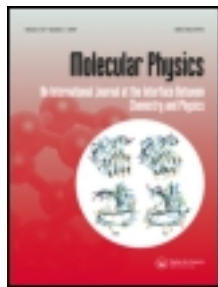


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RESEARCH ARTICLE

Molecular dynamic simulations of elastomer structure and its influence on anisotropic stress under time-varying strain

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We investigate the evolution of polymer structure and its influence on uniaxial anisotropic stress under time-varying uniaxial strain, and the role of external control variables such as temperature, strain-rate, chain length, and density, using molecular dynamics simulation. At temperatures higher than glass transition, stress anisotropy in the system is reduced even though the bond stretch is greater at higher temperatures. There is a significant increase in the stress level with increasing density. At higher densities the uncoiling of the chains is suppressed and the major contribution to the deformation is by internal deformation of the chains. At faster rates of loading stress anisotropy increases. The deformation mechanism is mostly due to bond stretch and bond bending rather than overall shape and size. Stress levels increase with longer chain length. There is a critical value of the functionality of the cross-linkers beyond which the uniaxial stress developed increases caused primarily by bond stretching due to increased constraint on the motion of the monomers. Stacking of the chains in the system also plays a dominant role in the behavior in terms of excluded volume interactions. Low density, high temperature, low values of functionality of cross-linkers, and short chain length, facilitate chain uncoiling and chain slipping in cross-linked polymers.

Keywords: cross-linked polymer; anisotropic uniaxial stress; time-varying uniaxial strain; molecular dynamics; polymer structure

1. Introduction

The behavior of cross-linked polymers can be attributed to the set of morphological constraints these material possess. Their molecular structure enables them to undergo nonlinear elastic strain. The major contribution to the strain comes from unfolding of the chains rather than the actual deformation of the bonds. To understand the effect of molecular structure on macroscopic stress requires accurate modeling and simulation of the evolving polymer structure.

Molecular dynamics (MD) together with statistical estimation techniques provide an insight into the microstructure and relate them to macroscopic parameters [1]. They have been used to evaluate the shear modulus and observe its decay [2, 3]. The role of cross-linkers in the mechanical behavior of cross-linked polymers has been studied using MD simulations in the context of failure stress [4], equilibrium stress [5], and glass transition temperature [6]. Entanglements depend on the polymer structure and topology and it is known that entanglement increases with density and so does the stress [7, 8].

The studies reported in literature earlier have dealt with the structure and topology of the cross-linked polymer and its influence on certain aspects of its behavior.

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A systematic study of the influence of various micro-structure parameters on the anisotropic stress developed in the cross-linked polymer has not been investigated. This work is concerned with the mechanisms that contribute to uniaxial stress in an cross-linked polymer under time-varying uniaxial strain, the evolution of its microstructure, the correlation between strain, microstructure, and stress, and the influence of external control variables such as temperature, strain-rate, and density on them. The numerical tool used is molecular dynamics.

2. Simulation

Use of MD simulation in the canonical NVT ensemble requires a modification in the equations of motion. This is achieved by introducing an additional degree of freedom [9, 10] representing kinetic mass in the equations of motion. We use a modified version of the velocity Verlet algorithm [11] to integrate the equations. While applying strain on the system, all atom positions are scaled in the same proportion as that of the cell dimensions. Here we assume the material to be incompressible. So if the stretch ratio in the x direction is λ then the stretch ratio in the y and z direction is $\frac{1}{\sqrt{\lambda}}$ due to symmetry. The equations of motion for the monomers which are involved in cross-linking is the same as that derived for the monomers belonging to the linear polymer chain [12]. An extra term is included in the momentum relation to account for contribution from cross-linkers.

The starting point of the simulation is to generate an initial equilibrated melt of polymer chains. Uniformly spaced points in the cell are selected as the center of mass of each chain. Chain growth takes place by generating a series of random bond vectors. A random bond vector in three dimensions is generated by using a random dihedral angle between 0° to 360° while keeping the bond angle and bond length of the chain at their equilibrium values. This helps in generating an initial structure of the polymeric system very close to the one corresponding to the minimum energy configuration. The position of the new monomer is obtained by adding these bond vectors to the previously generated sites. While chain growth takes place, a check is performed for the occupancy of the newly generated site. In other words, if the new generated position for the monomer is already occupied we go back one step and generate a new site position. A partial overlap of monomers is allowed during the chain growth which is later removed by subjecting the polymeric system to a soft repulsive potential to ensure that all the monomers are separated by a distance confirming the absence of overlap. After generating the series of linear polymer chains, we add stoichiometric number of cross-linkers with functionality f in the system by randomly placing them in the simulation cell. While placing the cross-linkers, checks are performed for occupancy of the randomly generated site. The monomers at the ends of the chains are active sites which are linked with the cross-linker when it comes within the reaction radius of these active sites. Before the cross-linking takes place, the linkers interact with other monomers through a Lennard-Jones (LJ) potential. Once the cross-linking takes place, we add a bonded potential, commonly known as finitely extended non-linear elastic (FENE) potential, between the cross-linked members.

