Molecular Dynamics Simulations of the Effect of Elastocapillarity on Reinforcement of Soft Polymeric Materials by Liquid Inclusions

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ABSTRACT: We use molecular dynamics simulations to study mechanical properties of polymeric nanocomposites of liquid inclusions in polymeric network matrix. The shear modulus of nanocomposite is shown to be a universal function of the elastocapillary number \( \gamma_{NL}/(G_N R_0) \), where \( \gamma_{NL} \) is the surface tension of the liquid/network interface, \( G_N \) is the shear modulus of the network and \( R_0 \) is the initial size of liquid inclusions. First, in the range of elastocapillary numbers, \( \gamma_{NL}/(G_N R_0) < 1 \), the composite shear modulus increases with increasing elastocapillary number. In this interval of elastocapillary numbers, liquid inclusions soften the network such that the composite modulus \( G_C \) is smaller than \( G_N \). However, for elastocapillary numbers \( \gamma_{NL}/(G_N R_0) \approx 2 \), the liquid inclusions begin to reinforce the network resulting in \( G_C > G_N \). In such composites, the surface energy of the deformed liquid inclusions stiffens the composite. When the elastocapillary number increases further, \( \gamma_{NL}/(G_N R_0) \gg 1 \), the interfacial energy of network/liquid interface dominates the mechanical response of the composite. Elongation ratio of the liquid inclusions monotonically decreases with increasing elastocapillary number \( \gamma_{NL}/(G_N R_0) \).

1. INTRODUCTION

Elastocapillarity is a manifestation of a fine interplay between elastic and capillary forces acting at the interface between soft compliant materials such as gels, elastomers and biological tissues. Recent studies have shown that it plays an important role in determining wetting and spreading conditions of liquid droplets at soft surfaces and interfaces, adhesion and contact mechanics of nano- and microsize objects, interface reinforcement by nanoparticles, resolution limit of the soft lithography, self-assembly conditions of filaments, and wrinkling instability of elastic interface. In all these crossovers, between capillarity and elasticity dominated regimes is controlled by the elastocapillary length, defined as a ratio of the surface tension \( \gamma \) to the elastic modulus of the material, \( G, l \propto \gamma/G \). Such that at the length scales \( r \) larger than the elastocapillary length, \( l \), the elasticity dominates deformation of interface while at shorter length scales, \( r < l \), the capillary forces provide a dominant contribution. Note that, for polymeric materials with a value of the modulus \( G \) on the order of 0.1 MPa and surface tension \( \gamma \approx 10 \text{ mJ/m}^2 \), this length scale is on the order of 0.1 \( \mu \text{m} \).

Elastocapillarity is also believed to be important for understanding mechanical properties of polymeric composites reinforced by nano- and microsize inclusions. The theoretical approach to the problem is based on the modification of the classical Eshelby’s theory of the inclusion which takes into account surface stress generated at the interface between inclusion and polymeric matrix. It was shown by Style et al. that the most pronounce effect of elastocapillarity on mechanical and thermodynamics properties of polymeric composites by molecular dynamics and Monte Carlo simulations few focused on the effect of elastocapillarity. In this paper, we use molecular dynamics simulations to study mechanical properties of polymeric nanocomposites with liquid inclusions. These simulations provide a unique opportunity to relate macroscopic mechanical properties of composites with network structure, inclusion size and the strength of molecular interactions. Molecular dynamics simulations highlight the role of elastocapillarity on mechanical properties of polymeric nanocomposites and provide assumption free model verification. The rest of the paper is organized as follows. In the next section, we discuss details of our simulation set up and show how to calculate macroscopic properties of materials such as shear modulus and interfacial tension of network/liquid interface as a function of the cross-linking density and strength of pairwise interactions. In section 3, we compare results of the molecular dynamics simulations for deformation of nanocomposites with a theoretical model by Style et al.

2. SIMULATION DETAILS

To study mechanical properties of polymeric nanocomposites we perform coarse-grained molecular dynamics simulations of composites in which liquid inclusions consisting of polymeric chains are placed in cross-linked polymeric matrix (see Figure [Figure])...
1). Polymeric networks making up the composite matrix and liquid inclusion are made from bead–spring chains with the bead diameter $\sigma$ and the degree of polymerization $N$ (see Table 1). The interactions between all beads in a system are modeled by the truncated-shifted Lennard-Jones (LJ) potential

$$U_{LJ}(r) = \begin{cases} 
4\varepsilon_{LJ} \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] + \frac{\varepsilon_{LJ}}{r_{cut}} & 0 < r < r_{cut} \\
0 & r > r_{cut}
\end{cases}$$

(1)

The cutoff distance for the bead–bead interactions is equal to $r_{cut} = 2.5\sigma$. The value of the Lennard-Jones interaction parameter for interactions between beads of the same type is set to $\varepsilon_{LJ} = 1.5k_B T$, where $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. The interaction parameter between beads belonging to network chains and polymer chains making up the liquid inclusions, $\varepsilon_{NL}$, is equal to 0.1$k_B T$, 0.4$k_B T$, 0.7$k_B T$, 1.0$k_B T$, and 1.2$k_B T$. This allows us to change the surface tension of the inclusion/network interface.

