chain elasticity, crystallite trapped chain elasticity and the elastic modulus of the crystallites. The model assumed a uniform chain length with highly symmetric, nearest neighbor-only chain connectivity.

With respect to silica-filled PDMS, theories that are formulated from Eq. (1) have an even more troubling issue; the experimental evidence raises questions about the assumption that the internal energy does not change under strain. Unlike conventional crosslinked rubber, silica-filled PDMS does not exhibit the linear increase in stress with temperature at low strains. The experiments by Galanti and Sperling [15–17] clearly reveal a negative or near zero temperature derivative for strains up to 40%. If the temperature derivative of the stress is zero, the origin of the stress cannot be due to changes in entropy. Accordingly, Galanti and Sperling concluded that most of the stress must be due to changes in internal energy. More recently Clement et al. [18] measured the stress/strain behavior of silica-filled PDMS at various temperatures. While they concluded that the elasticity was due to entropic effects, their data suggest that the derivative of stress with respect to temperature is zero up to about 10% strain. As they are presently constituted, we do not think that any of the existing models, described above, are directly applicable to silica-filled PDMS systems.

In this paper, we will focus on how the first two objections may be overcome, the inherent randomness of the filler particle positions and the chain lengths. We will present a numerical mesoscale network model that accommodates both random node positions and a distribution of chain lengths. Our goal will be to provide a realistic bridge between molecular level forces and micromechanical behavior. The resulting model will be shown to treat several types of strain including tensile, compressive, shear and swell. We shall compare the model predictions for tensile strain to experiments and provide representative stress/-strain calculations for compressive, shear and swell strains.

2. Model description

Based on representative experimental data for particle size and chain length and also computational limitations, we choose as a representative volume element a 1 μm cube, centered at the origin. This is large enough to smooth the interactions of individual particles but small enough that a reasonable density of particles and chains is computationally feasible. Physically, the volume element can contain over a million PDMS polymer chains of molecular weight (MW) of 500,000 Da, and between 10^3 and 10^4 filler particles for a silica concentration of 14% by volume. When fumed silica is used as the filler, the particles are composed of aggregates of small silica spheres having a diameter ~10 nm. The largest dimension of the aggregates is typically on the order of ~100 nm. We expect that explicitly treating on the order a few percent of this number will be statistically representative. The simulation begins by randomly placing nodes on two or more faces of the volume element depending on the type of strain. For tensile strains, the two opposing faces normal to the strain axis are chosen. The face nodes provide a convenient subset over which surface forces may be integrated to compute stresses. Throughout the strain cycles, the face nodes remain fixed on the volume element surfaces selected. Internal nodes are then placed randomly within the volume element. The only constraint applied to their placement is a minimum nearest neighbor distance, typically a few hundredths of a μm. If specified, crosslink nodes are also randomly dispersed subject to the same constraint.

The nodes, facial and interior, are then connected by chain segments to form a continuous network. Beginning with the face nodes, the nodes are processed sequentially, subject to the constraint that no face nodes are connected by the same chain. For each node, i, a random number of chains, drawn from a Gaussian distribution (mean and standard deviation supplied by input) are created and associated with the node being processed. The attachment point on the chain may be an end point or any point along the chain. The second node, j, that the chain is connected to, is chosen randomly from a list of neighbors of node i with a weighting factor of $1/R_{ij}$,^{2} where R_{ij} is the distance between the nodes i and j. Since the number of neighbors increases as the surface area of the enclosing sphere, this weighting factor assures that every neighboring node has equal probability of being chosen. Other weighting schemes can be readily implemented if desired. Every chain may have zero, one or two free ends. The process is repeated for each node subject to the constraints that only a single chain may connect any two nodes and that the total number of chains attached to any node be less than a maximum value (specified by input). The number of face nodes is determined by the constraint that the number of chains crossing a plane normal to a strain axis be approximately constant throughout the volume. Periodic boundary conditions are imposed appropriate to the type of strain being modeled. For tensile and shear strains, the axes transverse to the strain axis are periodic; for compression, the axis parallel to the strain axis is periodic. Periodic boundary conditions assure that all nodes have a spatially homogeneous set of neighbor nodes from which connections can be made. As we pointed out above, a 1 μm cube of PDMS can contain over a million polymers of MW 500,000 (number averaged). Although it is not computationally feasible to include this many chains in our simulations, we must take this deficiency into account when stresses are calculated. This is accomplished through a chain coarseness factor which is defined as