Once the initial structure is ready, we perform an MD simulation by subjecting the system to bonded and non-bonded potentials which describe the inter-atomic interaction. The van der Waals forces are modeled using a shifted and truncated Lennard-Jones potential which acts between all pairs of united atoms. The bonded interactions involved are bond stretching, bond bending, and bond torsional potentials. Stretching of bonds is modeled using FENE potential. This potential acts

between monomers which are directly bonded to each other in a chain and also between monomers which are cross-linked with each other. The bond bending potential is a harmonic function of the bond angle θ and the torsional potential is a four-body potential and is a function of the dihedral angle ϕ [13, 14].

In the present simulation we use a time step of 10^{-3} for the numerical integration of the equations of motion which is sufficient for the stability of the integration scheme and maintaining its accuracy. In order to simulate constant strain rate uniaxial deformation, the dimensions of the simulation cell in \mathbf{e}_1 direction, L_1 , was increased at a fixed rate. We assume that the cross-linked polymer is almost incompressible and apply the appropriate contraction in the transverse direction of the simulation cell. All the atom positions are scaled in the same proportion as the dimensions of the simulation cell changes. The average of the properties are taken over 200 steps of the simulation run. During the simulation the non-dimensional parameters used are time $\bar{t} = \frac{t}{\sigma} \left(\frac{\epsilon}{m} \right)^{\frac{1}{2}}$, number density $\bar{\rho} = \sigma^3 \rho$, pressure $\bar{p} = \frac{\sigma^3 p}{\epsilon}$, and temperature $\bar{T} = \frac{k_B T}{\epsilon}$. m is the mass of the united atom and in this case is 14 Da. σ and ϵ denote length and energy scale parameters, respectively, and their values are the same as for the Lennard-Jones potential. From here onwards, we drop the bar used for scaled symbols, and symbols without bar should be considered as denoting scaled parameters.

In general, in a cross-linked polymer, cross-linking can take place anywhere in the chain. However in the present simulation active sites for the cross-linking are only end monomers of the chain. Cross-linkers are added to the system to join various chains together through cross-links using the chain-end monomers. A cross-linker with functionality f implies that this cross-linker would join f united atoms, in different or the same chains, together. A stoichiometric number of cross-linkers links all the chains together including chain ends.

One of the objectives of this study was to investigate the effect of variation in the system parameters on the stress and structure. Therefore we chose a reference system. This reference system had $N = 1458$ polymer chains, each chain having $n = 10$ united atoms. Stoichiometric number of cross-linkers with functionality $f = 4$ were added to the system. This choice would lead to a highly cross-linked network of polymer chains. The temperature of this reference system was maintained at $T = 4.0$ in a thermal bath. The simulation cell had a volume consistent with a number density $\rho = 1.0$. This reference model was strained at a strain rate of $\dot{\epsilon} = 2.0 \times 10^{-3}$. The influence of varying the values of the system parameters was simulated by changing each of these parameters, independently, from their reference value, and measuring the resulting elastomer stress and structure.

3. Stress and structure

We considered two systems — one with no cross-linkers present $f = 0$ and the other with cross-linkers with functionality $f = 4$. Stoichiometric number of cross linkers — $N_c = 2N/f$ — were added to the system. The stress response of the two systems is shown in Figure 1(a). Cross-linkers with functionality $f = 4$ result in a highly cross-linked system. This puts an additional constraint on the motion of monomers. As a result the stress level increases significantly relative to the case where no cross-linkers are present. In a study presented by [4], it was reported that failure stress increases with increasing functionality of the cross-linkers below $f_{av}^\alpha < 4$. f_{av} is the average functionality of the cross-linkers as cross-linkers of different functionalities between 3 to 6 are added into the system. They also report

that above $f_{av}^\alpha = 4$, the failure mechanism itself changes, and as a result failure stress decreases with increasing functionality. The tangent modulus, obtained by differentiating this expression with respect to strain, too reflects the effect of cross-linking. Note that in both cases the tangent modulus is initially high and then decreases rapidly with strain. Beyond $\epsilon = 0.2$, there is no significant change in the modulus till $\epsilon = 0.8$, beyond which the tangent modulus once again increases. The increase in the modulus towards the end of the loading is because of entanglements as well as alignment of the chains in the loading direction.

Figure 1(b) shows the crosslinking kinetics. The simulation was run for 50000 time steps to allow cross-linking to take place. Actual functionality of the cross-linkers is less than 4 due to incomplete cross-linking and there are few dangling ends in the chains. Average value of the functionality is approximately 3.4.

The micro-structure shows distinct change in variation with strain as we move from a linear polymeric system to one with cross-linkers. The mean-square bond length increases almost linearly with strain and there is a notable difference in magnitude between the cross-linked polymer and a linear polymer. The bond angle is lower in the cross-linked system even before the strain is applied primarily caused by the extra constraints due to the cross-linkers — Figure 2(a). The mean-square end-to-end length and mean-square radius of gyration, Figure 2(b), are distinctly higher when no cross-linkers are present from the cases when cross-linkers are present. This indicates that chains open more freely when cross-linkers are absent — an expected result. A similar behavior was also observed by [6] wherein they report that mobility of monomers decrease and relaxation is hindered with increasing cross-linker density. Hence, straining the system with a higher functionality of cross-linkers, produces more internal strains in the chains resulting in increased stress levels.