The connectivity of beads into polymer chains and cross-linking bonds are represented by the finite extensible nonlinear

Table 1. System Parameters

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elastic (FENE) potential\(^\text{18}\) with attractive part of the potential described by

\[ U_{\text{FENE}}(r) = \frac{1}{2} k_{\text{spr}} R_{\text{max}}^2 \ln \left( 1 - \frac{r^2}{R_{\text{max}}^2} \right) \tag{2} \]

where \( k_{\text{spr}} = 30 k_{B} T / \sigma^2 \) is the spring constant and \( R_{\text{max}} = 1.5 \sigma \) is the maximum bond length. The repulsive part of the potential is modeled by truncated-shifted Lennard-Jones (LJ) potential with \( r_{\text{cut}} = 2^{1/6} \sigma \) and \( \epsilon_{\text{LJ}} = 1.5 k_{B} T \).

Simulations are carried out in the NVT ensemble with 3D periodic boundary conditions. The constant temperature is maintained by coupling a system to a Langevin thermostat. In this case, the equation of motion for the \( i \)th bead is

\[ m \frac{d \mathbf{v}_i(t)}{dt} = \mathbf{F}_i(t) - \xi \mathbf{v}_i(t) + \mathbf{F}_i^R(t) \tag{3} \]

where \( m \) is the mass of bead set to unity for all beads in a system, \( \mathbf{v}_i(t) \) is the bead velocity, and \( \mathbf{F}_i(t) \) represented the net deterministic force acting on the \( i \)th bead. The stochastic force \( \mathbf{F}_i^R(t) \) has a zero average value \( \langle \mathbf{F}_i^R(t) \rangle = 0 \) and \( \delta \)-functional correlations, \( \langle \mathbf{F}_i^R(t) \mathbf{F}_j^R(t') \rangle = 6 \delta_{ij} \sigma^2 \delta(t - t') \) (The friction coefficient \( \xi = \frac{6}{k_{B} T} \) for all beads in a system if two beads are within distance 1.15 \( \sigma \)). The velocity–Verlet algorithm with a time step \( \Delta t = 0.011 t_{\text{LJ}} \) is used for integration of the equation of motion. All simulations are performed using LAMMPS\(^{49} \).

**Composites.** In our simulation setup a spherical liquid inclusion with initial radius \( R_0 \approx 10 \sigma \) is placed at the center of cubic simulation box of size \( L_0 = 40 \sigma \) with space outside the inclusion filled with polymeric network as shown in Figure 1. This allows us to keep volume fraction of inclusions in a composite to be \( \phi \approx 6.5\% \). Preparation steps of a composite are shown in Figure 2a–d. A spherical inclusion is prepared by placing 125 or 62 polymer chains with degree of polymerizations \( N = 32 \) or \( N = 64 \) respectively into a confining cavity in a 3-D periodic simulation box with a repulsive cavity; (c) merging the spherical inclusion (orange) and the precursor polymer melt (light blue); (d) relaxation and cross-linking of the polymeric composite.

![Figure 2](image-url)

**Figure 2.** Snapshots of the simulation box during composite preparation process: (a) preparation of liquid inclusion (orange) in a confining cavity; (b) equilibration of precursor polymer melt (light blue) in a 3-D periodic simulation box with a repulsive cavity; (c) merging the spherical inclusion (orange) and the precursor polymer melt (light blue); (d) relaxation and cross-linking of the polymeric composite.

