

Theoretical Interpretation of Conformation Variations of Polydimethylsiloxane Induced by Nanoparticles

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Electronic Supplementary Information

Abstract There has been controversy as to whether the addition of nanoparticles to a polymer melt causes perturbed chain structure of polymers. In this work, the chain conformations of polydimethylsiloxane (PDMS) with addition of polyhedral oligomeric silsesquioxane (POSS) nanoparticles have been studied using a classical density functional approach. Under the strong interactions of POSS-PDMS, the radius of gyration of PDMS in the nanocomposites can either increase or decline depending on particle loading. After adding nanoparticles with larger size or weaker interactions, both the increasing and the declining amplitudes can be largely suppressed. The results provide a deep understanding of chain conformation in polymer nanocomposites.

Keywords Chain conformation; Radius of gyration; Polymer nanocomposites; Density functional theory

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INTRODUCTION

Polymer nanocomposites (PNCs) are known to have enhanced properties relative to neat polymers^[1–4]. Additionally, mechanical reinforcement in a polymer nanocomposite is related to chain conformations^[5]. Perhaps one of the most fundamental questions in this area is how the polymer radius of gyration, R_g , is affected by nanoparticles. The chain conformations in PNCs have been primarily measured by small angle neutron scattering (SANS) and small angle X-ray scattering (SAXS)^[6]. The answers to this question are controversial since there have been reports of expansion^[7–11], contraction^[12], or no change^[13–18] of polymer conformation. Nevertheless, it is known that the dimension of polymer chain depends on the particle size, concentration, dispersion of nanoparticles, as well as the particle-polymer interactions.

Beyond experimental studies, many efforts have been made to investigate the structure and conformation of polymer nanocomposites *via* theoretical models^[19–23] and molecular simulations^[24–31]. For instance, the polymer reference interaction site model^[22] suggested an expansion of chain dimensions under the condition of $r/R_g < 1$ and attractive interaction of particle-polymer. These results were discussed in conjunction with experiments^[9]. The expansion

is due to the effect of the excluded volume created by particles, where the particles act as good solvent to swell the polymers. Most of the simulation works show that addition of particles to a polymer melt could cause polymer chains to either expand or remain unaltered their dimensions. An excellent summary of these results can be found in a recent review^[32]. However, recent experimental measurements^[12] of polymer contraction appear to provide different results.

There is considerable interest in developing a theory capable of predicting the microscopic conformation of PNCs with various particle concentrations and sizes to decipher the expansion or contraction properties. Due to the interactions of particle-polymer, the interstices between adjacent polymer chains are filled with particles, which implies that the actual packing fraction is not equal to the summation of individual packing fractions. Therefore, the actual packing fraction should be corrected with special consideration of the asymmetric interactions. Packing fraction is indeed a fundamental thermodynamic property reflecting the entire spectrum of inter- and intramolecular interactions in PNCs. However, few theoretical investigations acknowledged such important issue^[33, 34]. As a consequence, the discrepancy between theory and experiment is inevitable, especially at highly asymmetric interactions.

In this work, we try to investigate the polymer chain conformation in a classical model system, polydimethylsiloxane (PDMS)/polyhedral oligomeric silsesquioxane (POSS) nanocomposites, which is representative of a large class of nanocomposites especially in term of filler dispersion

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and widely used for reinforcement. We design the system in which the presence of Si—O linkages in both PDMS and POSS is expected to provide the PNC with good compatibility. We apply a classical density functional theory (DFT) to deal with actual conformations of PDMS/POSS nanocomposites. DFT was originally proposed for description of inhomogeneous fluids by means of minimization of the grand free-energy function^[35, 36], which yields self-consistent structure and thermodynamic properties. The existing density functional methods for polymeric systems differ in whether the intramolecular interactions are accounted for in the ideal functional contribution, the excess contribution, or a combination of both. Further, a polymeric DFT can be formulated in terms of molecular density or segment density^[37–40], showing the advantages of theoretical self-consistency among inter- and intramolecular distribution functions^[41–43]. The radii of gyration of neat PDMS with different molecular weights are calculated and compared with the corresponding experimental data. Such comparison allows us to evaluate the reliability of the theory for polymer nanocomposites with delicate microstructures. Accordingly, the theoretical approach is then extended to evaluate the radii of gyration of PDMS in different environments, where the actual packing fraction of PDMS is corrected to improve the accuracy of theoretical predictions. The effects of POSS size, concentration, and POSS-PDMS interactions on the structures and swelling properties of PDMS/POSS nanocomposites are explored to illustrate their different contributions to the conformation of PDMS.