Chain alignment can be studied by observing two parameters, namely mass ratios and chain angle. The variation of mass ratios with strain, Figure 3, shows that chains are not spherical. Stretching of the system further reduces the mass ratios linearly which indicates that chains tend to take a one dimensional configuration with increase in strain. Very low values of g_3/g_1 indicates that chains take mostly a planar configuration. In the absence of cross-linking the mass ratios take on lower values indicating that they are less spherical. Cross-linking increases sphericity as the chains are pulled-in by their neighbors. Under axial strain the chains lose their sphericity for both systems. However cross-linked polymers lose their sphericity at a lower rate. The chain angle too decreases almost linearly with strain confirming that more and more alignment of end-to-end vectors of the chains in the loading direction. The presence of cross-linking has a very small effect on the chain angle. The chains with cross-linkers align in the loading direction slightly more as compared to those without cross-linkers.

Cross-linking significantly affects bond length distribution, Figure 4(a), across the polymer chain with chain-ends highly strained relative to the middle of the chain. This points to the effect of constraints at chain-ends due to cross-linking with other chains. The mean bond-angle similarly too increase towards chain-ends with an appreciable dip in the middle Figure 4(b). The mean bond length and mean bond angle at equilibrium before the application of strain are $b = 0.89$ and $\theta_0 = 108.86^\circ$. From the above two plots one notes that throughout, along the length of the chain, bonds are stretched. But bond stretching in the middle of the chain is less as compared to that at the ends of the chain. This additional stretching at chain-ends is because of constraints due to cross-linking. Chain-ends which were earlier free to move are now connected with each other through a cross-linker. As a result they start affecting the motion of each other and give additional forces to

the bonds near the chain ends. This is perhaps the cause of longer bond lengths and greater bond angles as we move towards the end of the chain. Since the chains are short, that is $n = 10$, the effect of the end motion gets diffused along the length of the chain and hence instead of an abrupt change in the bond length at the end, there is a uniform increase in the bond length from the middle of the chain towards either end. In the case of bond angles though, we notice an abrupt change in the bond angles.

4. Strain rate

The polymeric system was loaded at different strain rates to study its effect on its stress response. In Figure 5(a) faster the rate of loading, higher is the stress induced in the system, with a significant jump as we increase the strain rate from 2.0×10^{-3} to 5.0×10^{-3} . The corresponding tangent modulus also indicates that at low values of strain, the system is more stiff at higher rates of loading. During an intermediate range of strain, $0.2 \leq \epsilon \leq 0.8$, the tangent modulus close to zero at all strain rates. This primarily happens because of the uncoiling of the chains in this phase. From Figures 6(b) we observe that the amount of uncoiling is fairly low at the strain rate $\dot{\epsilon} = 5.0 \times 10^{-3}$. This keeps the number of new entanglements formed in the system very small. Hence the contribution to the strain is primarily due to deformation in the internal structure of the chain. This is also seen in Figure 6(a), in which a relaxation in the bond length is observed between $\epsilon = 0.2 - 0.5$ at low strain rates. In contrast, this is absent at higher strain rates. The balance between the contribution to stress due to bond deformations and excluded volume effects results in a very small increase in stress at faster strain rates.

In Figure 6(a) initially the evolution of the mean-square bond length is similar for all strain rates up to a strain of $\epsilon = 0.2$. Thereafter we observe that the bond length relaxes a little at the slower strain rates in the range $\dot{\epsilon} = 5.0 \times 10^{-4}$ to 1.0×10^{-3} . In the faster strain rate cases of $\dot{\epsilon} = 2.0 \times 10^{-3}$ and 5.0×10^{-3} , in the region of strain between $\epsilon = 0.2 - 0.5$, there is no relaxation similar to that observed at lower strain rates. However beyond $\epsilon = 0.5$ the rate of increase in the bond length is almost the same irrespective of the strain rate. At lower strain rates, time scale of external deformation and the time scale of the internal motion of the united atoms significantly differ, giving some time to relax the structure and acquire a lower energy state. In contrast, at a high strain rate, the time scale of external deformation and the time scale of the internal motion of the united atoms are very close and hence no relaxation is observed in such case. The effect of loading rate on the evolution of the bond angle is very mild.

The variation of mean-square end-to-end length, Figure 6(b), and mean-square radius of gyration, with strain is completely different at $\dot{\epsilon} = 5.0 \times 10^{-3}$ than at all other values of strain rates. In fact, at slower strain rates there is no significant difference in the variation of these two parameters. This indicates that uncoiling of the chains is suppressed at faster strain rates, and hence the major deformation in the system is due to the change in the mean-square bond length. Also, the overall arrangement of the chains in the system, and in turn the excluded volume interaction, plays a significant role in the response of the system at different rates. At $\dot{\epsilon} = 5.0 \times 10^{-3}$ the chains are more spherical during the stretch as compared to all other values of the strain rates. There is a small reduction in the mass ratios at this strain rate which indicates that the shape of the chains do not change significantly. At strain rates other than the above, the variation in the mass ratios with strain is similar and there is a larger reduction in the mass ratios at lower strains indicating the significant change in the shape of the chains. The evolution

of the chain angle is not affected much with the change in the strain rate.