During the initial run lasting 5 \( \times 10^2 t_{\text{LJ}} \) the interactions between beads are turned off in order for the chains to pass through each other and equilibrate their initial configurations. The interaction parameter between beads is then gradually increased to 1.5\( k_{B} T \) in the following run continued for 4 \( \times 10^3 t_{\text{LJ}} \). This is followed by the equilibration run lasting for 1.6 \( \times 10^3 t_{\text{LJ}} \). A composite is prepared by merging spherical inclusion and precursor polymer melt together (see Figure 2c). The system is equilibrated for 2.5 \( \times 10^4 t_{\text{LJ}} \) with all interactions turned on. After equilibration the precursor polymeric melt forming composite matrix is randomly cross-linked by FENE bonds. The cross-linking procedure is initiated if two beads are within distance 1.15 \( \sigma \) from each other and if none of them are at the chain end. One cross-link bond is allowed for each chain bead. New cross-links are added every 0.1\( t_{\text{LJ}} \) until the desired cross-linking density is achieved. After cross-linking, the composite is equilibrated for 8 \( \times 10^4 t_{\text{LJ}} \). The actual size of inclusions after relaxation \( R_0 \) is obtained from averaging the square of the radius of gyration (see eq 8 below). The final results for inclusion sizes are summarized in Table 1.

**Shear Modulus of Polymeric Matrix and Composites.** The shear modulus of the composite matrix is obtained from set of simulations of the uniaxial network deformation at a constant volume by affinely stretching simulation box along x-axis direction from \( L_0 \) to \( \lambda L_0 \) and compressing it in both y and z directions from \( L_0 \) to \( \lambda^{-1/2} L_0 \). For each matrix cross-linking density, a simulation of network deformation is performed by varying the elongation ratio \( \lambda \) between 1.00 and 1.10 with an increment \( \Delta \lambda = 0.02 \). This was done by stretching a network with a constant strain rate 0.0001\( t_{\text{LJ}}^{-1} \) to desired deformation. For soft networks, the interval of elongation (deformation) ratio \( \lambda \) is extended up to 1.40 to achieve a better signal-to-noise ratio in evaluation of the shear network modulus. After deformation, all systems, except for the softest ones with \( N = 64 \), and \( \rho_s = 0.022 \sigma^{-3} \), are equilibrated for 8 \( \times 10^4 t_{\text{LJ}} \) followed by the production run lasting 5 \( \times 10^5 t_{\text{LJ}} \) which is used for the data analysis. For the softest systems, the equilibration run is continued for 5.3 \( \times 10^5 t_{\text{LJ}} \) and is followed by the production run with duration 1.5 \( \times 10^6 t_{\text{LJ}} \).

The stress in uniaxially deformed networks is calculated from the pressure tensor \( P_{ij} \) as follows\(^{50–52} \)

\[ \sigma_{xx} = P_{xx} - \frac{1}{2} (P_{yy} + P_{zz}) \tag{4} \]

The shear modulus of the network, \( G_N \), is obtained by fitting the simulation data shown in Figure 3a to the stress-deformation function for uniaxially deformed networks at a constant volume\(^\text{5} \)

\[ \sigma_{xx} = G_N (\lambda^2 - \lambda^{-1}) \tag{5} \]

The obtained values of the network shear modulus, \( G_N \), are summarized in Table 1.

Similar approach is used for calculations of the shear modulus of the resultant composites as shown in Figure 3b. Since the softest composites with \( N = 64 \) and \( \rho_s = 0.022 \sigma^{-3} \) have relatively small signal-to-noise ratio, we prepare a larger system to get a better stress average. In the larger systems, eight spherical inclusions with initial radius \( R = 10 \sigma \) are arranged in a simple cubic lattice with the lattice constant 40\( \sigma \) in a simulation box with size \( L_0 = 80 \sigma \), to maintain volume fraction of inclusions to be close to \( \phi \approx 6.5\% \).

**Surface Tension.** The surface tension between polymeric matrix and liquid inclusion is obtained from the set of
simulations of composites in the initial undeformed state. In these simulations, each system is equilibrated for $8 \times 10^4 \tau_{LJ}$ followed by the production run lasting $5 \times 10^4 \tau_{LJ}$ which we use for data analysis. The production run is evenly divided into 10 blocks, with each time block being regarded as a single sample.

The surface tension, $\gamma_{NL}$, of spherical inclusion/network interface is calculated using the following equation\(^\text{54}\)

$$\gamma_{NL} = -\int_{-\zeta}^{\zeta} \frac{\zeta^2}{r^2} [P_N(r) - P_L(r)] \, dr$$

(6)

where

$$R_S = \int_{-\zeta}^{\zeta} \frac{r^2}{r^2} [P_N(r) - P_L(r)] \, dr$$

(7)

$\zeta$ defines the boundary of the interface determined from the stress profile where difference $P_N(r) - P_L(r)$ started to deviate from its bulk value (i.e., zero). The obtained values of the surface tension, $\gamma_{NL}$, are summarized in Table 1.