$$f_{\mathrm{coarse}} = V_{\mathrm{cell}}\rho_{\mathrm{PDMS}}/(M_{\mathrm{chains}}(1 - f_{\mathrm{bound}})(1 - f_{\mathrm{filler}})), \tag{3}$$

where V_{cell} is the volume of the simulation cell, ρ_{PDMS} is the density of PDMS, M_{chains} is the total mass of chains constructed, f_{bound} is the fraction of chains bound to at least two filler particles and f_{filler} is the volume fraction of the filler particles.

Chain crosslinking proceeds in much the same manner as node connections with the added complication that a crosslink may connect two separate chains (hetero-crosslink) or simply make a loop in a single segment (self-crosslink). The determination of which type of crosslink a particular crosslink node should be is determined randomly based on the probabilities supplied by input. For the case of a self-crosslink node, another network node is chosen from its neighbor list and a chain segment attached to this node is chosen randomly, subject to a length constraint. The candidate chain segment must be long enough to reach from the crosslinking node to each of the nodes that define its endpoints plus a minimum amount for a loop segment. The chain segment selected is then randomly divided into three new segments, a loop plus one segment to connect to each of the end nodes, again subject to the length constraints. Crosslinking between different chain segments (hetero-crosslinking) is accomplished in an analogous manner, except that two neighboring connecting chain segments are chosen. Initially, we have excluded free ends from participating as crosslinked segments and do not allow multiple crosslinks per chain.

Various strains may be imposed on the volume element such as tension, compression, shear and swell. The resulting stress is calculated by summing the appropriate force components over the facial nodes. For the case of tensile strain along the y axis, the net y component of force on each face is computed by summing over the facial nodes.

$$F_y = \sum_i^{\mathrm{Face}} \hat{y}\cdot\vec{f}_i, \tag{4}$$

The engineering stress is then computed as the difference between the net forces on the opposing faces divided by the area of an end face:

$$S = f_{\mathrm{coarse}}(F_- - F_+)/A_{xz} \tag{5}$$

where $f_{\mathrm{coarseness}}$ is the chain coarseness factor, $F_{-,+}$ are the average forces on the cell faces normal to the strain axis, and A_{xz} is the initial area of the volume element face.

Strain is applied in small increments to ensure that the maximum movement of any node is less than the distance over which a node–node force could change appreciably. In the case of the two-force model (described below), the limiting distance is the distance over which the force transitions from the chain-stretch to surface-slip value. Typically, this is set to 0.04 μm, which limits the maximum elongation factor to 1.002. The manner in which nodes are moved in response to the strain step depends on the type of strain being imposed. For tensile strain, the following procedure is used. At each strain step, an affine transformation ($\alpha = 1.002$) is applied to all nodes.

$$y = \alpha y', \quad x = \alpha^{-1/2}x', \quad z = \alpha^{-1/2}z', \tag{6}$$

where the primes refer to the original coordinate values. When the distance between two connected nodes reaches the length of the connecting chain segment, the segment is assumed to be taut. Node separation distances may be reduced by a constant value (provided by input) to account for the finite size of the filler particles. An optional node relaxation step may be applied if the net force on any node is above some threshold value. The tension of taut chains may be relaxed by moving the node an incremental distance in the direction of the net force. If there is a free end segment adjacent to the taut segment, an amount of chain length is transferred from the free end to the connecting segment sufficient to maintain the taut condition. If the length of the free end is too short to do this, then the chain is assumed to detach from the node and the status of the connecting segment is changed to that for a free end. The incremental chain lengths transferred from original free ends is summed at each strain step. We define a measure of permanent set as the ratio of the sum of the incremental chain length transfers to the total length of all chains in the volume element. The option exists to reverse the strain step at some strain value to effectively cycle the volume element back to zero strain. For the two-force node–node interaction model, this results in stress hysteresis. This is discussed in reference to Fig. 7.

