Uniaxial deformation of polystyrene–silica nanocomposites studied by hybrid molecular dynamics–finite element simulations

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ABSTRACT

This contribution investigates, based on molecular dynamics (MD), the mechanical deformation behavior of polystyrene-silica nanocomposites and focuses on the influence of micromechanical properties as e.g. filler particle size and filler mass fraction. With regard to simulations of macroscopic problems with system sizes not capable by pure MD approaches, our investigations are complemented by hybrid molecular dynamics – finite element (MD-FE) simulations. Our computational approach shows show that an increasing total interfacial area between the nanoparticles and the polymer matrix stiffens the nanocomposite. As expected, small nanoparticles have more significant impact on the macroscopic mechanical properties of nanocomposites than large ones. We show that, for the same mass fraction of nanoparticles, the Young's modulus increases by about 4–5% when the nanoparticle diameter is decreased from 5 to 2 nm. Furthermore, we find that: (i) the end-to-end distances of free polymer chains in the vicinity of nanoparticles are larger than in the bulk; (ii) the addition of nanoparticles slows down the global dynamics of free polymer chains; and (iii) the interphase thickness of nanocomposites is about 1–1.5 nm. Beyond that, we study structural properties at the microscale under uniaxial tension and find that the presence of nanoparticles hinders the orientation of free polymer chains under deformation. This hindrance is more pronounced for small nanoparticles and high mass fractions. Polymer structural descriptors as the chain end-to-end vector and a molecular anisotropy parameter largely change in line with the geometrical transformation of the whole sample.

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1. Introduction

Polymer nanocomposites [1–3] are produced by blending a polymer matrix with nanoparticles (e.g. spherical silica [4–6], carbon nanotubes [7–9] and delaminated clay [10–13]). In the past decades they have been applied extensively in different industries. However, it is still a challenge to understand the improvement of mechanical and other properties by nanoparticle inclusion at a molecular level. Due to their large surface, nanoparticles contact efficiently with polymer chains in nanocomposites. The interphase between the polymer matrix and the nanoparticles has a significant influence on the mechanical properties of nanocomposite materials. For instance, an interphase can hinder effectively the formation and propagation of fatigue cracks in nanocomposite materials [4]. This has been attributed to the fact that a strong interphase reduces the internal stress of polymer nanocomposites during a deformation process.

Experimental investigations [14–16] have demonstrated that an increase of the nanoparticle concentration leads to an increase of elastic moduli. However, above a certain threshold nanoparticle aggregation leads to a reduction of the contact area between the polymer matrix and the nanoparticles [15]. A good dispersion of the nanoparticles [17,18] in the polymer matrix attenuates effectively local stress concentrations. In addition, the influence of the nanoparticle size on the mechanical properties has been investigated by experimental methods. For polypropylene–$CaCO_3$ nanocomposites, Mishra et al. [19] have observed that the Young's modulus of composites with smaller nanoparticles has been greater than the one of composites with larger nanoparticles. In other contributions [20–22], similar results have been obtained for polyamide-6–silica thermoplastics, polysiloxane–silica coatings and epoxy–silica resins. A reduction of the nanoparticle size at a

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constant concentration causes an increase of the interphase area, which consequently enhances the overall surface energy between polymer chains and nanoparticles [21]. The grafting of nanoparticle surfaces by polymer chains is another way to modify the interaction between the polymer and the nanoparticles. Rong et al. [21,22] applied either ungrafted or polymer-grafted (i.e. polymethylmethacrylate or polystyrene) silica nanoparticles. They have found that grafted nanoparticles disperse better in the composites. In accordance with Rong et al., Bikiaris et al. [23] have also observed that isotactic polypropylene nanocomposites containing surface modified silica nanoparticles have improved mechanical properties such as the Young's modulus.

Simulation studies have been applied widely to investigate the mechanical and other properties of polymer nanocomposites. Papakonstantopoulos et al. [24,25] have employed a Monte Carlo (MC) approach to study the influence of the polymer-nanoparticle interactions on the mechanical properties of nanocomposites. They found that the average shear and Young's moduli of nanocomposites filled with inert or attractive nanoparticles were larger than those of the pure polymer. Raos et al. [26] have performed dissipative particle dynamics (DPD) simulations to examine polymer networks mixed with spherical particles at a volume fraction of 20%. Their results indicated that the polymer-particle interaction is a significant factor influencing the dynamic shear modulus of filler-cross-linked polymer networks [27–29]. Ndoro et al. [30,31] have demonstrated by atomistic molecular dynamics (MD) simulations that the size and the grafting density of silica nanoparticles have an influence on the interphase structure of nanocomposites. Due to the polymer-nanoparticle interaction, the properties of polymer chains in the interphase differ from those of the bulk. Ghanbari et al. [32,33] and Rahimi et al. [34] also formulated similar conclusions by coarse-grained MD simulations of polymer–silica nanocomposites.