The variation of the mean bond length and mean bond angle along the length of the chain does not show any remarkably different behavior for different strain rates.

5. Chain length

The stress induced is significantly affected by changes in length of the polymer chain — Figure 7(a). Long chain polymers have higher stress induced. In fact a large jump in stress occurs when we increased the chain length from $n = 5$ to $n = 10$. Thereafter this jump is smaller as the chain length is increased. In long chain polymers, as they are strained, chains get entangled very easily due to large number of constraints from the neighboring molecules. Short chains move very easily in the system and in case they get entangled, they can easily slip over one another. This is the primary mode through which short chains contribute to the overall deformation. As a result the stress induced in very short chain systems such as $n = 5$ is very low. In long chain polymers, slipping is very difficult as there could be the possibility of more than one entanglement in a single chain as chain size increases. As a result we observe higher stress induced in a long chain system. If the length of the chains is less than the entanglement length of the system, entanglement effects are not significant [2] and hence the stress is lower in short chain systems. The dynamics of the chain also completely changes across the entanglement length. Below the entanglement length, $n < n_e$, chains show Rouse behavior, where-as above the entanglement length, the behavior is better described by a reptation model [15]. A system with longer chain length is stiffer as compared to a short chain system Figure 7(b).

The variation of the mean-square bond length with strain is shown in Figure 8(a). We find a large change in the bond length with strain in long chain systems. This change is significant between $n = 5$ to $n = 10$. This is primarily because small chains can slip over one another very easily and as a result there is no bond deformation. Slipping gets increasingly difficult as the chain length grows and hence ways to contribute to deformation are through bond deformation and uncoiling of the chains. The variation of mean bond angle reveals that at higher chain lengths, the bond angles in the equilibrium configuration are smaller. This is shown in Figure 8(b), and is due to the increased constraints from the neighboring molecules. But as the system is strained, it is observed that there is a large change in the bond angle in a long chain system as compared to a short chain system. In fact, near $\epsilon = 1.0$, the bond angles at all chain lengths come close to each other even though the simulation starts at lower bond angles in long chain polymers.

The variation of the mean-square end-to-end length and radius of gyration are as expected. In long chain systems, there is better possibility for uncoiling of the chain due to the very fact that in the initial configuration, chains will be coiled. In very short chain systems chains are not coiled to the extent found in long chain systems in their initial configuration. As a result we observe a very small variation in both of the above parameters for very short chains. Chains are more and more spherical longer the length of the chain. This also indirectly indicates that the degree of coiling of the longer chains is more as compared to that for shorter chains. Also we note that a very short chain system takes almost a planar configuration as the mass distribution g_3 is very small. The change in the mass ratio with strain is greater in a long chain system indicative of more uncoiling as well as change in shape of the chains in such polymers. Furthermore, from $n = 20$ to $n = 50$, there is not enough change in the mass ratios which indicates that both are coiled approximately to

the same degree. Some more studies at longer chain lengths are needed to comment on the behavior of mass ratio with chain length at chain lengths beyond $n = 50$. Even though there is stretching of the bonds, the spherical shape of the chains does not give rise to stress anisotropy and hence we do not observe significant change in stress contribution due to this in systems at, and above, $n = 10$. Chains are oriented more in the loading direction as the chain length is increased. Alignment of the chains in the loading direction also increases with the length of the chain when the system is strained.

6. Density

The stress response of four different polymeric systems differing in their number densities ρ , having the same chain length, kept at the same reference temperature and subject to the same strain loading is shown in Figure 9(a). The stress-strain variation shows a quantitative change as move from $\rho = 1.2$ to $\rho = 1.5$. [16] also report a large jump in stress from $\rho = 1.0$ to $\rho = 1.5$ and they attribute this jump to glass transition. The tangent modulus values are higher for systems with larger densities in the initial phase of the loading $\epsilon < 0.3$. Beyond this value of the strain, the modulus is close to zero for all values of density. As the density increases chains cannot move easily as the monomers are closely packed. Hence any external deformation is caused by the internal deformation in the chain due to change in bond length and bond angle. Also for a high density system excluded volume effects are significant since monomers are very close to each other. Hence the observed increase in stress is the result of chain deformation as well as excluded volume effect [16]. Furthermore, at higher densities, contribution to the stress due to entanglement of the chains also increases [7]. Entropic contribution to the stress also goes up because of the increased packing entropy.

Figure 9(b) shows the variation of the mean-square bond length for polymers at different densities as they are stretched. The first thing one notices is that in the equilibrium configuration, that is without any imposition of strain on the cross-linked polymer, the mean-square bond length decreases for systems with higher values of density. This is due to the small space available at high density values. Then the bond lengths are smaller resulting in a compact configuration. Now as the system is stretched, in general the mean-square bond length increases strain for all the cases. However note the behavior at the density value $\rho = 1.5$. The mean-square bond length increases at a higher rate and in fact attains a value greater than that for the other systems with lower density at the end of the simulation, that is $\epsilon = 1.0$. At high densities, due to the compact configuration of the chain, there are constraints on the motion of the monomers that hinders the uncoiling of the chain. The deformation at high density values is therefore mainly due to the deformation of the internal degrees of freedom of the chains such as bond length and bond angle rather than the change in shape and size of the chains. At low densities, though, there is enough space available that chains can uncoil freely resulting in mild internal deformation. The bond angle too shows similar behavior at different densities.

