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Dimensions of matrix chains in polymers filled with energetically neutral nanoparticles

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Abstract

Simulations of dense one-component melts of coarse-grained polyethylene (PE) and polyoxyethylene (POE) chains have been modified so that some of the parent chains are collapsed intramolecularly to become filler particles. All intermolecular pairs of beads (filler–filler, filler–matrix, matrix–matrix) interact via exactly the same Lennard–Jones (LJ) potential. Filler particles are obtained by an increase in the strength of the minimum in their intramolecular LJ potential. The response of the mean square radius of gyration, $\langle s^2\rangle_{\text{matrix}}$, of the free matrix chains to disordered arrangements of the filler particles is evaluated for differences in the compactness and mobility of the filler particles, and for various relationships between the mass of matrix chains and filler particles. Even with this simple model, where distinctive surface—matrix interactions are completely suppressed, the response of $\langle s^2\rangle_{\text{matrix}}$ to the filler particles is complex. It depends on the completeness of the collapse of the chains that represent the filler particles, the mobility of these particles, their concentration, and the relationship between the number of beads in the matrix chains and filler particles. Expansion of the matrix chains is seen when the particles and matrix are both represented by a small number of beads, but contraction of matrix chains can be observed when both species contain a large number of beads. The mobility of the filler particles is likely to be an important issue when they are small, i.e. nanoparticles, and the matrix is not glassy.

Keywords: Composites; Filled polymers; Filler particles

1. Introduction

Decades ago it was demonstrated that the physical properties of amorphous polymers are often changed in beneficial ways by the addition of small filler particles [1,2]. Here, as in many areas of science, the nanoscale is particularly interesting. Nanoscale fillers can produce more interesting properties than micron sized fillers [3–6]. Part of this effect may be produced by the energetic interaction between the matrix chains and the filler particles. The energetic interaction might be attractive or repulsive, depending on the selection of the two components. This system-specific physical response is superimposed on a generic response, which may depend on the mean square radius of gyration ($\langle s^2\rangle_{\text{filler}}$), shape, porosity, and volume fraction (x_{filler}) of the filler particles, but suppresses any chemistry-specific special energetic interaction between the two components. The simulations reported here are designed to detect the generic response of the mean square radius of gyration of a matrix chain ($\langle s^2\rangle_{\text{matrix}}$) to the introduction of nano-sized filler particles. The manner in which the particles are treated in the simulation guarantees the complete suppression of any influence of special particle—matrix energetic effects.

Design of a simulation with this goal demands a precise definition of the chemical composition of a filler particle that will elicit only the generic response in the matrix chains, uncomplicated by any system-specific energetic effects. Our definition starts from an unfilled, one-component polymer melt, where all of the chains have the same composition and mean square unperturbed radius of gyration, denoted by $\langle s^2\rangle_0$. The intermolecular interactions in a one-component melt are the same for all pairs of chains. We define the 'generic' particle as one, which shares precisely these intermolecular interactions, so that a bead in matrix chain *i* does not discriminate between beads in matrix chain *j* and beads in filler particle *k*, insofar as the pair-wise energetic intermolecular interaction is concerned. With this definition, any difference between $\langle s^2\rangle_{\text{matrix}}$ and $\langle s^2\rangle_0$ must arise entirely from the size, shape, porosity, and concentration of the filler particle, uncomplicated

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by any special energetic effects. This definition leads naturally to a precise statement of the desired chemical composition for our ‘generic’ filler particles. The generic filler particles are collapsed representations of chains constructed from exactly the same repeat unit as the one found in the chains that appear in the matrix. A specific example is provided by polystyrene particles in a melt of linear polystyrene chains [7,8].

If a few chains are collapsed to spheres with the density, ρ, expected for that type of chain, they represent generic dense spherical filler particles that are impermeable to the matrix. Alternatively, they might be collapsed less severely, in which case they can represent generic nonspherical filler particles that are permeable to the matrix chains. Recently, we described the formation and properties of both impermeable and permeable filler particles obtained by the intramolecular collapse of a few coarse-grained polyethylene (PE) and polyoxyethylene (POE) chains in the melts [9]. Here, we identify several properties of the system that determine the response of $\langle s^2\rangle_{\text{matrix}}$ to these generic filler particles.