3. The two-force node–node interaction model

Previously, we have reported atomistic simulations of isolated PDMS molecules interacting with themselves or a hydroxylated silica surface [19,20]. These simulations suggested that the force required to straighten (or stretch) an isolated PDMS chain from a low energy conformation was approximately constant, i.e. the internal energy increased linearly. Changes in the internal energy were found to be dominated by the electrostatic and Van der Waals' terms in the classical potential used for the simulation. It was further found that a similar situation obtained for a single PDMS chain adhering to a hydroxylated silica surface. The force required to pull a chain away from the surface was found to be approximately constant and about a factor of three greater than the stretching force.

An analytic model was developed to describe the stress/strain behavior of a volume element of uncrosslinked silica-filled PDMS. In order to obtain agreement with experiment, it was found that the force required to slide a taut chain across a filler particle surface had to be increased by about a factor 6. Physically, this corresponds to assuming that every bound chain has ~6 contiguous dimethylsiloxane groups bonded to the silica particle surface by Van der Waals' and electrostatic forces. In order to move a chain across a particle surface, the Van der Waals' and electrostatic forces for all six units must be overcome simultaneously. This may be regarded as a molecular frictional force. We shall refer to the two force values as F_{stretch} and F_{slip}. This is the basis of the two-force node–node interaction model. Initially, the distance between connected nodes is greater than the connecting chain segment and the segment is slack. As the nodes move apart under an applied strain, the operative force is the stretching force, F_{stretch}. When the separation distance equals the length of the connecting chain segment, the chain becomes taut, and the force changes to the sliding force, F_{slip}. In practice, the change in the force is smoothed by joining the two force values with a third order polynomial constrained by zero derivatives at the endpoints. With the additional assumption that the distribution of connecting chain lengths is a Gaussian, the analytic model could be fit to the experimental data using reasonable parameter values. With only a single stretching force, this model does not contain a mechanism to account for the Mullins effect.

The simulation method used to obtain the forces may be criticized because it considered only isolated PDMS chains. Possibly, if a realistic environment of neighboring chains were included in the simulations, their presence would act as a constraint that could influence the value of the forces. This applies to both chain stretching and surface slip simulations. At this time, performing atomistic simulations with sufficient surrounding material to address these issues is a computationally challenging task. We consider this to be an area requiring further work. However, it may be argued that since PDMS is a viscous liquid, interactions between neighboring chains may be weak, and there is some experimental support for this. Boué et al. [21] dissolved deuterated PDMS chains in non-deuterated networks and used small-angle neutron scattering to see if the deuterated chains were influenced by the surrounding network as it was strained. They observed no detectable anisotropy for strains up to 45%, suggesting that a PDMS chain does not interact strongly with neighboring chains.

4. Discussion

At present, the network model can simulate four types of strain: tensile, compressive, shear and swell. For tensile strain, there are a number of experiments to which we can compare the model predictions; we chose to compare to the data of Boonstra et al. [22]. For the other types of strain, we were not able to find experiments that included sufficient detail to allow comparisons. We present representative calculations for these strain types for illustrative purposes only.

To simulate a tensile stress/strain experiment, we construct a representative volume element network (uncrosslinked) with nodes on the faces normal to the tensile axis (y) at $y = \pm 0.5$ μm, with periodic boundary conditions in the orthogonal dimensions (x, z). The volume element is sequentially distorted by the incremental affine transformation consisting of an extension factor of 1.002 along the y axis and a factor of $(1.002)^{-1/2}$ in the transverse dimensions. This is sufficiently small to resolve the transition from stretching to slipping as a connecting chain segment becomes taut. At each strain step, connecting chain lengths are compared to the node separation distance to decide if the chain has become taut. The engineering stress is computed according to Eqs. (4) and (5). The predicted tensile stress of a 1 μm^3 volume element for strains up to 9 is shown in Fig. 1, for five independent network constructs. The parameter values, listed in Table 1, were chosen to be consistent with the experimental conditions of Boonstra et al. for filled but uncrosslinked PDMS and, the predicted stress is in reasonable agreement with the experimental data (solid triangles). The predecessor analytic model [19] was also fit to this experiment with similar parameter values. The calculated stress reaches a maximum value at a strain of about 9, which is close to the observed failure point at a strain of 7. As explained above, a chain can detach from a