**Size of Liquid Inclusions.** The size of an inclusion in the initial (undeformed) state is calculated from the average value of the square of the radius of gyration

$$\langle R_g^2 \rangle = \frac{1}{N_{\text{mon}}} \sum_{i=1}^{N_{\text{mon}}} \langle (\vec{R}_i - \vec{R}_{\text{cm}})^2 \rangle$$

(8)

where summation is carried over all monomers $N_{\text{mon}}$ of liquid inclusion, $\vec{R}_i$ is a radius vector of the $i$-th monomer, $\vec{R}_{\text{cm}}$ is the radius vector of the center of mass of the inclusion, and brackets $\langle \ldots \rangle$ denote ensemble averaging during the simulation run. For a spherical particle with radius $R$ the radius of gyration is given by $R_g^2 = 3R^2/5$. In the deformed state we use components of the gyration tensor to calculate size of the deformed inclusion along $x$, $y$, and $z$ directions by considering inclusion as an ellipsoid with semiaxes $a$, $b$, and $c$ for which $R_g^2 = (a^2 + b^2 + c^2)/5$.

### 3. RESULTS AND DISCUSSION

Figure 4 shows variation of the inclusion shape in a polymeric network as a function of the network shear modulus $G_N$ and the strength of the LJ-interaction parameter between liquid/network pairs.
pairs. (Note that the surface tension of the inclusion/network matrix interface increases with decreasing value of the LJ-interaction parameter as shown in Table 1.) The inclusion shape was obtained from location of the boundary on which the local number density of inclusion beads is equal to the half of its bulk value. In the case of the weakly cross-linked networks which corresponds to small values of the network shear modulus, \( G_N = 0.025 \, \text{k_BT} / \sigma^4 \), liquid inclusions maintain almost spherical shape. This indicates that the stress generated in the composite during deformation is not sufficient to force inclusion shape deformation which is controlled by the inclusion surface energy. In the opposite limit of large values of the network shear modulus, \( G_N = 0.89 \, \text{k_BT} / \sigma^4 \), liquid inclusion adopt ellipsoidal shapes which also show little dependence on the strength of the LJ-interaction parameter. In this case system redistributes stress between matrix and inclusion through large deformation of the inclusion shape. In the intermediate values of the matrix shear modulus, \( G_N = 0.12 \, \text{k_BT} / \sigma^4 \), liquid inclusion gradually adopts a more spherical shape with decreasing the magnitude of the interaction parameter or increasing surface tension of the liquid/network interface.

Quantitative analysis of the inclusion shape deformation shows that elongation of the inclusion is a monotonic function of the elastocapillary number defined as a ratio of the liquid/network surface tension to network shear modulus \( G_N \) and inclusion initial size \( R_0 \), \( \gamma_{NL}/G_N R_0 \) as shown in Figure 5. According to theoretical model, inclusion deformation monotonically decreases with increasing the elastocapillary number \( \gamma_{NL}/G_N R_0 \):

\[
\lambda_i = 1 + \frac{10(\lambda - 1)}{6 + \frac{\gamma_{NL}}{G_N R_0}}
\]

(9)

![Figure 5. Dependence of the elongation ratio, \( \lambda_i \), of liquid inclusions on the elastocapillary number obtained for different values of the LJ-interaction parameter between liquid/network pairs: \( \varepsilon_{NL} = 0.1 \varepsilon \) (red circles), \( \varepsilon_{NL} = 0.4 \varepsilon \) (green circles), \( \varepsilon_{NL} = 0.7 \varepsilon \) (blue circles), \( \varepsilon_{NL} = 1.0 \varepsilon \) (pink circles), and \( \varepsilon_{NL} = 1.2 \varepsilon \) (light blue circles), and for composite elongation ratio \( \lambda = 1.1 \). The solid line is given by eq 9.](Image)

Comparison of the simulation results with eq 9 shows that analytical expression correctly predicts the general trend but slightly overestimate actual inclusion deformation.