The behavior of $\langle s^2\rangle_{\text{matrix}}$ in systems with filler particles of different compositions has been the topic of several neutron scattering experiments [10–13] and simulations [14–26]. The experiments demonstrate an intriguing dependence of the qualitative response of $\langle s^2\rangle_{\text{matrix}}$ to the details of the system. Thus, for polydimethylsiloxane (PDMS) filled with polysilicate particles, $\langle s^2\rangle_{\text{matrix}} < \langle s^2\rangle_0$ if the system is constructed so that $\langle s^2\rangle_{\text{matrix}}$ and $\langle s^2\rangle_{\text{filler}}$ are similar in size [12,13]. However, $\langle s^2\rangle_{\text{matrix}} > \langle s^2\rangle_0$ if longer PDMS chains are used, at least at low x_{filler} [12,13]. The extent of the expansion is reduced at higher x_{filler}. Simulations also show a rich variety of responses of the matrix to the filler. There is precedent for either $\langle s^2\rangle_{\text{matrix}} > \langle s^2\rangle_0$ [17,18,24] or $\langle s^2\rangle_{\text{matrix}} < \langle s^2\rangle_0$ [6,18,20–22,24], with the qualitative result sometimes dependent on the relationship between $\langle s^2\rangle_{\text{matrix}}$ and $\langle s^2\rangle_{\text{filler}}$ [18,24]. There is also a report that the distribution function for the end-to-end distance of the matrix chains experiences only an insignificant change in response to the filler particles [25]. The value of $\langle s^2\rangle_{\text{matrix}}$ need not respond in a monotonic fashion to the amount of filler, but may instead pass through a maximum as x_{filler} increases [24]. With the exception of the recent study of flow properties for polystyrene particles in polystyrene melts [7,8], prior experiments or simulations did not study systems that contain ‘generic’ filler particles, as that term was defined in the previous paragraph. The identification of properties of the system that affect the ‘generic’ behavior should serve as a useful reference point for understanding the physical basis of the varied response of more complicated systems. This report presents the first simulation of the ‘generic’ response of $\langle s^2\rangle_{\text{matrix}}$ to the presence of nano-sized generic filler particles.

2. Simulation method

The Monte Carlo (MC) simulations employ coarse-grained polyethylene (PE) or polyoxyethylene (POE) chains on a sparsely occupied high coordination lattice [27,28]. The chains are constrained so that any snapshot can be reverse-mapped to an atomistically detailed model at bulk density in continuous space [29]. Two consecutive chain atoms and their pendant hydrogen atoms are folded into each coarse-grained bead. The step length is 0.250 nm for PE [30] and 0.239 nm for POE [30]. Occupancies of 18% [32] and 20% [31], respectively, reproduce the experimental density (ρ) for PE melts and POE melts at the temperatures (T) used in the simulations (453 K for PE, 373 K for POE). All of the NVT simulations were performed at the experimental ρ of the one-component melts at these T. The simulations invoke the assumption that ρ is independent of x_{filler} when the filler is generic.

Two types of constraints cause the coarse-grained chains in a one-component melt to mimic the real chains they represent. The proper distribution function for the end-to-end distance of each chain, and all of its subchains, is enforced by a mapping [33] of the rotational isomeric state (RIS) models for PE [34] and POE [35]. The proper intermolecular structure of the one-component melt is imposed by use of a discretized Lennard–Jones (LJ) potential for the intermolecular interactions, as well as all intramolecular interactions not treated explicitly in the RIS model [32].

$$U_{\text{LJ}} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

The discretization, using input values of $\sigma = 0.44$ nm and $\varepsilon/k_{\text{B}} = 185$ K for PE, and $\sigma = 0.376$ nm and $\varepsilon/k_{\text{B}} = 154$ K for POE, produces interaction energies, u_i, for the various shells on the lattice [31]. These input LJ potentials specify $u_1 = 14.426$, $u_2 = 0.558$, and $u_3 = -0.626$ kJ/mol for PE, and $u_1 = 8.113$, $u_2 = -0.213$, and $u_3 = -0.339$ kJ/mol for POE, at the T employed in the simulations. The less significant u_i for $i > 3$ were ignored in the present simulations.

