Effect of van der Waals Interaction Strength and Nanocluster Size on the Dynamical and Mechanical Properties of 1,4-cis-polybutadiene Melts

Canan Atilgan, Ibrahim Inanc and Ali Rana Atilgan

Faculty of Engineering and Natural Science, Sabanci University, Istanbul, Turkey

ABSTRACT

Using molecular dynamics simulations, we have investigated the effect of embedding nanoclusters of radius 3-7 Å on the dynamical and mechanical properties of 1,4-cis-polybutadiene melts. To see the effect of polymer-nanocluster interaction strength on the bulk modulus, the van der Waals interactions (vdW) between the polymer chain and nanocluster have been varied from weak to very stong while keeping polymer-polymer and nanocluster-nanocluster interactions constant. The modulus depends on the interaction strength, but not on nanocluster size. Residence time of chains on the surface of the nanocluster (τ_r) has an increasing trend that reaches to a plateau as the vdW strength is increased. τ_r also doubles from 100 ps to 200 ps as the nanocluster size is increased from 3 to 7 Å. Our findings give clues on how the properties of polymeric materials may be controlled by nanoparticles of different chemistry and size.

INTRODUCTION

Polymer matrix based nanocomposites have been attracting research interest due to their promise to improve materials mechanical properties such as higher stiffness, impact and tensile strength, rheological, viscoelestic and physical properties [1-4]. Since it is a big challenge to characterize the structure and properties and manipulate the fabrication process, until now development of nanocomposites have mostly been empirical [5]. In the last decade, computer modeling and simulations have been holding an increasing role in understanding and controlling the underlying mechanism of such property changes and enhancements [6, 7]. Fundamental issues such as molecular origin of reinforcement, rheological behavior for better processing and structure and dynamics at the interface of the matrix and the filler are the main purpose of these modeling and simulation efforts. Different computational methods, ranging from molecular to macro scale, such as molecular dynamics (MD) [8-10], Monte Carlo [11, 12], dissipative particle dynamics [13], lattice Boltzmann [14], equalivant-continuum [15] and finite element methods [16], have been used for this purpose.

In nanocomposites, interplay of different parameters such as temperature, filler size and shape, mixing ratio of matrix and filler, polymer type and size play significant roles in the enhanced materials properties [17]. Yet, few computational approaches have addressed the affect of those parameters systematically. In this manuscript, results of a systematic study of a model polymer matrix reinforced by a nanoparticle are presented. The nanoparticle is modeled at the atomistic detail which allows us to determine the dynamical and mechanical properties. A nanoparticle that interacts via vdW with the chains are incorporated and the effect of interaction strength is varied. Furthermore, the effect of the size of the nanoparticle is studied.

MOLECULAR MODELING AND SIMULATION DETAILS

Nanoclusters having radii ranging from 3.16 Å to 7.12 Å (number of atoms from 10 to 150) are embedded in *cis*-1,4-polybutadine (PBD, 32 chains, each of 32 butadiene repeat units) to understand the effect of the nanocluster on the properties of the polymer (figure 1). Seven sets of clusters having size of N atoms (N = 10, 20, 30, 40, 70, 100 or 150) were studied. Pure PBD was also studied to provide baseline values of the properties studied. The results reported here were obtained at 330 K, well-above the T_g which is approximately at 170 K for *cis*-1,4-polybutadiene of 55000 g/cm^3 molecular weight [18].
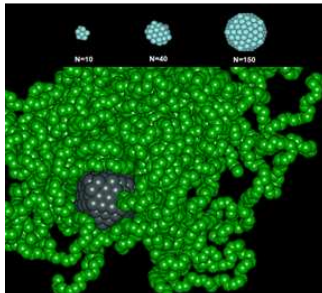

Figure 1. Nanoclusters in *cis*-1,4-polybutadine; (inset) atomic configurations of the nanoclusters of different sizes (N=10, 40, 150)

The fundamental properties of the atoms constituting the nanocluster are taken to be similar to that of silicon. Thus, the atomic mass of the atoms is 32 g/mol, and the well depth for non-bonded interactions between pairs of atoms occurs at 0.854 kcal/mol. The van der Waals radius is taken to be 4 Å. The particle coordinates of the nanocluster are obtained from the Cambridge Cluster Database [19] and those pairs that are within 2.23 Å of each other are connected by springs with spring constant k = 150 kcal/mol. These particles otherwise interact with each other and the rest of the polymeric chains via vdW forces depicted by the Lennard Jones potential. United-atom model was employed according to the work of Gee and Boyd [20], all forcefield parameters are given therein. With little sacrifice in accuracy, united-atom model provides a higher computational efficiency when compared to other all-atom force fields.