At a given value of strain the mean-square end-to-end length and mean-square radius of gyration are higher for low density polymers. This is since enough space is available in the representative volume. At a given density both these parameters increase with strain. However the rate of increase as the system is stretched is higher at $\rho = 0.8$. All these observations indicate that at higher densities internal degrees of freedom of the chains dominate in contributing to the overall deformation of the system whereas at lower densities uncoiling of the chains is the dominant

mechanism contributing to the deformation. The mass ratios too reflect the variation seen in the case of the radius of gyration. At a very low value of density — $\rho = 0.8$ — chains are almost two-dimensional as g_3 is very small. Also the mass ratios fall at a higher rate with strain at $\rho = 0.8$ relative to that at higher values of density. At the initiation of stretch, higher densities result in a more spherical mass distribution.

As noted earlier, the bond length is longer towards the ends of the chain and uniformly decreases from both sides towards the middle of the chain. Now this effect becomes more prominent at higher densities. At high densities, due to the limited availability of space, the bonds are subject to compression, but the presence of cross-linkers at the end of the chains put additional constraints on these monomers and they cannot move as freely as the monomers in the middle of the chains. In order to keep all chains connected through a cross-linker together, bonds at the ends of the chains are stretched more. The mean bond angle also shows a similar variation. Here also we find that bond angles are higher at the end of the chains and decrease towards the middle from both ends. But unlike the case of mean-square bond length we find that this effect is more predominant at a very high value of density namely $\rho = 1.5$.

7. Temperature

We now consider four systems maintained at four different temperatures $T = 2, 3, 4, 5$ with other parameters set at their reference values. The uniaxial stress response of the system at various temperatures is shown in Figure 10(a). Higher the temperature, the stress induced in the system reduces significantly. At high temperatures the system relaxes faster, but we also observe longer bond lengths at higher temperatures, as shown in Figure 10(b). Longer bond lengths should typically increase the stress level in the polymer. But what is observed here is a decrease in the stress that is contrary to expectation. The resultant stress is a contribution of bond stretching, bond bending, bond twisting, as well as excluded volume interaction. At higher temperatures, excluded volume interaction is less because of a more relaxed structure. Hence as a net effect we find a reduction in the stresses at higher temperatures. In a Monte-Carlo study, [17] report a reduction in the induced stress at higher temperatures. They also note that strain softening is due to intermolecular contribution whereas strain hardening is due to intramolecular interactions. The modulus starts increasing at strains close to $\epsilon = 1$. The increase in the modulus towards the end of the loading could be because of entanglements as well as alignment of the chains in the loading direction.

For a given value of strain, the mean-square bond length is greater higher the temperature of the polymer. At high temperatures, the kinetic energy of the atoms increases in comparison to the potential energy associated with the bond between them and hence the atoms vibrate with a larger amplitude at high temperatures. Also note that the mean-square bond length increases almost linearly with strain at all temperatures. The end-to-end length as well as the radius of gyration too show similar behavior. The bond angle though does not show significant change in variation with strain at different temperatures. At a given temperature the mass ratios decrease with strain implying that chains tend to take a one-dimensional configuration under uniaxial tension. With increase in temperature this effect is enhanced and at $\epsilon = 1.0$ the chains have almost taken a planar configuration as the contribution of g_3 is very low. The effect of temperature on the chain angle has almost no effect on the alignment of the chains in the loading direction as the variation in the chain angle is very small with temperature.

In summary, we observe a large change in bond length with temperature while at the same time a better relaxation of the structure at higher temperatures. Increase in the mean-square bond length with temperature is not reflected as higher stress in the system. Dominance of excluded volume effects due to greater relaxation of the structure results in lower stresses at higher temperatures. Therefore even with large internal deformation of the polymer chains, the response is dominated by the excluded volume effect at elevated temperatures.

With increase in temperature the bond lengths of the chain are greater, with very little difference between bonds at the edges and the middle of the chain. This is due to the higher kinetic energy of the monomers that helps in resisting the bond stretching potential. A similar variation is also found in the bond angles along the length of the chain. Again we note that bond angles are greater at higher temperatures because of the higher kinetic energy of the monomers. But then the effect of temperature is not so significant on the bond angle as it is on the bond length of the chain.