The collapse of selected chains to become filler particles was handled in the manner introduced recently by Lin et al. [9]. The maximum attraction of the discretized LJ potential, which appears in the third shell, is separated into two terms, denoted $u_{3,\text{inter}}$ and $u_{3,\text{intra}}$ in Fig. 1. Within a given collapsed chain, long-range intramolecular interactions not treated explicitly with the RIS model use $u_{3,\text{intra}}$, which is obtained from $u_{3,\text{inter}}$ in the manner shown in Eq. (2).

$$u_{3,\text{intra}} = \lambda u_{3,\text{inter}} \tag{2}$$

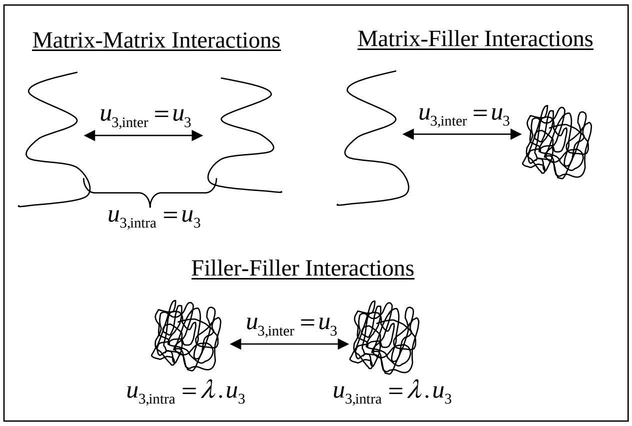

Fig. 1. Depiction of the distinction between $u_{3,\text{inter}} = u_3$ and $u_{3,\text{intra}}$.

All of the intermolecular interactions continue to use the unaltered $u_{3,\mathrm{inter}}=u_3$. The assignment $\lambda>1$ enhances the short-range attraction between two beads in the collapsed chain. If λ is large enough, $\langle s^2\rangle_{\mathrm{filler}}$ approaches $(3/5)(3M/4\pi\rho N_{\mathrm{A}})^{2/3}$, which is the value expected for a uniform sphere with the specified mass (M/N_{A}) and density. The extent of the collapse at a specified value of λ is characterized using the term defined in Eq. (3).

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

In the one-component melt, before any collapse has occurred, $c=0$ because $\langle s^2\rangle_0$ and $\langle s^2\rangle_{\mathrm{filler}}$ are indistinguishable. Complete collapse to a spherical, impenetrable particle of the desired density yields $c=1$. A consequence of the definition in Eq. (3) is that a spherical particle with $c=1$ has precisely the same density as the matrix. Collapse of a matrix chain to such a particle in the melt does not affect the space available to the uncollapsed matrix chains. It rearranges the available space, but does not change the total amount.

The reduction in dimensions must be accompanied by a change in the anisotropy of the instantaneous conformations. For long unperturbed chains, the average principal moments of the radius of gyration tensor are in the ratio $\langle L_2^2\rangle/\langle L_1^2\rangle=0.23$ and $\langle L_3^2\rangle/\langle L_1^2\rangle=0.08$ [36]. Complete collapse to a dense sphere not only decreases the value of $\langle s^2\rangle_{\mathrm{filler}}$; it also causes the asymmetry to approach $\langle L_2^2\rangle/\langle L_1^2\rangle=\langle L_3^2\rangle/\langle L_1^2\rangle=1$, as sketched in Fig. 2. In the simulation, the value of λ is not allowed to become so large that it produces unphysical values of c that are significantly larger than 1. However, values of c between 0 and 1 are of interest, because this range includes incompletely collapsed, permeable particles with asymmetries intermediate between those of the unperturbed chain and a sphere [9].

The filler content, x_{filler}, is the fraction of the beads that are in collapsed chains.

Single bead moves [29] and pivot moves for 2–6 beads [37], along with the Metropolis rules [38], were employed for equilibration of the systems. Equilibration is judged by the absence of any systematic trend for $\langle s^2\rangle_{\mathrm{filler}}$ and $\langle s^2\rangle_{\mathrm{matrix}}$, mean square displacement of the centers of mass over a distance that exceeds $\langle s^2\rangle_{\mathrm{filler}}$ and $\langle s^2\rangle_{\mathrm{matrix}}$ and decay of the orientation autocorrelation function for the end-to-end vectors, $\langle\mathbf{r}\cdot\mathbf{r}\rangle$, to values close to 0. On average, each bead is tried once for a single bead move, and once for a pivot move, during a single MC step (MCS).

