

# A molecular dynamics simulation study of inclusion size effect on polymeric nanocomposites

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## Abstract

The elastic behavior of polymeric nanocomposites is investigated with molecular dynamics simulations. Inclusions are modeled as spherical nanoparticles. It is demonstrated with numerically performed tensile tests that Young's moduli of nanocomposites are strongly affected by the size of the nanoparticle as well as by the interaction strength between polymer chains and the nanoparticle. The Young's modulus of the nanocomposite is enhanced as the size of the nanoparticle decreases as long as the strength of polymer–nanoparticle interaction is stronger than or equal to that of the polymer–polymer interaction. The analysis of stresses on polymer monomers shows that the composite modulus enhancement by smaller nanoparticles is attributed to the stiffer layer of polymer of higher densities around the nanoparticle.

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## 1. Introduction

Filled polymeric composites are widely used in aerospace, automobile and marine applications due to their excellent mechanical properties. In recent years, various nanomaterials with unique properties have been produced. Due to their much greater reactive surface area per unit volume compared to that of larger particles [1], nanoparticles together with polymers have been explored to form nanocomposites. As a result, mechanical and physical properties of nanocomposites have gained great interest for their structural applications.

The molecular simulation has been employed as an important tool for analyzing and understanding material

behavior at nanoscale. From studies of molecular simulations, interfacial conditions between polymer chains and nanoparticles and size of nanoparticles have been considered to have significant influence on the mechanical properties of nanocomposites. Smith et al. [2] showed with a model polymer nanocomposite in melt condition that the composite shear modulus and viscosity dramatically increase with attractive nanoparticle–polymer interactions relative to the pure polymer melt, exhibit little change for neutral systems, and decrease for repulsive systems. Brown et al. [3] investigated polymer structures and bulk modulus around a SiO<sub>2</sub> nanoparticle of about 4.4 nm in diameter with a simplified linear polyethylene. In their simulations, polymer–polymer and polymer–nanoparticle interactions were all repulsive, while the attractive interactions were compensated by applied pressures. It was shown that a layer of oriented polymer chains is formed around the nanoparticle; the bulk modulus of the polymer layer is lower than that of the pure polymer; and the elastic modulus of their nanocomposite is lower than that of the pure polymer matrix [3]. Odegard et al. [4] attempted to model

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the mechanical properties of SiO<sub>2</sub>/polyimide nanocomposite based on the Mori–Tanaka micromechanical in conjunction with a molecular simulation of the interface between the nanoparticle and the polymer matrix. Various interfacial chemical treatments and different sizes of the nanoparticle were considered. It was demonstrated in [4] that the predicted Young's modulus increases as the nanoparticle size increases and asymptotically approaches to the result of the Mori–Tanaka model without incorporating molecular simulations.

Recently, we investigated experimentally and numerically the particle size effect on the elastic properties of particulate polymeric composites with particle size ranging from 15 nm to 500 μm [5]. From experimental results, it was observed that the Young's modulus of the composite increases as particle size decreases in nanoscale, while for composites with micron size particles the Young's modulus show little dependence on particle size [5]. The trend found in [5] is opposite to that found in [3,4]. A possible explanation of this phenomenon is that nanoparticles may have more constraints on the surrounding polymer chains than micron size particles.

The purpose of this study is to employ molecular dynamic (MD) simulations to investigate the particle size effect on the behavior of polymer surrounding the particle. Representative nanocomposites are studied using the MD simulation, in order to further our understanding of the effect of particle-size as well as polymer–nanoparticle interaction on the elastic behavior of nanocomposites. Model nanocomposites consisting of amorphous linear glassy polymer chains and rigid nanoparticles are considered. Polymer chains are modeled as coarse-grained polymers [6], and nanoparticles of different sizes are constructed to be roughly spherical. Various levels of interfacial strength between the polymer chain and the nanoparticle are assumed by varying the energy unit (well depth) of the Lennard–Jones potential [2,7]. These interfacial strengths are chosen to represent stronger, neutral, and weaker interactions, respectively, relative to the interaction strength among polymer chains themselves. Numerical tensile loadings are simulated on these nanocomposite models. Young's moduli are calculated for the nanocomposites with different particle sizes, particle volume fractions, and interfacial strengths. The density distribution of polymer atoms and stress distributions around the nanoparticle are examined to understand the mechanism that effects the increase of the composite Young's modulus with a reduction in the size of nanoparticles.

## 2. Molecular simulations

### 2.1. Overview of simulation methodology

All simulations were performed using a molecular dynamics simulation package LAMMPS that was developed at Sandia National Laboratories [8].

The simulation started with preparing a nanocomposite by generating amorphous linear polymer chains and a nanoparticle in a simulation box at the melt temperature. After relaxing the polymer chains, the nanocomposite was quenched to the glassy state. Subsequently, simulations of tensile tests were performed by applying strain on the simulation box.

For all the simulations, periodic boundary conditions were applied to the simulation box so as to make it as a representative volume element imitating the bulk phase of the nanocomposite.

The equations of motion of polymer and nanoparticle atoms were integrated by the velocity-Verlet integrator [9]. The temperature and pressure of nanocomposites during simulation were controlled using Nosé–Hoover thermostat and barostat [10–13].

Thermodynamic quantities were expressed in reduced units that are convenient in molecular simulations as the state of a simulation with reduced units can represent many combinations of thermodynamic quantities [14]. For the polymer matrix of a Lennard–Jones system with basic units of length  $l_r$ , energy  $u_0$ , temperature  $u_0/k_B$  and mass  $m$ , the units of time, energy, temperature, pressure, and density are defined as follows:

$$t^* = l_r \sqrt{\frac{m}{u_0}}, \quad U^* = \frac{U}{u_0}, \quad T^* = T \frac{k_B}{u_0}, \quad P^* = \frac{Pl_r^3}{u_0}, \quad \rho^* = \rho l_r^3. \quad (1)$$

In Eq. (1), the reduced units are denoted with superscript \*.

In molecular simulation studies, virial stress averaged over the total volume  $V_t$  or of a local region of interest is often found to be useful to study macroscopic material behavior under uniform mechanical loading conditions or to analyze stress distribution inside the system. The average virial stress given by

$$\bar{\sigma}_{ij} = -\frac{1}{V_t} \sum_{\alpha} \left( m^{\alpha} v_i^{\alpha} v_j^{\alpha} - \frac{1}{2} \sum_{\beta \neq \alpha} f_i^{\alpha\beta} r_j^{\alpha\beta} \right) \quad (2)$$

allows one to avoid using the arbitrarily sized atomic volume. In Eq. (2),  $m^{\alpha}$  is the mass,  $v_i^{\alpha}$  and  $v_j^{\alpha}$  are the  $i$ - and  $j$ -components of the velocity of atom  $\alpha$ , respectively;  $f_i^{\alpha\beta}$  is the  $i$ -component of the force between atoms  $\alpha$  and  $\beta$ ; and  $r_j^{\alpha\beta}$  is the  $j$ -component of the central distance between atoms  $\alpha$  and  $\beta$ .

The kinetic energy term in the virial stress definition is small compared with the interatomic force term for solids but is dominant for gases [15]. Moreover, in this study, we modeled a polymeric composite material in the glassy state where molecules or atoms in the material are assumed to be basically frozen so that the momentum flux of particles crossing a spatial plane is assumed to make little contribution to the physical stress. Thus, in this study, the mechanical stress was calculated with the interatomic potential energy only. Also, in order to avoid the ambiguous volume size of atoms and investigate macroscopic material behavior, average stresses were adopted.

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