Nanoparticle atom-polymeric chain atom interactions are normally obtained via geometric mean for the well-depth, and arithmetic mean for the vdw radii. The vdw strength between nanocluster and PBD chains, ϵ, is also modified in a second series of simulations. This series is carried out for the largest sized nanocluster only, with N = 150 atoms, while -ϵ is modified with the values of 0.1, 0.2, 0.3, 0.5, 0.75, 1.0, and 1.5 kcal/mol. The standard value in the previous sets of simulations was -ϵ_{Si-C}=0.3 kcal/mol. We note that the intramolecular interactions are fixed throughout the simulations, and only the intermolecular interaction strength (well-depth) is varied.

In all simulations, cutoff distance on non-bonded interactions are 10 Å, which are smoothed with a switching function set on at 8 Å. Time step is 2 fs and data are recorded at intervals of 1000 steps. Each simulation was carried out for 40 ns. Periodic boundary conditions are imposed on the constructed boxes which contain 4096 PBD beads and the nanocluster. Calculations are carried out under the NPT ensemble. The isotropic box sizes are in the range of 47-50 Å throughout the simulations.

One nanocluster was embedded into the polymer matrix and this polymer-nanocluster composite was equilibrated for 2 ns at 1 atm pressure. This procedure was repeated for nanoclusters with sizes from 10 to 70 atoms. For the nanoclusters with more than 70 atoms, since they cannot be embedded directly into the polymer matrix, the nanocluster is first located on the edge of the polymer box. The resulting larger periodic box was simulated for 1 ns under 1000 atm pressure until a homogenous mixture was obtained and further equilibrated under 1 atm pressure to reach room temperature density.

Dynamical properties

Time correlations (τ_c) from the ^{13}C-NMR experiments are calculated from the time decay of the second orientational autocorrelation function (OACF), M_2 (t), of the butadiene C-H bond vectors via:

$$M_2(t) = \frac{1}{2}[3 < cos^2\theta(t) > -1] \tag{1}$$

where $\theta(t)$ is the angle between two orientations of the C-H bond at times 0 and t. τ_c is obtained from the integral of the OACF as [21]:

$$\tau_c = \int \frac{M_2(t)-M_2(\infty)}{M_2(0)-M_2(\infty)} dt \tag{2}$$

Residence time (τ_r) which is an average time of an atom/molecule to escape from a given region [22] is used to obtain information on the dynamical behavior of polymer chains that are close to the surface of the nanocluster. We have calculated τ_r by monitoring the decrease in the number of atoms residing at a distance of one vdw radius from the nanocluster surface (N_r). A simple exponential decay function fits the curve of number of such atoms as a function of time:

$$N_r = < N_r > \exp{(-t/\tau_r)} \tag{3}$$

where $< \cdot >$ denotes ensemble average.

Mechanical properties

For small deformations, the relationship between the stresses and strains may be expressed in terms of a generalized Hooke's law:

$$\sigma_{lm} = C_{lmnk}\varepsilon_{nk} \tag{4}$$

where ε is the strain tensor and C is the stiffness matrix. For the isotropic case, the Shear Modulus, G, can be written in terms of the Lame coefficients that are obtained from C. In this work we use the implementation of the work of Theodorou and Suter by the Materials Studio Program for all shear modulus calculations [23].

Another mechanical property of interest is the bulk modulus, K, defined by:

$$K = -V \frac{\partial P}{\partial V}\Big|_T \tag{5}$$

where P is pressure, V is volume, and partial derivative is at constant temperature. Here we calculate the bulk modulus from the fluctuations of the periodic box volume using simulations at constant pressure by the relationship,

$$K = \frac{k_B T <V>}{<V^2>-<V>^2} \qquad (6)$$

RESULTS AND DISCUSSIONS

Dynamical Properties

The effect of nanocluster size on the dynamical behavior of polymer chains is studied through the residence times, τ_r (equation 3) (figure 2a), which increases two-fold (~100 ps to ~200 ps) as the size of the nanocluster increases from ~3 to ~7 nm radius. Thus, the larger the nanocluster size, the more time chains spend in the vicinity of the probe. This, in turn, indicates additional effective nanocluster - polymer interactions, as corroborated by the radial distribution functions (RDFs) for the nanocluster center – PBD repeat units shown in figure 2b. We find that the effective radius of the nanocluster does not have a simple dependence on its size. The first coordination shell is split into two peaks; however, the strength of the peak depends on the geometry of the nanocluster. The second peak is stronger for $N = 10$ and 30, the inverse is true for $N = 70$, while they have nearly merged for $N = 150$. The range where there is enhanced concentration of PDB chains is also is variable, commensurate with the shape of the peak.
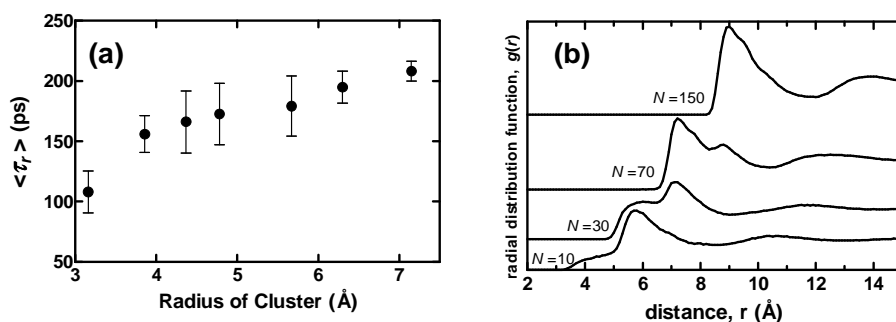