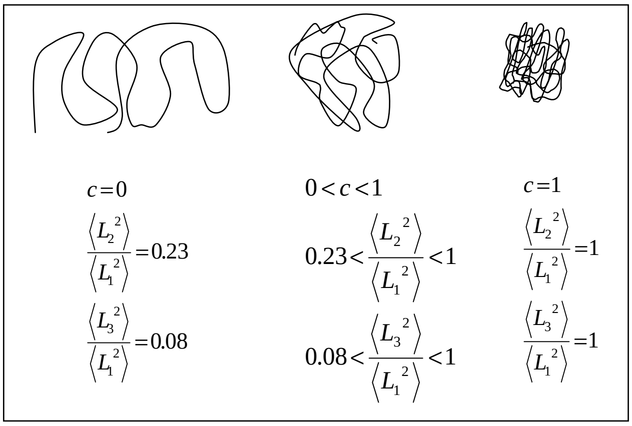

Fig. 2. Sketch of the change in mean square dimensions and asymmetry when c changes from 0 to 1.

The collapsed particles studied in the simulation are somewhat similar to the highly crosslinked polystyrene particles in a polystyrene matrix [7,8]. However, there is one important difference. The collapse of the polystyrene particles is enforced by covalent crosslinks, which occupy permanent positions in the particles. The collapse of the particles in the simulations is enforced by noncovalent interactions, which are transitory in nature. Therefore, the particles in the simulations [10] have access to internal degrees of freedom that are not accessible to the crosslinked polystyrene particles studied in the experiments [7,8].

3. Results and discussion

3.1. Response of the matrix chains to the completeness of the collapse of the filler particles

The single point at $c=0$ in Fig. 3 depicts $\langle s^2\rangle_0$ for the chains in a dense POE melt. Each of the 43 parent chains is represented by 52 coarse-grained beads, and $\lambda=1$ is used for all of these chains. At values of c larger than 0, a single parent chain ($x_{\mathrm{filler}}=0.023$) is subjected to a value of λ that is larger than 1, producing a smaller value for its $\langle s^2\rangle$ that is now denoted $\langle s^2\rangle_{\mathrm{filler}}$. The value of $\langle s^2\rangle_{\mathrm{filler}}$ for this ‘filler particle’ after equilibration with the new value of λ determines the value of c via Eq. (3). The remaining parent chains, which continue to use $\lambda=1$, experience an increase in their mean square dimensions to a new value denoted by $\langle s^2\rangle_{\mathrm{matrix}}$. There is no physically sensible value of c, $0<c<1$, where $\langle s^2\rangle_{\mathrm{matrix}}<\langle s^2\rangle_0$. The data suggest a lengthy plateau for $\langle s^2\rangle_{\mathrm{matrix}}$ at intermediate c, and an increase in $\langle s^2\rangle_{\mathrm{matrix}}$ as $c\to1$. The largest $\langle s^2\rangle_{\mathrm{matrix}}$ is seen when the particles are completely collapsed, with c near 1.

The suggestion of a lengthy plateau for $\langle s^2\rangle_{\mathrm{matrix}}$ at intermediate values of c in Fig. 3 raises the interesting possibility that, for suitable perturbation in the construction of

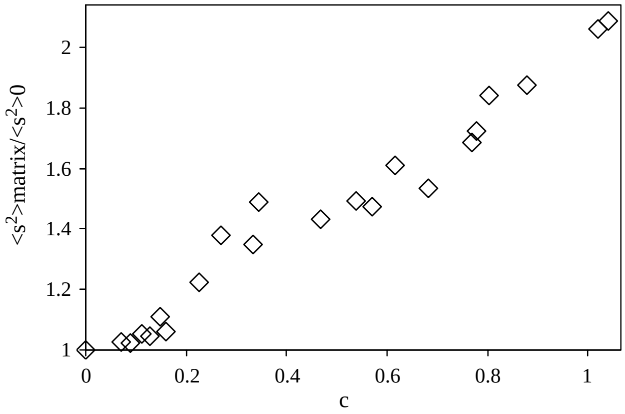

Fig. 3. Change in $\langle s^2\rangle_{\mathrm{matrix}}$ when the filler particle, at $x_{\mathrm{filler}}=0.20$, is collapsed to varying degree in the physically sensible range. Filler particle and matrix chains are each represented by 52 coarse-grained beads of POE.