MODEL AND APPROACH

Herein we apply a coarse-grained model to describe PDMS chains. Each polymer chain can be represented by a series of bonded Kuhn segments. The diameter of the coarse-grained bead representing a polymeric segment, σ_p , is chosen such that $(\pi/6)\sigma_p^3$ equals the volume per Kuhn segment in the bulk polymer, as calculated from the mass corresponding to a Kuhn segment and the experimental mass density (approximately $\sigma_p = 0.72$ nm). The POSS particles are distributed at randomly selected positions with diameter σ_n . The coarse-grained potential between any two spheres of species can be derived from the Hamaker theory with suitable Hamaker constants^[27]. A major advantage of this approach is that the existence of accurate atomistic potentials describing interactions between the sites constituting the two coarse-grained entities is exploited. The integrated potentials are computationally effective^[44]. The calculation details have been listed in Ref. [27], which are restated in the electronic supplementary information (ESI) of the present paper. The Hamaker constant governing the interaction between two coarse-grained bodies can be calculated as $A = 4\pi^2\epsilon_{LJ}(\rho_{LJ}\sigma_{LJ}^2)^2$, where ϵ_{LJ} and σ_{LJ} are the atomistic Lennard-Jones interaction parameters, and ρ_{LJ} is the density of atomistic interaction sites in the macroscopic body. The Lennard-Jones parameters for Si, O, and CH₃ sites of PDMS and POSS are used^[45, 46], which have been summarized in Table 1. Electrostatic interactions are not taken into account either for POSS or for PDMS.

Using the extended test-particle method^[41–43], we allow one segment from an arbitrarily selected chain to be fixed at the origin. The system considered is equivalent to a mixture of three polymeric components (*F*, *C* and *D*) and particles in a symmetric external field due to the fixed segment, as depicted in Fig. 1.

Table 1 Force field parameters for PDMS and POSS

Site	σ_{LJ} (nm)	ϵ_{LJ} (kJ/mol)
Si	0.429	0.5481
O	0.330	0.3347
CH ₃	0.373	0.8134

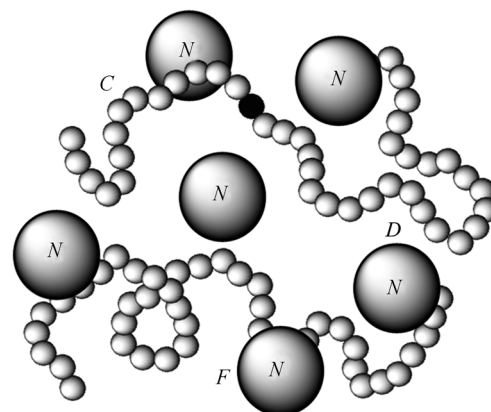


Fig. 1 Schematic of the polymer and nanoparticle model used in this work

Here a middle segment from a polymer chain (filled black sphere) is fixed at the origin. The nanoparticles are distributed at randomly selected positions. The density distributions of segments from the tethered fragments (*C* and *D*) and the free chains (*F*) are related to the intra- and intermolecular segment-segment correlation functions.

The free chains are represented by *F* composed of m_F segments, while the tethered fragments are represented by *C* and *D* composed of m_C and m_D segments, respectively. The equations for m_C and m_D are as follow: $m_F = m_C + m_D + 1$. At equilibrium, the density distributions of free chains, the tethered fragments and particle should satisfy the variational relations

$$\frac{\delta\Omega}{\delta\rho_i^{(F)}(\mathbf{r})} = \frac{\delta\Omega}{\delta\rho_i^{(C)}(\mathbf{r})} = \frac{\delta\Omega}{\delta\rho_i^{(D)}(\mathbf{r})} = \frac{\delta\Omega}{\delta\rho_n(\mathbf{r})} = 0 \quad (1)$$

where Ω stands for the grand free-energy, $\rho_i^{(l)}(\mathbf{r})$ ($l = F, C, D$) is the density profile of i^{th} segment on chain l at position $\mathbf{r}$, $\rho_n(\mathbf{r})$ is the density profile of particle at position $\mathbf{r}$.

The grand potential is related to the Helmholtz free-energy $A[\rho(\mathbf{r})]$ for polymer/particle blend

$$\begin{aligned} \Omega[\rho_\alpha(\mathbf{r})] = & k_B T \sum_\alpha \int d\mathbf{r} \rho_\alpha(\mathbf{r}) [\ln[\rho_\alpha(\mathbf{r})] - 1] \\ & + A^{\text{hs}}[\rho_\alpha(\mathbf{r})] + A^{\text{att}}[\rho_\alpha(\mathbf{r})] + A^{\text{chain}}[\rho_\alpha(\mathbf{r})] \\ & - \sum_\alpha \int d\mathbf{r} (\mu_\alpha - V_\alpha(\mathbf{r})) \rho_\alpha(\mathbf{r}) \end{aligned} \quad (2)$$

