Molecular dynamics study of cavitation in carbon nanotube reinforced polyethylene nanocomposite

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Abstract. Carbon nanotubes (CNTs) have proved to be very promising fillers for polymer nanocomposites. However, because of the lack of a detailed understanding of the principles of the nano inclusion interaction with polymer matrixes, the properties of such materials are poorly understood. In the present study, within the coarse-grained molecular-dynamics methods, aspects of the interaction of amorphous polyethylene matrix with carbon nanotubes and the influence of CNTs on the cavitation during the nanocomposite deformation are studied.

1. Introduction

Properties of polymer chains in contact with a nanoscale filler surface inevitably differ from the properties of a pure polymer \([1, 2]\). Because of the large area of their effective surface, even at small concentrations of nainclusions (on the order of several weight percent), the interfacial area may cover a substantial part of the polymer matrix. In this case, the material properties are affected by several parameters: the shape and size of nanoparticles, the distribution of particles in the polymer matrix, the type and force of interaction of the polymer matrix with the nanoparticles, the temperature regime, entanglement of polymer chains, etc \([3]\). A considerable role in the change of the properties of the contact between a matrix and a nanotube may be played also by local irregularities of the nanotube itself, such as surface curvature and defects of its atomic structure \([4]\). Such defects can form additional mechanical barriers comparable with direct covalent bonding. In practice, the main way to increase the contact strength is surface modification of the carbon nanostructure by different functional groups \([5, 6]\). Carbon nanotubes (CNTs) and other graphene-based nanostructures \([7]\) have a wide range of applications, including mechanical reinforcement discussed here or, for example, energy storage \([8]\). High applicability also aroses interest to the modeling of carbon nanomaterials growth \([9, 10]\).

The abundance of the above-listed factors indicates that a special approach should be applied to the numerical analysis of nanocomposite properties. In the last decade, because of the rapid development of supercomputer technologies, atomistic modeling methods become widespread in the field of materials science \([11, 12]\). One of the early examples of application of the classical molecular dynamics for the analysis of interfacial-layer parameters in CNT-based nanocomposites is provided in \([13]\). Molecular dynamics makes it possible to follow the evolution of conformational changes at the level of valence angles and lengths of interatomic bonds and
to reveal local plastic rearrangements [14, 15]. On the coarser, mesoscopic level, the method of dissipative particle dynamics (DPD) is widely used to study the processes of nanoparticle agglomeration and their influence on the elastic properties of polymer matrices [16, 17].

In the present study we model the process of nanocavitation during the deformation of polyethylene (PE) and PE–CNT composites using classical molecular dynamics. Extending our previous results on PE–CNT deformation [11] we study the influence of nanofillers on nanopore nucleation using so-called primitive path (PP) analysis.

2. Model and calculation method

Main parameters of the computational setup are similar to [11]. Polyethylene molecules are presented in a simplified geometry: CH$_2$ and CH$_3$ groups were considered as atomic units of the polymer chain (so-called united-atom model). To model PE–PE and PE–CNT interaction the analytical equations of the Dreiding force field were used. Parametrisation of the force field is described in [11].

The initial topology was obtained with the use of a radical-like polymerization [18]. Chain growth was initiated in a cell initially containing only monomers and a set of CNTs with the given parameters corresponding to the equilibrium configuration at $T = 300$ K. During chain growth, the coordinates of CNT atoms were fixed. Additionally, the chain growth through walls of the nanotubes was prohibited. When polymerization was completed, each cell was relaxed for 5 ns at $P = 1$ atm and $T = 300$ K—below the temperature of glass transition, which for pure PE model was $T_g \approx 350$ K. All subsequent MD simulations of deformation were performed in microcanonical (NVE) ensemble.

Molecular-dynamics calculations were performed using LAMMPS. The integration step of atom-motion equations for the coarse-grained model was 1 fs. The system was derived for the desired parameters (temperature and pressure) with the use of a Nose–Hoover thermostat and a Parrinello–Rahman barostat.

