

# A molecular dynamics simulation study to investigate the effect of filler size on elastic properties of polymer nanocomposites

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## Abstract

The influence of filler size on elastic properties of nanoparticle reinforced polymer composites is investigated using molecular dynamics (MD) simulations. Molecular models for a system of nanocomposites are developed by embedding a fullerene bucky-ball of various sizes into an amorphous polyethylene matrix. In all cases, bucky-balls are modeled as non-deformable solid inclusions and infused in the matrix with a fixed volume fraction. The interaction between polymer and the nanoparticle is prescribed by the Lennard-Jones non-bonded potential. The mechanical properties for neat polymer and nanocomposites are evaluated by simulating a series of unidirectional and hydrostatic tests, both in tension and compression. Simulation results show that the elastic properties of nanocomposites are significantly enhanced with the reduction of bucky-ball size. An examination at the atomic level reveals that densification of polymer matrix near the nanoparticle as well as the filler-matrix interaction energy play the major role in completing the size effect.

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## 1. Introduction

Recently, nanoparticle reinforced polymeric composites have generated considerable attentions among materials scientists and engineers due to their potential of producing superior physical, chemical, and mechanical properties in composites structures. It appears from current experimental investigations that improvements in mechanical properties, specifically the elastic properties, of nanocomposites depends on a set of factors including nanoparticle size, shape, volume fraction, degree of dispersion, characteristics of polymer matrix and interactions between filler and matrix at their interface [1]. The influence of nano-scale filler size on elastic properties is, however, somewhat surprising because this type of effect is not seen in conventional composite materials. It is also not possible to explain such effect from continuum mechanics [2–4]. Moreover, it is dif-

ficult to find plausible correlations between filler size and mechanical properties from the reported experimental results.

Cho et al. [5], for example, conducted a systematic experimental and numerical study to address the effect of particle size on elastic modulus, tensile strength and particle/matrix debonding fracture toughness of particulate composites. They varied the size of particles from macro (0.5 mm) to nano (15 nm) scale and found that particle size at micro scale impart no influence on Young's modulus of the composite. However, the Young's modulus increased as the size of the particles decreased at nano-scale. Similar results were obtained by Chisholm et al. [6] who infused micro and nano sized SiC particles in epoxy matrix. They claimed that higher elastic modulus in nanocomposites was attained due to higher surface energy of nanoparticles. While it apparently shows that reduction in size would yield stiffer nanocomposites, reports are available where it is demonstrated that decreasing filler size has no effect [7] or some cases has negative effect [8] on elastic properties.

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It was reported that poor nanoparticle dispersion and weak filler-polymer interface adhesion were the reasons why nanocomposites could not perform over microcomposites [8]. The size issue appears to be further complicated from the work of Vollenberg et al. [9,10] where they have claimed that in the case of polymer infused with surface-treated filler, the elastic modulus is independent of the size of the inclusions. However, the modulus seems to be significantly dependent on the particle size when reinforced by untreated particle.

It appears that when size of filler reduces to nano-scale, it is difficult to identify any definite mechanism that could portray how size influence elastic properties of nanocomposites. This is partly because of challenges in processing nanocomposites, and unavailability of sophisticated tools to inspect closely their *in situ* manufacturing as well as characterization process. In this regard, several researchers have attempted to perform molecular level computations to visualize the deep insight of mechanics of nanocomposites [11–14]. While there has been quite a few computational works done in the field of polymer nanocomposites, there is yet to address the effect of filler size on mechanical properties of nanocomposites.

The purpose of this study is to investigate the effect of nanoparticle size on elastic properties of polymeric nanocomposites using MD simulations. For this, molecular models of a nanocomposite were constructed by reinforcing amorphous polyethylene (PE) matrix with nano sized buckminster fullerene bucky-ball (or simply bucky-ball). Bucky-balls of three different diameters (0.7, 1.2 and 1.7 nm, respectively) were utilized to incorporate size effect in the nanocomposites. To represent them as a generic nanoparticle system, all bucky-balls were configured as rigid body. This is necessary because a bucky-ball embedded inside the polymer matrix may deform excessively depending on its size and may overshadow the composite mechanical properties attributed to filler size. The assumption of rigid bucky-ball will ensure that the shape of filler does not contribute to variation in elastic properties. The assumption may be unrealistic for large diameter bucky-balls, it is a reasonable assumption for small bucky-balls and solid nanoparticles. In addition to this shape constraint, the volume fraction of the filler, matrix characteristics (density, molecular weight, molecular weight dis-

tribution, branch content, degree of crystallinity, etc.) and their force interaction with the nanoparticle were kept constant in all nanocomposites. Molecular models of the neat PE matrix were also developed for comparison. Elastic properties of the neat and nanocomposite systems were then evaluated using four different modes of deformation, namely, unidirectional tension and compression, and hydrostatic tension and compression, respectively.

## 2. Molecular dynamics simulations

### 2.1. Molecular models

Molecular models of nanocomposites were developed by symmetrically placing a spherical fullerene bucky-ball in the PE matrix, as shown schematically in Fig. 1a. The dashed box in Figs. 1a and b indicates the periodic cell or unit cell that was simulated by MD. Three types of bucky-balls,  $C_{60}$ ,  $C_{180}$  and  $C_{320}$  (subscripts denote number of carbon atoms), were used to incorporate the size effect. All bucky-balls were infused in matrix by approximately 4.5 vol%. Periodic boundary conditions were employed to replicate the unit cells in three dimensions. In nanocomposites, the PE matrix was represented by united atom (UA) –  $CH_2$ – units. The initial structure of the matrix was constructed by positioning the bucky-ball at the center of the unit cell and by randomly generating PE chain(s) on a tetrahedron lattice surrounding the bucky-ball. The method can be considered as a modified version of the conventional self-avoiding random walk (SARW) technique [15]. Three types of polymer chains were thus constructed for different nanocomposites. The characteristic features of the polymer chains are shown in Table 1. It can be observed from Table 1 that the lengths and thereby the molecular weights (MW) of the chains in different unit cells are almost constant. The reason of maintaining such a structure was to establish consistent matrix properties [16,17]. The same chain structures were used to describe polymer in three different neat systems.

### 2.2. Force field

Once the molecular structures were developed, corresponding molecular mechanics force fields were then

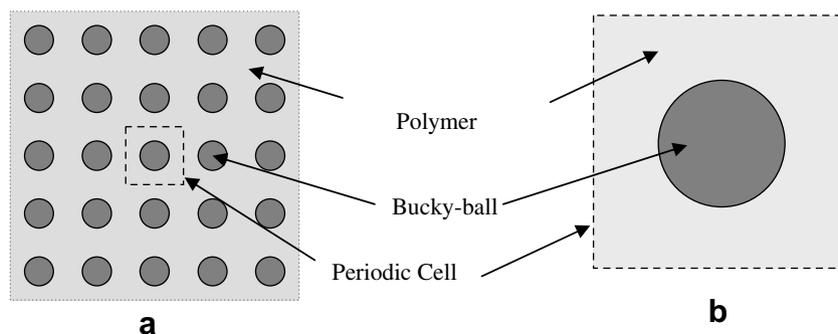


Fig. 1. (a) Schematic diagram of polymer nanocomposites, (b) periodic cells used for MD simulations.

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