Response of matrix chains to nanoscale filler particles

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ABSTRACT

A new generation of on-lattice MC simulations for dense melts of coarse-grained POE chains has been developed so that the MC simulations include nanoscale filler particles. In this novel approach, filler particles and polymer chains are built from the same chemical structural building unit. Early simulations pointed an ambiguous behavior for the response of the matrix chains to the introduction of the nano-particles. When the size of nanoparticles is comparable to that of matrix chains, or even smaller, a significant amount of chain expansion (for matrix chains) is always the case, which challenges the current theoretical considerations in this field. Our recent simulations show that the chain expansion behavior is not triggered by an artificially created "extra volume" effect. Furthermore, the relation between chain expansion behavior and a potential enhancement in the free volume is found to be irrelevant based on our analysis on the pair correlation and scattering functions.

1. Introduction

Amorphous polymers can be filled with particles with a wide variety of compositions, both inorganic and organic. This fact implies that the energetic interaction between a matrix chain and a filler particle is subject to wide variation by the use of different combinations of chains and fillers. It seems useful to introduce a conceptual reference point provided by a system in which all the pair-wise interactions (filler–filler, filler–matrix, and matrix–matrix) are identical, so that the properties of the filled system respond solely to the space-filling requirements of the dense filler particle, with that response uncomplicated by any preferential energetic interaction. Recently, there has been interest, from both theoretical and experimental point of view, on the behavior of systems filled with particles that meet this requirement.

The experimental system used by Mackay and coworkers [1–3] is based on atactic polystyrene. The polystyrene chains that constitute the filler particles contain numerous intramolecular crosslinks, causing them to behave as compact nanoparticles. These particles are then suspended in conventional, uncrosslinked atactic polystyrene to form a filled system in which styrene is the only repeat unit present.

We have reported results from simulations of a filled system that is created from an equilibrated model for a dense melt of either polyethylene (PE) or polyoxyethylene (POE) [4,5]. The attractive part of the intramolecular Lennard–Jones potential is then

strengthened for a subset of the chains, causing these chains to collapse. The intermolecular interactions are not altered. The extent of the collapse is described by c, defined using the mean square radii of the filler particle, $\langle s^2 \rangle_{\text{filler}}$, and chain of the same molecular weight, M, in its unperturbed melt, $\langle s^2 \rangle_0$, as:

$$c \equiv \frac{\langle s^2 \rangle_0^{3/2} - \langle s^2 \rangle_{\text{filler}}^{3/2}}{\langle s^2 \rangle_0^{3/2} - (3/5)^{3/2}(3M/4\pi\rho N_{\text{A}})} \quad (1)$$

With this definition, $c = 0$ when there is no collapse ($\langle s^2 \rangle_{\text{filler}} = \langle s^2 \rangle_0$) and $c = 1$ when the selected chains have collapsed to the extent where their mean square radius of gyration has the value expected for a uniform sphere with the bulk density, ρ, of 1.06 g/cm³ and the mass, M/N_{A}, of that chain ($\langle s^2 \rangle_{\text{filler}} = (3/5)^{3/2}(3M/4\pi\rho N_{\text{A}})$). The properties of filler particles produced in this manner have been described elsewhere [4].

The crosslinks that produce the collapse of selected polystyrene chains in the experimental system are permanent, since they are produced by covalent bonds. In contrast, the "crosslinks" that create the collapse of selected PE or POE chains in the simulation are transitory and mobile, because they are produced by enhancing the attractive part of a Lennard–Jones potential. It is gratifying that both systems find an expansion in the mean square dimensions of the matrix chains in response to the presence of the small (nano-scale) filler particles, $\langle s^2 \rangle_{\text{matrix}} > \langle s^2 \rangle_0$, where $\langle s^2 \rangle_{\text{matrix}}$ denotes the mean square radius of gyration of the matrix chain in the filled system and $\langle s^2 \rangle_0$ denotes their mean square radius of gyration in an unfilled melt. This observation is particularly noteworthy because all conceivable types of behavior of the matrix chains (contraction: $\langle s^2 \rangle_{\text{matrix}} < \langle s^2 \rangle_0$ [6–11], expansion: $\langle s^2 \rangle_{\text{matrix}} > \langle s^2 \rangle_0$ [6,11,12], or no

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change: $\langle s^2 \rangle_{\text{matrix}} \sim \langle s^2 \rangle_0$ [13,14]) have been reported in other experimental and simulation studies in which the particle and matrix were composed of different materials.