8. Conclusion

We have presented a study of the correlation of the structure of a cross-linked polymer network with its stress response when subject to a uniaxial constant strain-rate loading. The tool used for this study is a united atom molecular dynamics simulation. This perspective provides a detailed insight of the deformation mechanisms in the polymeric system. We observe that temperature reduces the stress anisotropy in the system even though the bond stretch is greater at higher temperatures. This is caused by the randomness in the bond orientation at higher temperatures. Chain uncoiling is also more at higher temperatures. Density has a very significant effect on stress. There is a large change in the stress level with increasing density. This is due to the large changes in the mean-square bond length and mean-square bond angle. Also at higher densities the uncoiling of the chains is suppressed and the major contribution to the deformation is by internal deformation of the chains. The rate of loading affects the response of the system. At faster rates of loading stress anisotropy increases. At a very high strain-rate we observe that uncoiling of the chain is suppressed by a significant amount. The deformation mechanism is mostly internal deformation rather than overall shape and size. We notice that stress levels increase with increasing chain length of the polymer. However this increment in the stress level decreases with increasing chain length. At very small chain lengths the internal deformation in the chains ceases to exist and contribution to the overall deformation is due to slipping of the chains over one another or by uncoiling of the same. Chain opening is not very significant at very low chain lengths because in the equilibrium configuration itself chains are not significantly coiled. As a result a very small amount of stress is induced in short polymer chain networks. As the chain length increases contribution to the stress increases. For longer chain lengths there are internal deformation in the chains together with their uncoiling. Internal deformation such as bond stretching and bond bending are dominant and affect the stress response of the system. Stacking of the chains in the system also plays a dominant role in the behavior in terms of excluded volume interactions. In an overall sense excluded volume interactions play a significant role in the response. Low density, high temperature, and small chain length, facilitate chain uncoiling and chain slipping in cross-linked polymers.

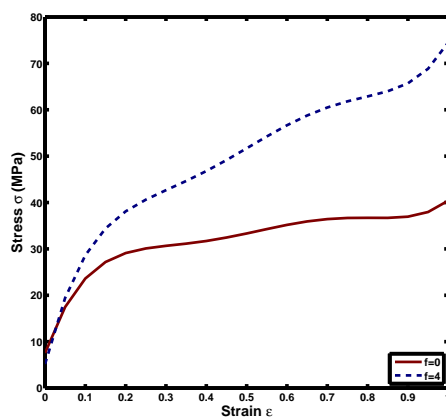
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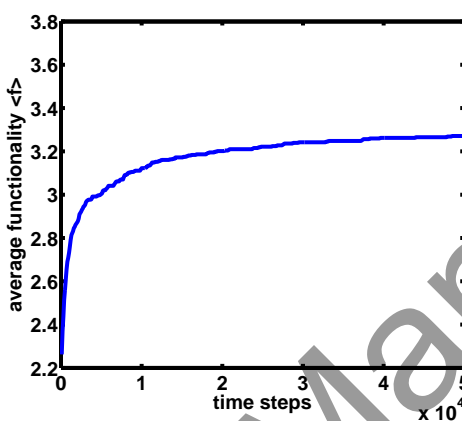
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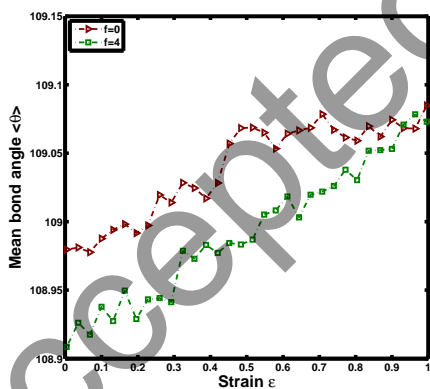