3. Results and discussions

The influence of nanoinclusions on the elastic properties of the polymer composite and nanocavitation was studied via simulation of the deformation of pure PE and the composite formed on its basis with the addition of different types of CNTs.

3.1. Pure PE deformation

Computational cell of $25 \times 10 \times 200$ nm$^3$ and periodic boundary conditions contained about 1.7 million coarse-grained atoms. Every polymer chain contained on average two thousand units. The uniaxial deformation (stretching along the z axis of the cell) of the system was performed at an extension rates of $\dot{\varepsilon} = 5 \times 10^7$ and $1.25 \times 10^9$ s$^{-1}$; the dimensions of the cell along the two other axes were fixed ($\dot{\varepsilon}_y, \dot{\varepsilon}_z = 0$). Figure 1(a) shows the stress-strain diagram for the pure PE at $\dot{\varepsilon} = 5 \times 10^7$ s$^{-1}$, in the insets the corresponding density diagrams representing the process of nanovoid nucleation are shown.

The potential energy change during the deformation is shown in figure 1(b).

Energy components corresponding to non-bonded (van der Waals forces between polymer chains) and bonded (angle- and bond-length-dependent) interactions are separated to show that the elasticity of linear polymer systems is mostly determined by the non-bonded component (evolution of different energy components during PE deformation is discussed in detail in [19]). Moreover, from [19] one can see that the lower is deformation rate the lower is the bonded contribution. Therefore, it could be stated that in the limit of macroscopic times of deformation in elastic regime for PE (in our case $\varepsilon < 0.05$), the elastic properties are affected predominantly by inter-chain interactions.
Figure 1. (a) Stress–strain curve for a pure PE. (b) Evolution of energy components during the deformation. (c) Detailed picture of chain configuration near one of the pores at $\varepsilon = 0.15$.

Cavitation in polymers differs much from that in simple liquids: motion of polymer chains and their ability to increase the free volume is highly restricted by the entanglement topology. Even higher alkenes with molecular weights much lower than discussed here for PE show a lot of peculiarities in relaxation and transport properties [20, 21]. Zones with weak entanglement network are first candidates for nanovoid formation. The process of disentanglement is governed by chain reptations. It is known that the characteristic time of reorientation of a single monomer unit is $t \approx 10^{-11}$ s, thus, the relaxation time of a chain containing $N$ units is $T = tN^2$ according to the Rouse model. In the case of a chain of $N = 1000$ units, the characteristic time of macromolecular relaxation can reach $10^{-5}$ s. It results in significant dependence of the rate of nanopore nucleation on the deformation rate, figure 2(a, b). To show the dynamics of nanovoid nucleation in PE during the deformation we also calculate pore size distribution (PSD, for the details on the computational procedure see e.g. [22])—figure 2(c).
3.2. **PE–CNT composite deformation**

To study the role of nano inclusions on the cavitation stress-strain diagrams and PSD were calculated for PE–CNT system. Two types of CNT with different interfacial shear strength (ISS) were used: with regular surface and functionalized one (details on ISS calculations could be found in our previous work [11]).

The tension of the composite with different configurations of the filler (CNTs) was analyzed within the cell with a volume of $25 \times 10 \times 200$ nm$^3$ containing two parallel nanotubes 175 nm in length and 2.5 nm in diameter (an aspect ratio of 70). The total amount of coarse-grained atoms was about 1.7 million. Every polymer chain contained on average two thousand units. The uniaxial deformation of the system was performed at an extension rate of $\dot{\varepsilon} = 5 \times 10^7$ s$^{-1}$. It was applied along to the longest axis; the dimensions of the cell along the two other axes were fixed. The mass fraction of the filler was 8%.