The fact that other works, either simulation or experiment, often produced qualitatively different results might produce some concern as to whether our simulations have been interpreted correctly. For example, private comments from other experts have voiced the concern that additional free volume is somehow produced in our simulations when some of the chains collapse and the matrix chains expand in response to that increase in free volume. Here we report results from our recent simulations that deny the validity of this hypothetical conjecture.

2. Simulation method

The *NVT* Metropolis Monte Carlo simulations were performed with the same general method employed in our recent investigation on the behavior of melts containing collapsed chains constructed from the same monomer unit [4,5]. The coarse-grained methyl terminated POE chains are simulated on a high coordination lattice ($10i^2 + 2$ sites in shell i, step length $L = 0.239$ nm) using one coarse-grained bead for every second chain atom. Except when stated specifically to the contrary below, the *NVT* simulation imposes a density, ρ, of 1.06 g/cm^3 on the system, which is the experimental melt density of POE at the temperature (373 K) of the simulation. The exception occurs when we investigate the consequences of the intentional introduction of additional free volume into the system by an increase in the length of one side of the periodic box, without a corresponding increase in the number of chains. This procedure intentionally introduces new, and artificial, free volume into the system, which in turn lowers the density of the model. Periodic boundary conditions are used in all dimensions. The collapse of selected chains, causing them to form dense particles, is achieved by an enhancement of the short-range intramolecular attraction of coarse-grained beads in these chains that are separated by at least two other beads. The extent of the collapse described by c is defined in Eq. (1). The properties of filler particles produced in this manner have been described previously. The fraction of all beads in the system that reside in the collapsed chains defines the filler concentration, x_{filler}, expressed as a number fraction.

3. Results and discussion

The possible influence of extra free volume can be determined by a set of simulations in which additional free volume is intentionally introduced into the system. Here we initially equilibrate the melt in an *NVT* simulation in a periodic box of length $22L = 5.30$ nm on each side, with L chosen to produce the physical density (1.06 g/cm^3) for a POE melt at the temperature (373 K) of the simulation. The 43 independent parent chains are each represented by 52 coarse-grained beads. After equilibration, the mean square radius of gyration of the uncollapsed matrix chains, $\langle s^2 \rangle_{\text{matrix}}$, is 1.49 ± 0.02 nm^2. Then the length of one side of the box is extended by one unit (0.239 nm) so that the new *NVT* simulation of the same system is performed in a box with dimensions 5.30 nm in two directions and a third dimension of 5.50 nm. The density is decreased by approximately 4%, which implies a substantial increase in free volume. After the system is reequilibrated in the larger box, the new value of $\langle s^2 \rangle_{\text{matrix}}$, 1.50 ± 0.02 nm^2, is indistinguishable from the result obtained in the original box, where $\langle s^2 \rangle_{\text{matrix}} = 1.49 \pm 0.02$ nm^2.

The same recipe is followed for a filled system where an identical system is used, but 9 of 43 parent chains are collapsed, so that the volume fraction of filler particles is $x_{\text{filler}} = 0.21$. The original 52-bead system with $x_{\text{filler}} = 0.21$ showed that matrix chains
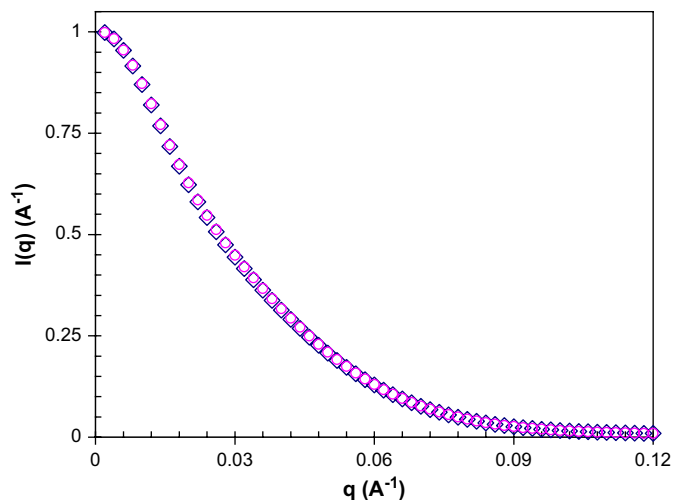