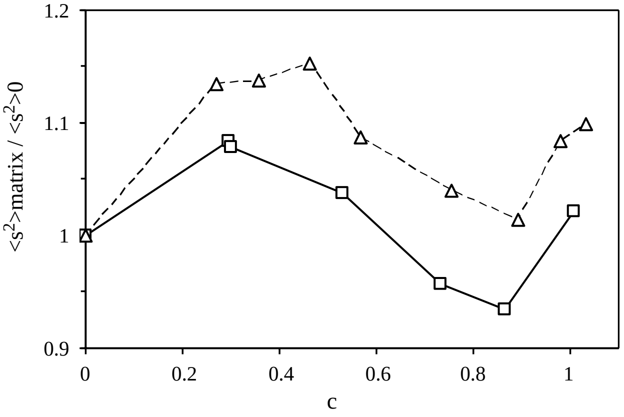

Fig. 4. Change in $\langle s^2\rangle_{\mathrm{matrix}}$ when the filler particles are collapsed to varying degree in the physically sensible range, using $x_{\mathrm{filler}}=0.32$ (open squares) or 0.6 (open triangles). Filler particles and matrix chains, respectively, are represented by 14 and 58 coarse-grained beads of PE.

the system, $\langle s^2\rangle_{\mathrm{matrix}}$ might pass through local maxima and minima as c increases. That possibility is realized in Fig. 4 for two systems constructed from coarse-grained PE. In this figure, the filler particles are smaller than the matrix chains, with the numbers of coarse-grained beads being 14 and 58, respectively. Furthermore, the concentration of the filler particles, either $x_{\mathrm{filler}}=0.32$ or 0.6, is as much as an order of magnitude larger in Fig. 4 than it was in Fig. 3. These larger value of x_{filler} required representation of the filler particles with multiple parent chains. These parent chains are mobile, producing various random arrangements during the simulation. The differences in the depths of the local minima in the two data sets depicted in Fig. 4 become significant when they are compared with the dimensions of the unperturbed chains, at $c=0$. When $x_{\mathrm{filler}}=0.6$, $\langle s^2\rangle_{\mathrm{matrix}}$ is always larger than $\langle s^2\rangle_0$, but when x_{filler} is 0.32, there is a small range of c at which $\langle s^2\rangle_{\mathrm{matrix}}$ is smaller than $\langle s^2\rangle_0$.

3.2. Mobile vs. immobile filler particles

In the MC simulation of the one-component melt, the same attempt frequency is used for moving all of the beads in all of the chains. This condition is not changed when some of the chains are subjected to $\lambda>1$. Obviously, individual chains could not collapse if one no longer attempted to move their beads after changing the numerical value of λ. The same attempt rate is maintained throughout the simulation, even after completion of the collapse, which causes the particles to be mobile [9]. This condition seems physically sensible, especially for cases where the particles are smaller than the matrix chains. Most of the prior simulations of filled systems have used stationary arrays of filler particles. Therefore, it becomes important to inquire whether $\langle s^2\rangle_{\mathrm{matrix}}$ is affected by the mobility of the nanoparticles.

The mobility of the nanoscopic filler particles can be important, as shown in Fig. 5. The system uses a high concentration ($x_{\mathrm{filler}}=0.6$) of partially collapsed ($c=0.53$) nanoscopic filler particles of 14 PE beads, randomly dispersed in a matrix of PE chains represented by 58 beads. This composition is near the local maximum in $\langle s^2\rangle_{\mathrm{m}}$ in Fig. 4. The numbering of the Monte Carlo steps (MCS) in Fig. 5 begins after the system has reached a steady state.