where k_B is the Boltzmann constant and T is the temperature. α denotes a nanoparticle or a segment in polymer chain. The terms on the right hand side represent the ideal gas free energy contribution, $A^{\text{hs}}[\rho_\alpha(\mathbf{r})]$ due to volume exclusion/short range hard sphere repulsion^[47], $A^{\text{att}}[\rho_\alpha(\mathbf{r})]$ due to long-range attraction^[48], and $A^{\text{chain}}[\rho_\alpha(\mathbf{r})]$ due to chain connectivity^[49]. The details of these contributions are included in ESI. The final term is the Legendre transformation in which μ_α is the bulk chemical potential of species α , and the external field $V_\alpha(\mathbf{r})$ is the pair potential between species α and the fixed segment, which is derived from the Hamaker theory. The functional derivatives of the free-energies, $\partial\Omega/\partial\rho_\alpha(\mathbf{r}) = 0$, are employed to obtain the equilibrium density profiles. As a result, the Euler-Lagrange equations can be written as

$$\ln \rho_\alpha(\mathbf{r}) + \frac{\delta\beta A^{\text{hs}}}{\delta\rho_\alpha(\mathbf{r})} + \frac{\delta\beta A^{\text{att}}}{\delta\rho_\alpha(\mathbf{r})} + \frac{\delta\beta A^{\text{chain}}}{\delta\rho_\alpha(\mathbf{r})} = \beta(\mu_\alpha - V_\alpha(\mathbf{r})) \quad (3)$$

This equation can be written to give the density profile

$$\rho_\alpha(\mathbf{r}) = \exp(\beta\mu_l) \exp[D_\alpha(\mathbf{r}) - \beta V_\alpha(\mathbf{r})] I_{1,\alpha}(\mathbf{r}) I_{2,\alpha}(\mathbf{r}) \quad (4)$$

with

$$D_\alpha(\mathbf{r}) = \frac{1}{2} \sum_l \sum_{\gamma=1}^{m_l} \sum_{\gamma'}^{\{\gamma\}} \int \rho_\gamma(\mathbf{r}') \frac{\delta \ln y^{\gamma\gamma'}(\mathbf{r}')}{\delta\rho_\alpha(\mathbf{r})} d\mathbf{r}' - \frac{\delta\beta A^{\text{hs}}}{\delta\rho_\alpha(\mathbf{r})} - \frac{\delta\beta A^{\text{att}}}{\delta\rho_\alpha(\mathbf{r})} \quad (5)$$

where $\mu_l = \sum_{\alpha=1}^{m_l} \mu_\alpha$ is the bulk chemical potential of the chain

l ($l = F, C, D$). The multiple integrals $I_{1,\alpha}(\mathbf{r})$ and $I_{2,\alpha}(\mathbf{r})$ for the free chains ($l = F$) are solved in a recursive fashion and are given by

$$\begin{cases} I_{1,1}(\mathbf{r}) = 1 \\ I_{1,\alpha}(\mathbf{r}) = \int I_{1,\alpha-1}(\mathbf{r}') \exp[D_{\alpha-1}(\mathbf{r}') - \beta V_{\alpha-1}(\mathbf{r}') \Delta_{\alpha-1,\alpha}(\mathbf{r}', \mathbf{r}) \left(\frac{\mathbf{r}' \Theta(\sigma - |\mathbf{r}' - \mathbf{r}|)}{r} \right)] d\mathbf{r}' \end{cases} \quad (6)$$

$$\begin{cases} I_{2,\alpha}(\mathbf{r}) = \int I_{2,\alpha+1}(\mathbf{r}') \exp[D_{\alpha+1}(\mathbf{r}') - \beta V_{\alpha+1}(\mathbf{r}') \Delta_{\alpha,\alpha+1}(\mathbf{r}, \mathbf{r}') \left(\frac{\mathbf{r}' \Theta(\sigma - |\mathbf{r}' - \mathbf{r}|)}{r} \right)] d\mathbf{r}' \\ I_{2,m_F}(\mathbf{r}) = 1 \end{cases} \quad (7)$$

with $\Delta_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') = KF_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') y_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}')$. Here α' denotes the neighboring segment that will bond to segment α , K is a geometric constant that accounts for the volume available for bonding between segments, and $F_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}')$ represents the association Mayer f -function. $y_{\alpha\alpha'}$ is the cavity correlation function between the two segments in the reference fluid. The function $\Theta(r)$ is the Heaviside step function. When applied to the tethered fragments ($l = C, D$), $I_{1,\alpha}(\mathbf{r})$ and $I_{2,\alpha}(\mathbf{r})$ can be expressed as