In contrast to particle-based methods, continuum-based approaches (i.e. micromechanics [35] and the finite element (FE) method [36]) tackle macroscopic problems by applying continuous meshing units. Fornes et al. [37] have adopted a micromechanically based model to simulate a nylon-6–layered-clay system. They concluded that the exfoliated clay contributed to a mechanical reinforcement of nylon-6. The reinforcement, however, decreased when the number of clay platelets per stack grew. By using a three-dimensional FE approach, Mortazavi and coworkers [38] have evaluated the influence of the interphase on the elastic modulus of nanocomposites containing either unidirectionally or randomly oriented particles. They demonstrated that the interphase effects for spherical nanofillers were stronger than for the anisometric nanofillers.

While particle-based methods address appropriately molecular and mesoscopic structures of soft materials, their computational cost is prohibitive when facing macroscopic problems. Continuum-based methods allow a macroscopic modeling of soft materials, frequently relying on finite element meshes for numerical solution. Thereby, a microstructural resolution in terms of particles and their interactions is not accessible. Hybrid particle-continuum methods have been developed to overcome their intrinsic drawbacks: a small particle domain with a high resolution for analyzing quantities of interest is coupled to an extended surrounding continuum that makes macroscale simulations computationally affordable. They may be categorized into sequential and concurrent couplings [39–42]. Sequential coupling [43] provides a bridging solution in which hierarchical methods are coupled by passing material parameters (e.g. elastic moduli) derived from one scale in an off-line way to another scale. Yang et al. [44] developed such a combined framework based on MD, FE and micromechanics. In their approach, the bulk modulus of nanocomposites calculated by an atomistic MD simulation was used to parameterize the FE model. The results reflected qualitatively the influence of the nanoparticle size on the mechanical properties of nanocomposites. Concurrent coupling combines simulation methods at different scales in an on-line way [45]. A bridging domain method has been developed by Xiao and Belytschko [46] to couple the continuum with molecular models. Their investigations have indicated that such a bridging domain approach can reduce the spurious wave reflections at the interphase region. Zhang et al. [47], Khare et al. [48] and Davydov et al. [49] have demonstrated that the bridging domain method addresses appropriately deformation problems of crystalline materials. Ben Dhia et al. [50,51] have proposed the Arlequin method in which the energies of the particle and continuum domains are coupled. Both the bridging domain and the Arlequin method do not require a lattice description in the particle domain. Therefore, they have been applied by some researchers (i.e. Bauman et al. [52] and Chamoin et al. [53]) to simulate soft materials such as polymers.

Different to the aforementioned methods, some of us [54,55] have developed a hybrid MD-FE framework based on the Arlequin approach. A large number of so-called anchor points are introduced in this scheme to communicate information (i.e. forces and displacements) between the MD and FE computations when performing the staggered iteration cycles. Details of the present MD-FE coupling [54–56] are explained in Section 2. Recently the hybrid method has been employed to simulate pure polystyrene and polystyrene nanocomposites containing a single ungrafted silica nanoparticle [55]. In the present contribution, this method is applied to investigate the influence of the mass fraction, size and grafting density of nanoparticles on the mechanical properties of polystyrene–silica nanocomposites in a coarse-grained resolution. At first, standard periodic MD simulations without coupling to the FE domain are performed to identify the effective mechanical parameters (i.e. Young's modulus and Poisson's ratio) of polystyrene–silica nanocomposites. In addition, the influence of nanoparticle inclusion on structural and dynamic properties of polymer chains is also investigated. Subsequently, the considered nanocomposite systems are elongated at a constant deformation step size by the hybrid MD-FE method. The changes of the mean normal stress with the strain are monitored, too. Furthermore, a geometrical transformation model is proposed to analyze the changes of structural polymer properties at a glassy state during a uniaxial elongation. These results allow us to understand from a molecular perspective the improvements in the mechanical properties by nanofiller inclusion as well as the changes of polymer properties as a function of the applied deformation.

2. Simulation method and computational details

2.1. Hybrid molecular dynamics-finite element method

The hybrid simulation space consists of three regions, i.e. the outer FE, the inner MD and the intermediate dissipative particle dynamics (DPD) region (Fig. 1). The FE region allows an application of an external load to deform the entire box during the hybrid simulation. The particles in the MD region move under classical Newtonian mechanics. The interactions between the beads in the MD region are described by a coarse-grained force field [57] developed by Ghanbari et al. [33]. In our recent simulations [34,54,55,58], the applicability of the adopted force field has been investigated either with the help of qualitative scaling relations (Young's modulus) or quantitative property predictions (e.g. Poisson ratio and the interphase thickness). It should be mentioned that the Young's modulus derived from the present MD simulations is somewhat lower than the experimental number. This is reasonable, as the coarse-grained potential is softer than the