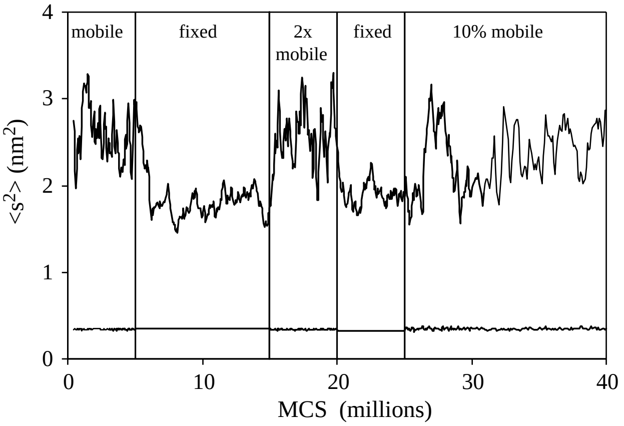

Fig. 5. Behavior of $\langle s^2\rangle_{\mathrm{matrix}}$ and $\langle s^2\rangle_{\mathrm{filler}}$ when the mobility of the small partially collapsed PE particles (14 beads, $c=0.53$, $x_{\mathrm{filler}}=0.6$) is turned off and on. The lower trace, at about 0.35 nm^2, is $\langle s^2\rangle_{\mathrm{filler}}$. The upper trace is $\langle s^2\rangle_{\mathrm{matrix}}$ for the uncollapsed matrix chains, each represented by 58 beads. Mobility of the beads in the particles is suspended at 5 and 20 million MCS. The suspension is lifted at 15 and 25 million MCS. Between 15 and 20 million MCS, the attempt frequency for moves of the beads in particles is twice as large as it was before 5 million MCS. After 25 million MCS, the attempt frequency for beads in particles in only 10% of what it was at 0–5 million MCS.

The $\langle s^2\rangle_{\mathrm{filler}}$ for the filler particles fluctuate within a narrow range near 0.35 nm^2. These fluctuations are barely visible on the scale used in Fig. 5. At 5 million MCS, the attempt to move beads in the filler particles is suspended, and remains suspended until 15 million MCS. The trace for $\langle s^2\rangle_{\mathrm{filler}}$ is a precise flat line during this time interval in Fig. 5. From 15 to 20 million MCS, the suspension is lifted, and the attempt rate for beads in filler particles is twice as large as it was initially. The small fluctuations in $\langle s^2\rangle_{\mathrm{filler}}$ are reestablished. They are about the same size as they were at 0–5 million MCS, and $\langle s^2\rangle_{\mathrm{filler}}$ is not affected, with c remaining close to 0.53. Then the attempt rate for filler particles is again suspended from 20 to 25 million MCS. The suspension is again lifted at 25 million MCS, but now the attempt rate for the beads in the particles is only 10% as large as it was initially.

The matrix chains show a reproducible relaxation in $\langle s^2\rangle_{\mathrm{matrix}}$ in response to the changes in the mobility of the filler particles. During the first 5 million MCS, $\langle s^2\rangle_{\mathrm{matrix}}$ is about 2.5 nm^2, which implies a slight expansion of the matrix chains in response to the filler. But when the filler particles are frozen, $\langle s^2\rangle$ for the matrix chains relaxes to a smaller value of about 1.8–1.9 nm^2, which implies a small contraction of the matrix chains in response to the filler. In this system, the qualitative response of the matrix chains (expansion or contraction) depends on whether or not the particles retain the same potential mobility that they had in the one-component melt, before collapse.

The physical origin of this effect is demonstrated in Fig. 6. The curve with negative slope is the orientation autocorrelation function for the end-to-end vector in the matrix chains. This correlation function implies a relaxation time, τ, on the order of

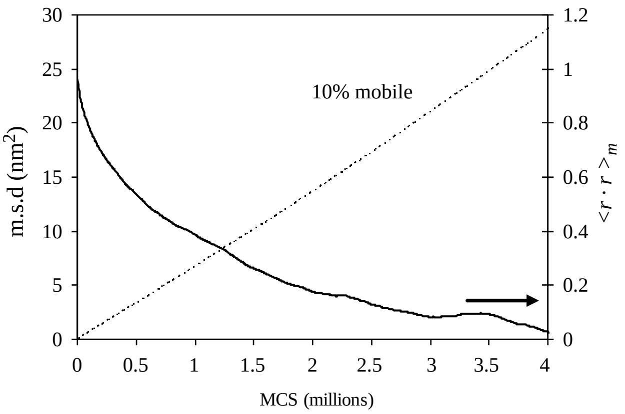

Fig. 6. Orientation autocorrelation function for the end-to-end vector of the matrix chains (PE, 58 beads) and mean square displacement of the center of mass of the collapsed chains (PE, 14 beads) when $c=0.53$, $x_{\text{filler}}=0.6$, and the attempt rate for moving a bead in the particle is only 10% as large as the attempt rate for moving a bead in the matrix chain.