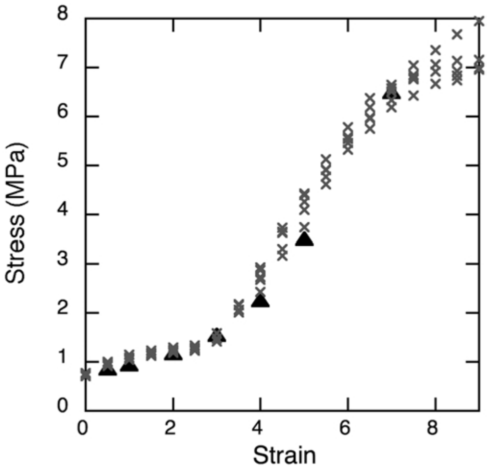

Fig. 1. Predicted tensile stress (x's) for filled, uncrosslinked PDMS–silica and experimental values of Boonstra et al. [22] (solid triangles) for parameter values listed in Table 1. Five independent random networks were simulated.

Table 1
Principal input parameters and values used for simulations of Boonstra experiment [22]

Parameter	Simulation	Experiment
Polymer MW_n (dalton)	400,000 ± 30,000	500,000
Filler particle density (μm^{-3})	1500	1000–10000 ?
Filler volume fraction	14%	14% (35 phr)
Fraction bound	0.75	0.85, Single particle
Minimum node separation (μm)	0.03	NA
Neighbor cutoff distance (μm)	0.13	NA
Chain stretching force, F_{stretch}	5×10^{-6}	NA
Chain slipping force, F_{slip}	5.3×10^{-6}	NA
Chain coarseness factor	142	NA
Chain density (μm^{-3})	9320	$>1 \times 10^6$

filler particle after all of the available material in an adjacent free end slips over the surface as the node separation distance increases in response to the strain. In the simulations, the maximum stress occurs when the rate that chains detach from network nodes exceeds that of chains becoming taut. For strains above the peak stress point, commonly referred to as the strain-softening region, the model predicts lower stresses. Silica-filled PDMS usually does not exhibit this behavior and we assume that tensile failure occurs when the strain exceeds the maximum stress point.

The fact that a lower average value for the MW of the PDMS chains (400,000 vs. 500,000 Da for the experiment) was necessary to obtain agreement with the experiment, is not surprising. A PDMS chain of MW 500,000 Da has an extended length of nearly 2 μm, so it is reasonable to expect that some of them can adhere to more than two filler particles, resulting in more than one connecting segment per chain. The effect that this would have on the simulations would be to lower the average MW of connecting chain segments. To the extent that multiple node connections occur commonly, one could argue that the simulation value of 400,000 is actually too high. More difficult to reconcile is the very low value for the required width of the Gaussian distribution of chain MW, 30,000 Da, since the polydispersity of PDMS is typically found to be two or greater. In the process of varying the values of the simulation parameters to achieve agreement with experiment, it was found that the calculated ratio of the connecting segment length to node separation distance, L/R, had a strong correlation with the shape of the stress strain curve. It is this ratio that determines the amount of extension that an individual chain can accommodate before the tensile force changes from f_{stretch} to f_{slip}. Apparently, the algorithm employed to choose connected node pairs results in sufficient variation in this ratio to achieve a fit with the experimental stress/strain. Increasing the distribution width for the chain MW results in an excessive amount of variation in L/R_{ij} We considered this an area requiring further study.