(a) Stress-strain curve

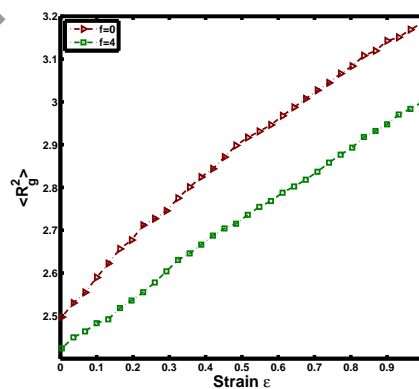


(b) Crosslinking kinetics

Figure 1. Stress response under uniaxial constant strain rate loading



(a) Mean bond angle



(b) Radius of gyration

Figure 2. Variation of mean-square bond angle and radius of gyration with strain

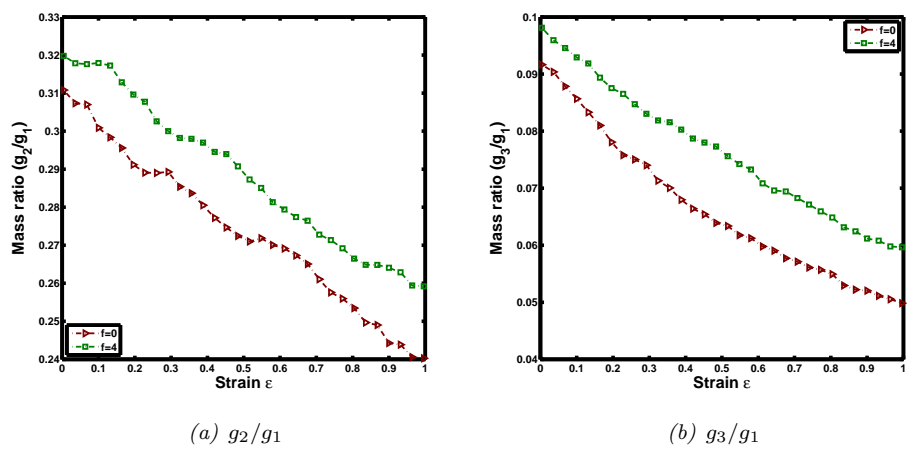


Figure 3. Variation of mass ratios with strain

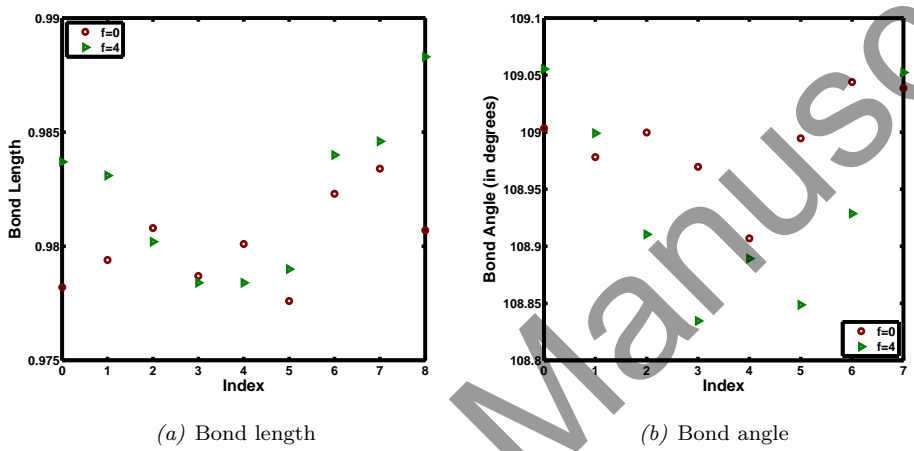


Figure 4. Distribution of bond length and bond angle along the chain

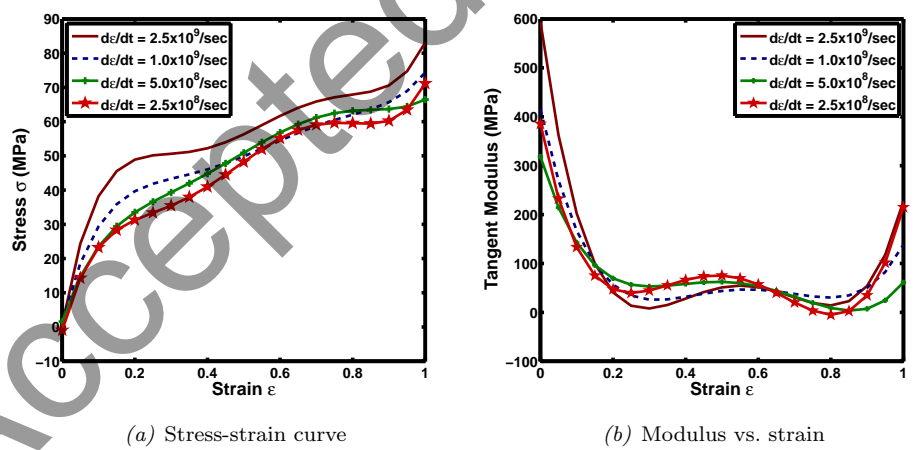


Figure 5. Effect of strain rate on stress response