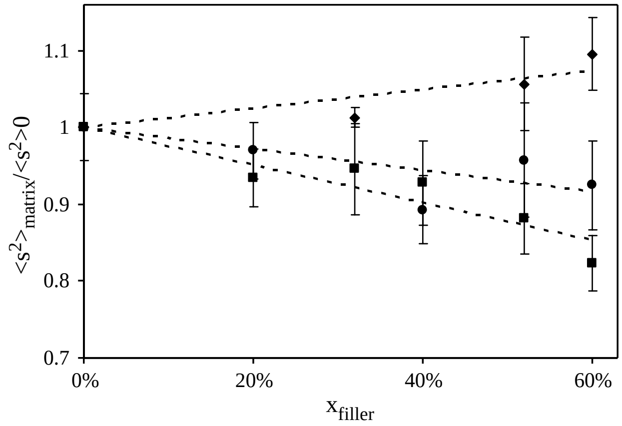

Fig. 7. Change in $\langle s^2\rangle$ for matrix chains represented by 58 coarse-grained PE beads upon the introduction of completely collapsed ($c=0.98$–1.03) PE filler particles composed of 14 (upper data set), 58 (middle data set), or 174 beads (bottom data set).

10^6 MCS. The line with a positive slope is the mean square displacement of the center of mass of the nanoparticles, evaluated under the condition where the attempt rate for a move of a nanoparticle is only 10% as large as the attempt rate for moving a bead in a matrix chain. In the time specified by τ, the mean square displacement of a nanoparticle is over an order of magnitude larger than $\langle s^2\rangle_{\text{filler}}$. Under these conditions, the comparatively slow relaxation of the matrix chains does not allow them to adjust completely to the positions of the mobile nanoparticles. The disturbance of the matrix by the mobile particles produces $\langle s^2\rangle_{\text{matrix}} > \langle s^2\rangle_0$. In contrast, if the matrix can adjust completely to the coordinates of the nanoparticles, which happens if the mobility of the nanoparticles is suppressed, the inequality changes to $\langle s^2\rangle_{\text{matrix}} < \langle s^2\rangle_0$. Only when the longest relaxation time for the matrix chains is much shorter than the diffusion time for the particles it will be appropriate to model the particles as being in a static array. Very small particles may not fit this limiting condition. Perhaps a part of the special effects attributed to filled system containing very small nanoparticles might arise from the fact that their mobility affects the steady state dimensions of the matrix chains. That effect is an expansion in the dimensions of the matrix chains, as seen in Fig. 5.

All of the remaining simulations reported here use mobile particles, in which all beads are subject to exactly the same attempt rate that was employed in the one-component melt, with $\lambda=1$ and $c=0$.

3.3. Expansion and contraction of the matrix chains

Fig. 7 shows the response of $\langle s^2\rangle_{\text{matrix}}$ for the matrix chains represented by 58 beads of coarse-grained PE when the filler particles, also PE, are completely collapsed, with c in the range 0.98–1.03. As filler content increases, $\langle s^2\rangle_{\text{matrix}}$ increases when the filler particles are very small (14 beads, or about 1/4 as large as the number of beads in a matrix chain). However, a decrease in $\langle s^2\rangle_{\text{matrix}}$ is seen if the filler particles contain the same number (58) of beads, or three times as many beads (174), as a matrix chain.