Figure 2. (a) Size dependence of chain residence times (τ_r) in the vicinity of nanoprobe. (b) sample RDFs between atom at the bead center and PBD units; each curve converges to the bulk value of 1; curves are nudged for better view of peak positions.

The effect of interaction strength on the dynamics is depicted by τ_r and τ_c (figure 3). τ_r has an asymptotic exponential association type behavior, increasing in value two-fold from ~100 ps) to ~200 ps, stabilizing in this escape dynamics at moderate interaction strengths. On the other hand, τ_c increases from 20 ps (pure PBD) to ~80 ps, stabilizing at higher interaction strengths -ϵ > 0.75 kcal/mol. The presence of the cluster slows down the overall orientational motions of the chains, except at low interaction strengths whereby the chains flow more freely around nanocluster. Strengthening the interactions, on the other hand, directly affects local chain dynamics. The chains which are thus condensed to the first coordination shell of the nanocluster have a saturated CH-bond vector relaxation rate. Sample RDFs are shown in figure 3c. The curves for strengths -ϵ > 1.0 kcal/mol are nearly identical.
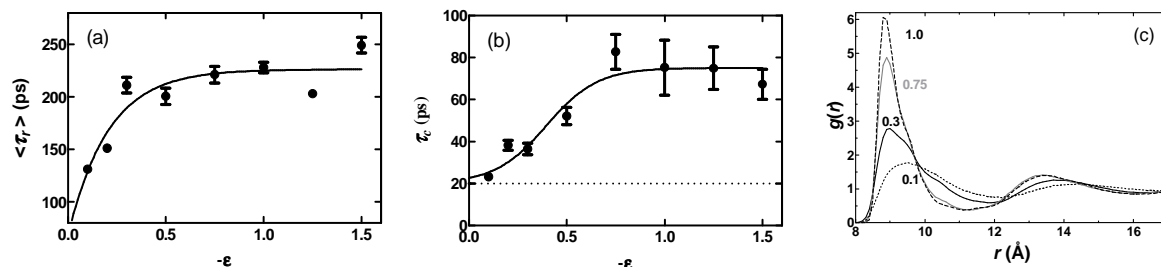
Figure 3. Effect of intermolecular interaction strength ϵ on (a) τ_r, (b) τ_c, and (c) RDF. $T = 330$ K, N=150 atoms corresponding to cluster radius of 7.15Å. Lines in (a,b) are drawn to guide the eye.

Mechanical Properties

We next investigate how the above-mentioned chain distributions around nanoclusters affect mechanical properties. The effect of nanocluster size at moderate interaction strength is displayed in figure 4a. As the cluster size is increased, there is an initial increasing trend in the modulus, followed by a plateau, as indicated by the dotted lines. This behavior is due mainly to the competing entropy/enthalpy contributions to the free energy, which in turn affects the volumetric fluctuations. Energetically, the number of interactions between the nanocluster and PBD chains increases with the surface area of the latter. Entropically, the volume of the cavity formed by the nanocluster leads to an unfavorable contribution to the free energy, which is compensated by energetic for small clusters, but takes over for larger ones. On the other hand, increasing -ϵ for a fixed cluster size ($N = 150$ in this case) affects mainly the energetics, leading to the nearly linear trend observed in figure 4b. We have also calculated the Poisson's ratio, ν, of all these systems using the shear modulus calculation strategy implemented in Materials Studio [23]. All calculations lead to the incompressible value of $\nu = 0.5$ which is valid for elastomers.
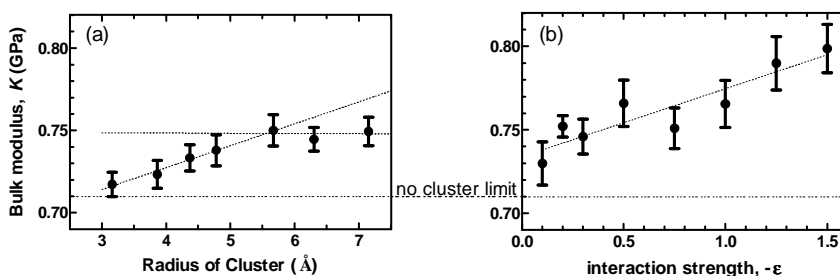

Figure 4. (a) Effect of cluster size and (b) vdw interaction strength on bulk modulus.