Figure 3 shows the corresponding stress-strain diagram for three systems: pure PE, the nanocomposite with smooth (non-functionalized) nanotubes and with modified functionalized nanotubes. The addition of CNTs with a high aspect ratio leads to a noticeable increase in the elastic modulus of the composite. The higher the value of ISS, the more noticeable the strengthening effect is. Nanotubes are long enough to interact with sufficiently large number of PE chains and transfer stress between chains which do not have shared entanglements due to the distance. Therefore CNT act as a single aggregator of stress.

As seen from the nanovoid nucleation analysis, figures 4 and 5, CNTs parameters significantly affect the process of nanocavitation during the nanocomposite deformation. Introducing inhomogeneity, they behave as additional centers of pore nucleation (especially at CNT tips), but at the same time CNTs slow down the growth of nanopores and subsequent crack formation. Final macroscopic properties of the material, depending on the nano inclusions’ parameters, will be defined by the interplay between intensified nanovoid formation on the one hand, and increased rheological parameters of the interface (due to high ISS) on the other.
3.3. Primitive path analysis
In amorphous polymer systems nanovoid formation could be considered as a result of local topological degradation of polymer network that starts from acts of disentanglement. It is
conjectured [23] that analysis of the interchain entanglement network of the undeformed polymer could predict the spots where nanovoid formation starts during the deformation. The idea is that regions depleted with entanglements are more predisposed to the nanovoid nucleation. The same concept could also be applied to the case of polymer nanocomposite, where nanoinclusions bring inhomogeneity into the spatial distribution of interchain entanglements. We utilize here one of the most commonly used technique of entanglement structure analysis—primitive path (PP) method. Doi and Edwards [24] introduced the concept of a PP as the shortest path between chain ends that is consistent with the restriction of chain uncrossability. Sukumaran et al. [25] provided a method for constructing a PP through modified MD simulations by fixing chain ends while slowly tightening polymer bonds. During this process thermal motion allows chains to shrink and create a network of interconnected links, figure 6.

Here we use PP analysis to calculate the average molecular weight between entanglements, \( N_e \). The value of \( N_e \) is calculated in accordance with

\[
N_e = (\mathcal{N} - 1) \frac{R_{ee}^2}{\mathcal{L}_{pp}^2},
\]

where \( R_{ee} \) is end-to-end distance and \( \mathcal{L}_{ee} \) is the length of the chain in its primitive path configuration (so-called “statistical” interpretation of \( N_e \) [26]).

The system was a cube with 80 nm side, figure 6. The total amount of coarse-grained atoms was about 18000 which were divided between 10 PE chains. The uniaxial deformation of the system was performed at an extension rates of \( \dot{\varepsilon}_x = 8 \times 10^7 \) and \( 8 \times 10^6 \) s\(^{-1}\); the dimensions of the cell along the two other axes were fixed (\( \dot{\varepsilon}_y = \dot{\varepsilon}_z = 0 \)). Every 100 ps we stored the configuration of the system and analyzed its primitive path network. In each configuration we fixed tail atoms of the chains and then gradually reduced bond length parameter between monomers. It comes from the definition of \( N_e \) that larger values of \( N_e \) correspond to less entangled structures. As one can see in figure 7, the slower is stretching the larger is number of disentanglements. This result is in accordance with the picture of nanovoid nucleation dependence on the deformation rate, figure 2: the slower deformation is—the larger fraction of entanglements has enough time to disentangle and thus we observe more pronounced picture of nanovoid formation.
Figure 6. Initial computing cell with PE molecules and corresponding primitive path network.

Figure 7. Evolution of the entanglement molecular weight $N_e$ during uniaxial stretching for two deformation rates: $\varepsilon_x = 8 \times 10^7$ and $8 \times 10^6$ s$^{-1}$.

4. Conclusions
In the present paper, the process of nanocavitation in PE–CNT nanocomposites during the tensile deformation was studied. Results of calculations show that both elastic properties and
cavitation process are highly influenced by CNT inclusions even at their low mass fraction. CNTs affect the mechanical properties of composite via two competing mechanisms: intensifying nanovoid formation in the vicinity of CNT surface, and increasing adhesion parameters of the PE–CNT interface.

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