Fig. 8 presents a pictorial summary of the manner in which the qualitative change in $\langle s^2\rangle_{\text{matrix}}$ produced by filler particles is affected by the relationship between the masses of the two species. All of the data is from strongly collapsed filler particles, with c lying in the range 0.77–1.00. The main diagonal in the figure (from lower left to upper right) addresses cases where the matrix chains and filler particles have the same degree of polymerization. If this degree of polymerization is small, $\langle s^2\rangle_{\text{matrix}} > \langle s^2\rangle_0$, but the inequality switches to $\langle s^2\rangle_{\text{matrix}} < \langle s^2\rangle_0$ as the degree of polymerization increases. The trend produced by the introduction of inequalities in the degrees of polymerization of the two species is revealed by inspection of the diagonal running from upper left to lower right. Causing the matrix to have a degree of polymerization larger than the

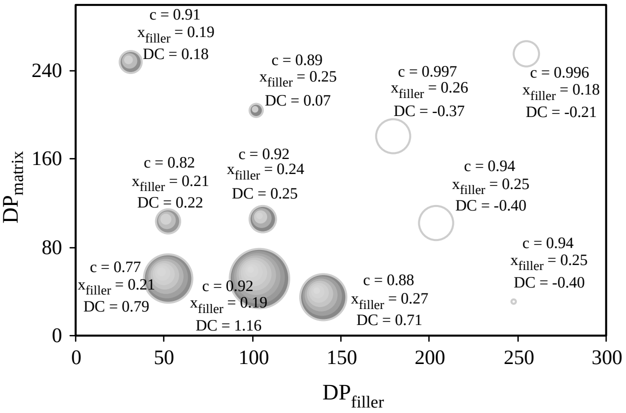

Fig. 8. Depiction of the effects of the degrees of polymerization (DP) of the matrix chains and filler particles on the relationship between $\langle s^2\rangle_{\text{matrix}}$ and $\langle s^2\rangle_0$ for PEO. The points are plotted with shaded circles if $\langle s^2\rangle_{\text{matrix}} > \langle s^2\rangle_0$ and with open circles if $\langle s^2\rangle_{\text{matrix}} < \langle s^2\rangle_0$. The value of DC associated with each point is $\langle s^2\rangle_{\text{matrix}}/\langle s^2\rangle_0 - 1$. Larger symbols denote points for which the values of DC lie farther from 0. The values of x_{filler} are in the range 0.22 ± 0.05, and the values of c are in the range 0.88 ± 0.12.

degree of polymerization of the filler particles favors $\langle s^2\rangle_{\text{matrix}} > \langle s^2\rangle_0$, consistent with the behavior of PDMS chain with polysilicate particles [12,13]. Placement of large filler particles in small matrix chains favors $\langle s^2\rangle_{\text{matrix}} < \langle s^2\rangle_0$.

4. Conclusions

The response of the dimensions of matrix chains to filler particles depends on a nonmonotonic fashion of the degree of collapse of the particles. It also depends on the mobility of the particles, where rapid diffusion of the filler particles tends to increase the dimensions of the matrix chains. The response of the matrix chains to the filler particles depends on the relationship between their masses. When these masses are identical, and the filler concentration is in the range $x_{\text{filler}} = 0.22 \pm 0.05$, matrix chains are expanded if the masses are small, but increase in the masses leads to systems in which the matrix chains contract. Inequalities in the masses lead to expansion of the matrix chains for large chains and small particles, and contraction of matrix chains for short chains and large particles. For nanoparticles immersed in long matrix chains, the simulations find expansion of the matrix chains, and this expansion of the matrix chains is enhanced if the nanoparticles are mobile.

All of the results obtained here have been obtained with filler particles and matrix chains that are small enough so that the particular character of the materials is important. This fact is incorporated in the simulations, because, as demonstrated elsewhere [29], the applied method permits accurate recovery of atomistically detailed models in continuous space. Our nanoparticles do not assume idealized shapes such as perfect spheres with a smooth surface. Even when $c = 1$, the particles retain a rough surface and have a detectable asphericity in their shapes. Except when specifically stated to the contrary, our particles are able to diffuse in a natural manner, to the extent expected for their size and the viscosity of the matrix. This diffusive motion of the particles affects the dimensions of the matrix chains. Most other coarse-grained simulations neglect the influence of the mobility of the filler particles on the dimensions of the matrix chains. For all of these reasons, our results may be somewhat different from those anticipated by simulations with much more idealized systems. We believe that our approach is closer to reality than results obtained with more highly idealized systems, especially when one is concerned with nano-composites in which the filler particles are very small.

Acknowledgements

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