CONCLUSION

We systematically investigate how nanoclusters may be used to manipulate the mechanical properties of PBD chains by changing the interaction strength between the two and the size of the former. To understand the underlying mechanisms that lead to modified properties, we first study the distribution of the PBD chains in the vicinity of the nanoclusters. We find that the effective radius of the nanocluster does not have a simple dependence on its size (figure 2b), while increased -ϵ has an organizing effect which is saturated by 0.75 kcal /mol (figure 3c). The

latter is reflected in local chain relaxations, manifested by τ_c of CH-vectors (figure 3b). However, both the escape times also reach a plateau as the interaction strength increases. Since the polymer chains stick to the surface tightly, their translational and orientational movements are restricted.

The effect of the chain distributions and dynamical behavior are manifested in the increase in mechanical properties. Although the mixtures studied here comprise of volume fractions op to 1.5 %, and the interactions are only short ranged van der Waals type, we achieve enhancement of up to 12 % in the bulk modulus, and 25 % in the shear modulus. The effect of nanocluster size is more modest, and saturates for relatively small clusters containing ~70 atoms.

We conjecture that nanocluster properties may be tuned to manipulate many of the properties relevant in applications involving nanocomposites. In this work, we show that even for an isotropic, incompressible system such as PBD, and using short-range interactions only, significant enhancements may be achieved. The property modification may further be modified by incorporating longer-ranged interactions (e.g. by including charged particles into the system), as well as incorporating anisotropy, either in the chains or in the nanoclusters. Finally, our preliminary results indicate that contradicting reports in the literature for nanocomposites on the increase/decrease in T_g under similar conditions [24], may well be explained by the interplay between cluster geometry and interaction strength. We shall direct our future research efforts in this direction.

REFERENCES

[1] E. P. Giannelis, Advanced Materials 8 (1996) 29-&.
[2] S. Komarneni, Journal of Materials Chemistry 2 (1992) 1219-1230.
[3] R. Khrisnamoorti, R. A. Vaia, Polymer Nanocomposites: synthesis, characterization, and modeling, American Chemical Society, Washington DC, 2001.
[4] Polymer Nanocomposites Handbook, CRC Press, Taylor & Francis Group, Florida, 2010.
[5] T. A. Vilgis, Polymer 46 (2005) 4223-4229.
[6] G. Allegra, G. Raos, M. Vacatello, Progress in Polymer Science 33 (2008) 683-731.
[7] C. R. Picu, Keblinski, P., Modeling of Nanocomposites, Wiley-VCH, Weinheim, 2003.
[8] F. W. Starr, T. B. Schroder, S. C. Glotzer, Macromolecules 35 (2002) 4481-4492.
[9] S. Sen, J. D. Thomin, S. K. Kumar, P. Keblinski, Macromolecules 40 (2007) 4059-4067.
[10] G. D. Smith, D. Bedrov, L. W. Li, O. Byutner, Journal of Chemical Physics 117 (2002) 9478-9489.
[11] M. Vacatello, Macromolecules 34 (2001) 1946-1952.
[12] Q. Zhang, L. A. Archer, Journal of Chemical Physics 121 (2004) 10814-10824.
[13] D. Long, P. Sotta, Macromolecules 39 (2006) 6282-6297.
[14] G. Raos, Macromolecular Theory and Simulations 12 (2003) 17-23.
[15] H. D. Wagner, Chemical Physics Letters 361 (2002) 57-61.
[16] A. A. Gusev, Macromolecules 39 (2006) 5960-5962.
[17] D. C. Edwards, Journal of Materials Science 25 (1990) 4175-4185.
[18] T. Kanaya, T. Kawaguchi, K. Kaji, Physica B-Condensed Matter 182 (1992) 403-408.
[19] D. J. Wales, The Cambridge Cluster Database, in.
[20] R. H. Gee, R. H. Boyd, Journal of Chemical Physics 101 (1994) 8028-8038.
[21] C. Baysal, B. Erman, I. Bahar, F. Laupretre, L. Monnerie, Macromolecules 30 (1997) 2058.
[22] F. Ghirelli, B. Leckner, Chemical Engineering Science 59 (2004) 513-523.
[23] D. N. Theodorou, U. W. Suter, Macromolecules 19 (1986) 139-154.
[24] D. R. Paul, L. M. Robeson, Polymer 49 (2008) 3187-3204.