While the two-force node–node model enforces a yield stress, it does so at the expense of having an unphysical discontinuity at zero strain. This could be remedied by giving the stretching force a finite turn-on length, analogous to the transition length for switching to the slipping force. In fact, some of the atomistic simulations displayed such transitions. Physically, we would interpret this to mean that chains are not completely natured, i.e. collapsed on themselves, allowing some extension at near zero force. This is not included in the initial version of the model because we have no good estimate of what the transition length should be from simulations. Considerable variation in the initial modulus is found in the experimental literature as well. Including a turn-on parameter in the model at this stage would simply result in yet another parameter to be fit to experiment. We anticipate that further simulations and low strain experiments will provide guidance for estimating this parameter.

Material that is crosslinked as well as filled is treated by the addition of cross linking nodes, having a functionality of four. Each crosslink creates a junction in two connecting segments associated with neighboring filler nodes. To fit the filled and crosslinked stress/strain data of Boonstra et al., we added about 800 hetero-crosslinks in addition to the 1500 interior nodes. This resulted in about 16% of the chains being crosslinked. The predicted stress/strain for this case, shown in Fig. 2, is in reasonable agreement with the experimental data, with the exception that the simulations do not predict a stress maximum near the experimental failure point. The concentration of dichlorobenzoyl peroxide reported for the experiment was 3.2 parts-per-hundred (phr). If every peroxide molecule resulted in a chemical crosslink, a chain of MW 500,000 Da would have, on average, 35 crosslinks, and a typical connecting segment comprised of one third of the length would have ~12 crosslinks. However, the actual efficiency of the peroxide crosslinking process was not reported. While this may

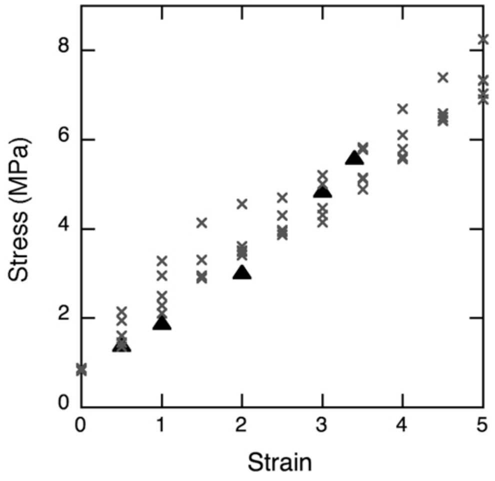

Fig. 2. Predicted tensile stress (x's) for filled and crosslinked PDMS–silica and experimental values of Boonstra et al. [22] (solid triangles) for parameter values listed in Table 1. Five independent random networks were simulated.

appear to be a significant discrepancy, it may not be totally inconsistent with experiment. It is commonly found that the tensile strength for crosslinked but unfilled material is as much a factor of 10 lower than that for filled and crosslinked material [23]. This, too, is considered an area requiring further study. We expect that the network model will allow quantitative studies on the mechanical effects of crosslinks.

Because the model does not include the compressibility of the polymer, compressive strain is simulated as a two-dimensional expansion normal to the compression axis. Face nodes are placed on the four faces transverse to the compression axis during the network build. As in the case of tensile strain, strain is applied via incremental affine transformations of all nodes and stress is computed analogous to Eq. (5). A plot of stress vs. compressive strain is shown in Fig. 3 for the parameter set listed in Table 1. Since we have no experimental data to which the predictions can be compared, the plot is for illustrative purposes only.

Uniaxial shear strain is applied by the transformation

$$z = z' + \frac{\Delta z_{\text{face}}}{0.5Y_{\text{box}}}y, \tag{7}$$

where z' and z and are the initial and final z coordinates of the node, y is the node y coordinate, Δz_{face} is the shear translation of a face of the volume element and Y_{box} is the width of the volume element. A representative shear stress/strain prediction is shown in Fig. 4 for illustrative purposes.