Fig. 1. Scattering function vs. scattering vector data for systems composed of 21 POE parent chains, each represented by 106 beads. Diamonds are for the melt ($x_{\text{filler}} = 0$) and circles are for the filled system with $x_{\text{filler}} = 0.19$.

experience a significant amount of increase in their dimensions ($\langle s^2 \rangle_{\text{matrix}}/\langle s^2 \rangle_0 = 1.79 \pm 0.09$). When we include some artificially generated free volume in the simulations, it turns out that the resulting increase in the dimensions ($\langle s^2 \rangle_{\text{matrix}}/\langle s^2 \rangle_0 = 1.78 \pm 0.06$) is statistically equivalent to the one that comes from our previous simulations. Besides, based on our recent simulations that report $\langle s^2 \rangle_{\text{matrix}}$ could increase by as much as a factor of 2 when some of the chains were collapsed to nanoparticles (see Fig. 3 in Ref. [5]), it is inconceivable that this collapse can be attributed to an increase in the free volume of simulated system.

The same point can be made in an alternative manner by searching for the onset of density fluctuations within the simulation cell when some of the chains are collapsed to nanoparticles. One approach would be looking for changes in intermolecular pair correlation functions. A related approach is to calculate the scattering functions, which are sensitive to density fluctuations. Both approaches have been performed. Fig. 1 depicts two scattering
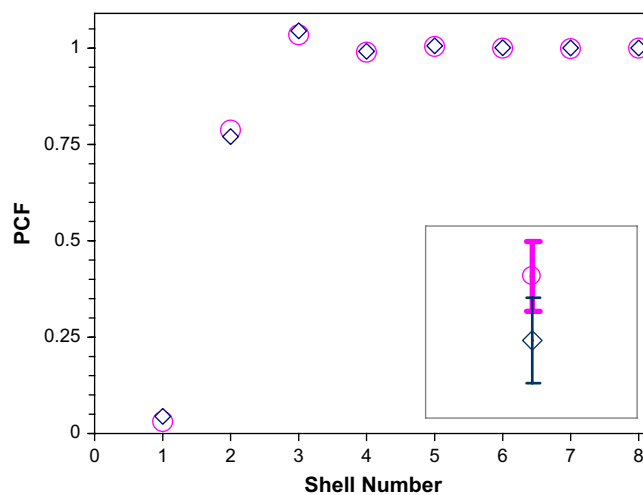

Fig. 2. Bead-to-bead pair correlation functions for the identical systems used in Fig. 1. Diamonds are for the melt ($x_{\text{filler}} = 0$) and circles are for the filled system with $x_{\text{filler}} = 0.19$. The error bars in the inset depict the statistical significance of the results for the second shell interactions. Simulation error is determined based on a simple standard deviation calculation for the values that come from a set of simulations that have been performed for the identical systems.

functions (which are indistinguishable from one another) for a POE system in which the 21 parent chains are each represented by 106 beads, and $x_{filler} = 0.19$. Within our simulation error, the scattering function does not change when some of the chains are collapsed to become particles. The intermolecular pair correlation functions, Fig. 2 may show a slight change in the second shell when some of the chains collapse to nanoparticles, but this possible change is smaller than the simulation error in the individual points, which is clearly depicted in the inset in Fig. 2. In conclusion, the simulation detects neither density fluctuations, nor convincing changes in intermolecular pair correlation functions, when a subset of the chains is collapsed to nanoparticles.

4. Conclusions

Traditionally, most people believe that the matrix chains should experience a huge reduction in their dimensions when they are subject to a confined geometry whose boundaries are defined by the rough surfaces of nanoscale filler particles. Our previous simulations show that numerous systems can produce an opposite behavior when the size of nanoparticles is comparable to that of matrix chains. We design a new set of simulations in order to check the presence of some artificially created effects that may trigger the chain expansion behavior. Our analysis with pair correlation and scattering functions for the filled and unfilled systems proves that there is no substantial deviation in the density fluctuations in both systems. Furthermore, the simulated behavior does not change extensively in magnitude even when some additional free volume is artificially inserted into the filled and unfilled systems. So, we strongly argue that the chain expansion behavior cannot be attributed to the changes in the free volume of system that might take place during the collapse of a subset of linear chains to become nanoparticles.

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