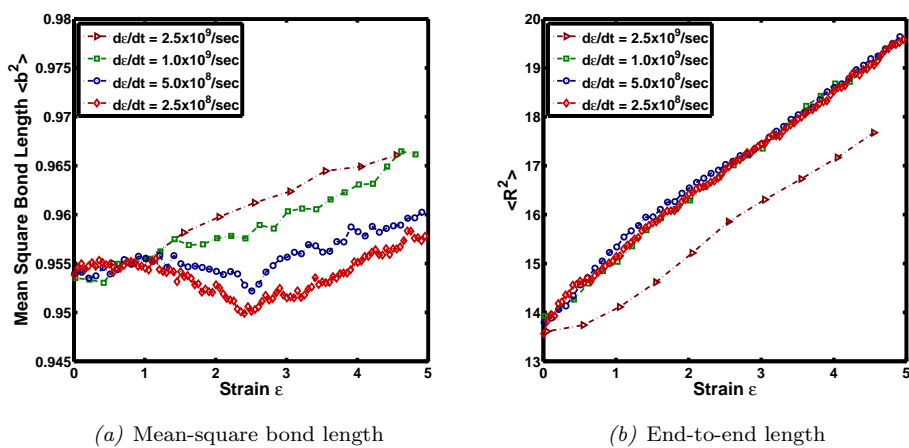


Figure 6. Effect of strain rate on mean-square bond length and end-to-end length

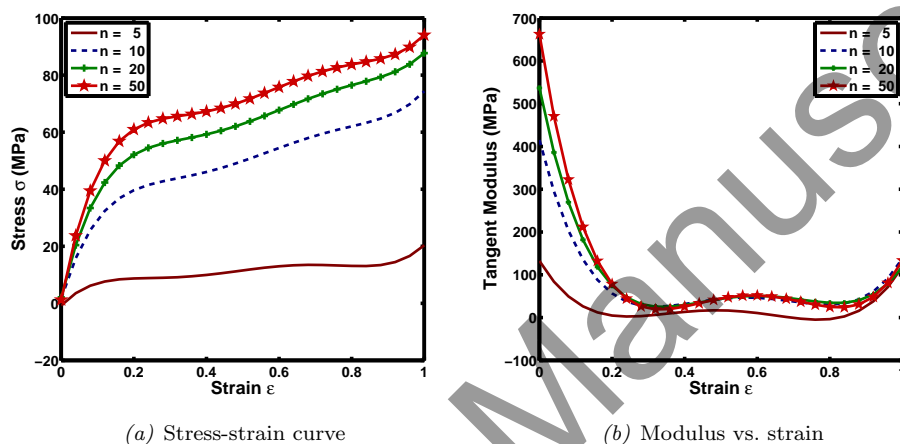


Figure 7. Influence of chain length on stress response

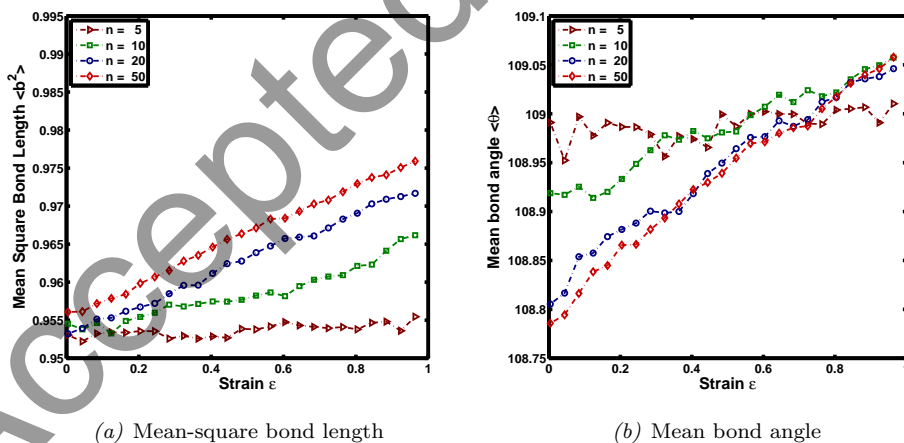


Figure 8. Effect of chain length on mean-square bond length and bond angle

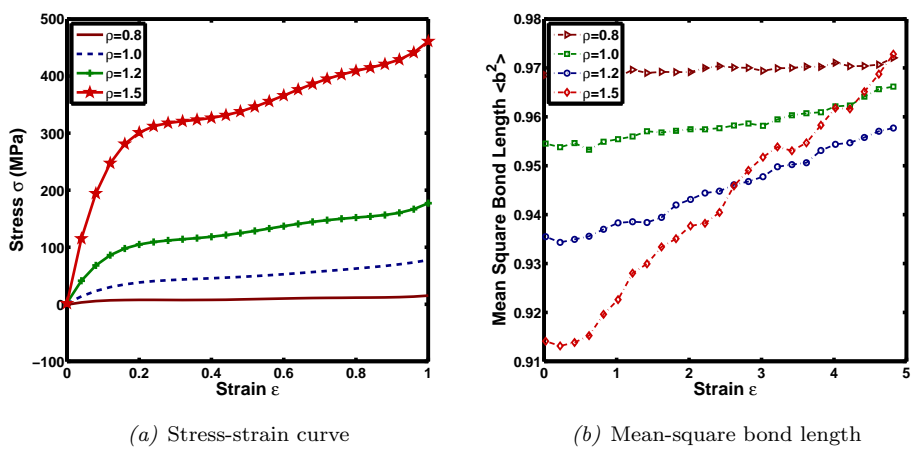


Figure 9. Effect of density on stress response

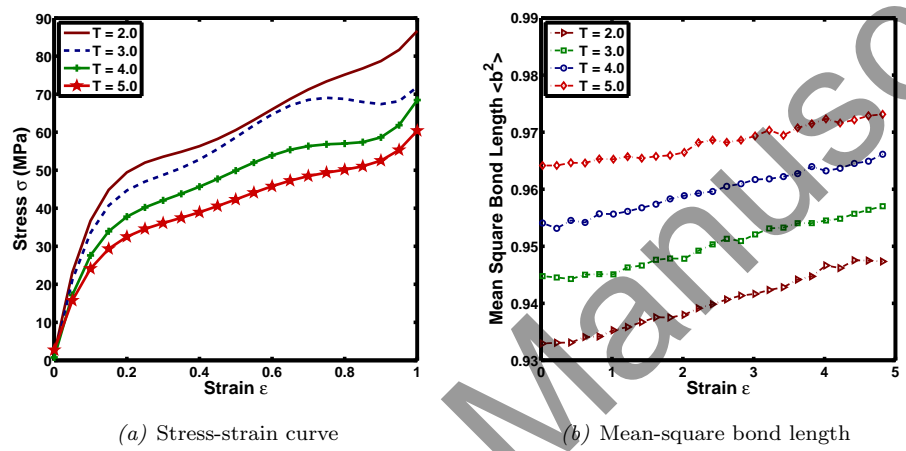


Figure 10. Effect of temperature on stress response

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