Swelling a filled polymer in a good solvent is often used as qualitative measure of the crosslink density. Swell strain is simulated by placing face nodes on all six faces of the volume element, and sequentially applying a multiplicative factor to all of the node coordinates. Physically, we interpret swell strain as being due to the solvation of the connecting segments, essentially neutralizing the stretching force, allowing the network to expand until the chains become taut and the stronger force, F_{slip}, prevents further swelling.

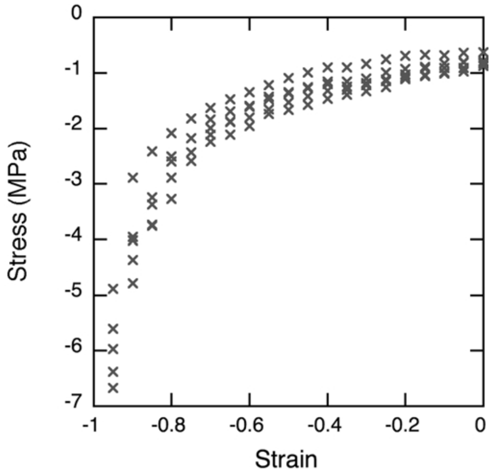

Fig. 3. Predicted compressive stress for filled and crosslinked PDMS–silica using parameter values listed in Table 1. Five independent random networks were simulated.

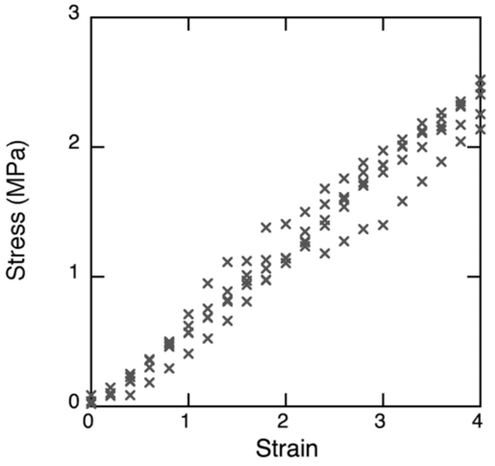

Fig. 4. Predicted shear stress for filled and crosslinked PDMS–silica using parameter values listed in Table 1. Five independent random networks were simulated.

In our simulations, stress is computed analogous to Eq. (5) at each strain step. We assume that the slipping force is not affected by the solvent. The simulations for swell strain, shown in Fig. 5 are consistent with these assumptions. We expect that the maximum swell factor should be close to the strain value at which the stress begins to increase sharply. A representative plot of this is shown in Fig. 5 for parameter values listed in Table 1.

Permanent set is the phenomenon characterized by the incomplete recovery of a material to its original length after being strained. This can be as much as 20% or more of the original length, and often has an adverse effect on the performance of elastomers. A possible mechanism for this exists in our model by virtue of the fact that material can be transferred from a free end chain segment to the connecting segment, as a taut chain is further extended. We suggest that the local accumulation of this material between connected filler particles will tend to prevent them from returning to their original separation, resulting in permanent set. In the

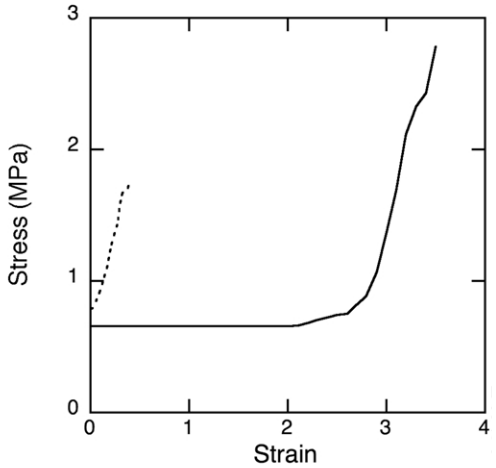

Fig. 5. Predicted stress due to swelling for filled, uncrosslinked PDMS–silica (solid line), and for filled and crosslinked (dashed line), using parameter values listed in Table 1. Strain is extension along one axis.

case of tensile strain, this can be easily computed at each strain step. A representative plot of this is shown in Fig. 6, again, for illustrative purposes.