The shear stress concentration factor distribution around inclusions and its redistribution with varying the elastocapillary number is shown in Figure 6 a. The shear stress concentration factor is defined as the ratio of local maximum shear stress, \( \tau_{max} \), to total maximum shear stress acting on the simulation box, \( \tau_{max}^{\text{tot}} \), where the maximum shear stress is one-half of the difference between the maximum and minimum principal stress. It follows from this figure that with increasing the elastocapillary number the stress is concentrated close to the interface between liquid inclusion and network matrix. As elastocapillary number decreases the stress begins to concentrate more uniformly in a polymeric matrix. Note that concentration of the stress at the interface is a characteristic feature of the rigid inclusions, thus liquid inclusions with large values of the elastocapillary numbers could serve as stress concentrators in polymeric composite materials. This is further confirmed by evolution of the deformation fields as a function of the elastocapillary number shown in Figures 6 b and c. This field distributions are obtained by averaging the displacement field of each bead defined as \( \Delta \mathbf{u} = u_{\hat{e}_f} + r \sin \theta \, \hat{e}_f \), where \( \hat{e}_f \), \( \hat{e}_o \), and \( \hat{e}_r \) are unit vectors in spherical coordinates. The origin of the coordinate system is placed at the center of mass of the inclusion, and the angle \( \theta \) is measured from the elongation direction. The increments of the radial and tangential displacement with respect to the value corresponding to affine deformation of a pure network are shown in Figure 6, parts b and c. At low elastocapillary numbers, the inclusion deforms more than the network, so that the excess of radial displacement of polymeric network surrounding the inclusion is positive. As the elastocapillary number increases, the large inclusion surface energy contribution prevents the inclusion shape deformation and the excess of radial displacement changes its sign from positive to negative.

Finally, Figure 7 shows our results for composite shear modulus as a function of the elastocapillary number. It confirms that for large values of the elastocapillary numbers the liquid inclusion could reinforce polymeric networks. The crossover from composite weakening regime in which liquid inclusions decrease the composite modulus in comparison with that of pure network, \( G_C/G_N < 1 \), to reinforcement regime takes place at \( \gamma_{NL}/G_N R_0 \approx 2 \). At larger values of the elastocapillary numbers the mechanical properties of the composite materials are superior to that of neat polymeric networks. Comparison of our simulation results with Style et al. model\(^3\) indicates that the model capture correctly the general trend in composite reinforcement by liquid inclusions, however, the simulation data are scattered around the theoretical curve

\[
G_C = \frac{6 + \frac{\gamma_{NL}}{G_N R_0}}{\frac{\gamma_{NL}}{G_N R_0} (1 - \phi) + (6 + 10\phi)}
\]

(10)

This data scattering could be explained by heterogeneities in network mechanical properties associated with fluctuation of the degree of cross-linking resulting in deviation of the local network shear modulus from its average value and by the finite thickness of the inclusion/network interface that are neglected in theoretical model.

4. CONCLUSIONS

We have presented results of the molecular dynamics simulations of deformation of nanocomposites reinforced by liquid inclusions. Analysis of our simulation data shows that the effective composite modulus, \( G_C \), is a universal function of the elastocapillary number \( \gamma_{NL}/G_N R_0 \) describing relative contribution of the capillarity and elasticity into composite deformation (see Figure 7). At small values of the elastocapillary numbers, \( \gamma_{NL}/G_N R_0 < 1 \), the composite shear modulus \( G_C \) is smaller than the modulus of the corresponding bulk sample made of polymeric network with the same concentration of cross-links, \( G_N \). In this range of elastocapillary numbers the liquid inclusions weaken the composite mechanical properties by...
reducing the average density of the stress supporting polymeric chains making up the composite matrix. With increasing elastocapillary number the contribution to the composite mechanical properties coming from surface energy of the deformed inclusion/matrix interface begins to improve composite strength. The capillary forces compensate for the loss of the stress supporting strands in polymeric network when the elastocapillary number $\gamma_{NL}/G_N R_0 \approx 2$. For large elastocapillary numbers, $\gamma_{NL}/G_N R_0 \gg 1$, the liquid inclusions reinforce composite material. In this range of parameters the stress distribution in the composite is concentrated around liquid inclusions as shown in Figure 6a. This stress concentration is qualitatively similar to the case of the composite reinforcement by rigid inclusions. Our results are in a good agreement with experimental data, and predictions of the theoretical model of composites with liquid inclusions and provide further justification for the use of liquid inclusions in polymeric network reinforcement.

Figure 6. Distribution of shear stress concentration factor (a), excess radial displacements (b), and excess tangential displacements (c) around liquid inclusion in network matrix calculated for the system with different values of the elastocapillary numbers and $\lambda = 1.30$.

Figure 7. Dependence of the normalized composite shear modulus on the elastocapillary number obtained for different values of the LJ-interaction parameter between liquid/network pairs: $\varepsilon_{NL} = 0.1k_B T$ (red circles), $\varepsilon_{NL} = 0.4k_B T$ (green circles), $\varepsilon_{NL} = 0.7k_B T$ (blue circles), $\varepsilon_{NL} = 1.0k_B T$ (pink circles), and $\varepsilon_{NL} = 1.2k_B T$ (light blue circles). The solid line is given by eq 10.

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Notes
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