Stress hysteresis is observed in both silica-filled PDMS and carbon black rubber and its origin is still an outstanding question. We performed a simple cyclic tensile strain simulation using the parameter set listed in Table 1. As is clear from Fig. 7, the two-force node interaction model appears to have an intrinsic mechanism for stress hysteresis. For this simulation, a filled but uncrosslinked network was stretched by a factor of 6 and then returned back to its original length. The strain deformation was accomplished by incremental affine transformations with a relaxation step as explained above. The abrupt drop in stress, as the strain is reversed (i.e. the extension factor is changed from 1.002 to 0.998), is due to the response of taut chains. As the separation distance between connected nodes is decreased, taut chain segments are flagged as slack and the chain force changes abruptly from the slip value to stretch. Further scrutiny and testing will be necessary to determine whether or not this offers a viable explanation of stress hysteresis.

5. Conclusions

An explicit three-dimensional, molecular level polymer and node network model has been developed to simulate the micromechanical response of a mesoscale volume element of a filled and crosslinked polymer system in response to various strains. For comparison to experimental data and demonstrations of code functionality, a two-force node–node interaction model was assumed, however, any force model that depends on the distance between network nodes would be compatible. The model captures the inherent randomness of filler particle dispersion and the nonuniformity of polymer chain lengths. Predictions for tensile stress/strain are in quantitative agreement with experiment. We have also shown that compressive, shear and swell type strains can be treated quantitatively. With the assumption of the two-force node–node interaction model, the network model contains intrinsic mechanisms that may predict the phenomena of yield stress, tensile failure, permanent set and stress hysteresis. Because the model can quantitatively treat a multitude of strain types and associated phenomena, we expect that a self-consistent set of molecular-level, material parameter values can be inferred with high confidence. We anticipate that the numerical model will provide insight into how the molecular interactions affect elasticity in filled polymers and will be useful in developing simpler, more computationally efficient engineering models. We expect that the model will be made available to other investigators.

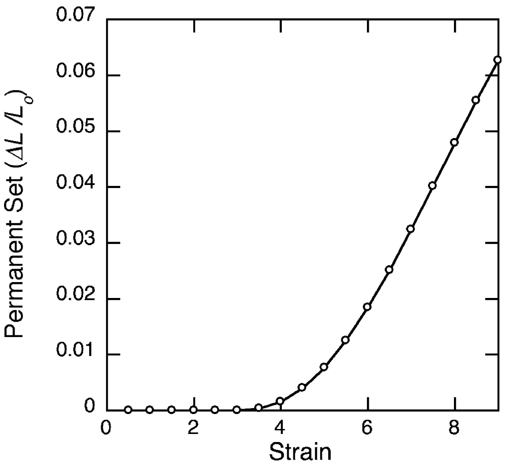

Fig. 6. Predicted permanent set for filled, uncrosslinked PDMS–silica using parameter values listed in Table 1. Permanent set was computed as the fractional increase in connecting chain lengths due to chain material moved from a free end to a taut, connecting segment.

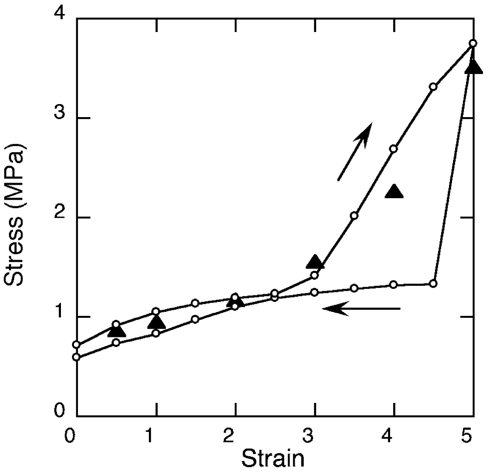

Fig. 7. Predicted tensile stress during an extension/relaxation cycle (solid lines) for filled, uncrosslinked PDMS–silica using parameter values listed in Table 1. Relaxation cycle exhibits an abrupt hysteresis as the network is unloaded. Experimental values [22] for extension are shown by solid triangles.

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