$$\begin{cases} I_{1,1}(\sigma) = 1 \\ I_{1,2}(\mathbf{r}) = \exp[D_1(\sigma) - \beta V_1(\sigma)] \Delta_{1,2}(\sigma, \mathbf{r}) \left(\frac{\sigma \Theta(\sigma - |\sigma - \mathbf{r}|)}{r} \right) \\ I_{1,\alpha}(\mathbf{r}) = \int I_{1,\alpha-1}(\mathbf{r}') \exp[D_{\alpha-1}(\mathbf{r}') - \beta V_{\alpha-1}(\mathbf{r}') \Delta_{\alpha-1,\alpha}(\mathbf{r}', \mathbf{r}) \left(\frac{\mathbf{r}' \Theta(\sigma - |\mathbf{r}' - \mathbf{r}|)}{r} \right)] d\mathbf{r}' \end{cases} \quad (8)$$

$$\begin{cases} I_{2,1}(\sigma) = \int I_{2,2}(\mathbf{r}') \exp[D_2(\mathbf{r}') - \beta V_2(\mathbf{r}') \Delta_{1,2}(\sigma, \mathbf{r}') \left(\frac{\mathbf{r}' \Theta(\sigma - |\mathbf{r}' - \sigma|)}{\sigma} \right)] d\mathbf{r}' \\ I_{2,\alpha}(\mathbf{r}) = \int I_{2,\alpha+1}(\mathbf{r}') \exp[D_{\alpha+1}(\mathbf{r}') - \beta V_{\alpha+1}(\mathbf{r}') \Delta_{\alpha,\alpha+1}(\mathbf{r}, \mathbf{r}') \left(\frac{\mathbf{r}' \Theta(\sigma - |\mathbf{r}' - \mathbf{r}|)}{r} \right)] d\mathbf{r}' \\ I_{2,m_l}(\mathbf{r}) = 1 \end{cases} \quad (9)$$

The chemical potentials of the free chains ($l = F$) are obtained directly from Wertheim's first-order thermodynamic perturbation theory equation of state^[50]. The chemical potentials of the tethered fragments C and D can be determined using the normalization conditions $\int 4\pi r^2 \rho_\alpha(\mathbf{r}) d\mathbf{r} = 1$ ($\alpha = 1, 2, 3, \dots, m_l$, $l = C, D$). For the first tethered segment (segment '1' of $l = C, D$), it can be written as

$$\int 4\pi r^2 \{ \exp(\beta\mu_l) \exp[D_1(\mathbf{r}) - \beta V_1(\mathbf{r})] I_{1,1}(\mathbf{r}) I_{2,1}(\mathbf{r}) \} d\mathbf{r} = 1 \quad (10)$$

which yields $\exp(\beta\mu_l) = 1/[\exp(D_1(\sigma)) I_{1,1}(\sigma) I_{2,1}(\sigma)]$. Using other segments yields equivalent results for μ_l . Combining μ_l with Eq. (4) thus gives

$$\rho_1^{(C)}(\mathbf{r}) = \rho_1^{(D)}(\mathbf{r}) = \frac{\delta(r - \sigma)}{4\pi\sigma^2} \quad (11)$$

which matches the known condition for the tethered segment. Solving for the other segments ($\alpha = 2, 3, \dots, m_l$, $l = C, D$) gives

$$\rho_\alpha(\mathbf{r}) = \frac{1}{\exp[D_1(\sigma)] I_{1,1}(\sigma) I_{2,1}(\sigma) \exp[D_\alpha(\mathbf{r}) - \beta V_\alpha(\mathbf{r})] I_{1,\alpha}(\mathbf{r}) I_{2,\alpha}(\mathbf{r})} \quad (12)$$

In the theoretical calculations, we fix the segments of a polymer chain one by one and the density distribution around the fixed segment is calculated using Eqs. (4)–(12). Because of symmetry, only $m_F/2$ (if m_F is even) or $(m_F + 1)/2$ (if m_F is odd) calculations are required for predicting the detailed local structures of polymer chains consisting of m_F identical segments. The density profile is solved using the Picard-type iterative method. At every iteration step, a new estimate of the density profile was calculated employing Eq. (4), and then mixed with the old one. The result is used as the new guess for the next iteration. This procedure is iterated until numerical self-consistency can be achieved in a sense that the difference of density profiles between the preceding step and the present

step is less than 1.0×10^{-3} . All the convolution results of the equations are directly evaluated in real space.

The segment distribution of the free chains (F) around the fixed segment is related to the intermolecular segment-segment distribution function $g_{ij}(r) = \rho_{i,j}^{(F)}(r) / \rho_b^{(F)}$, where $\rho_{i,j}^{(F)}(r)$ is the density profile of segment i on chain F around the fixed segment j , $\rho_b^{(F)}$ is the bulk density of segment i . On the other hand, the distribution of segments from the fragments C and D is related to the intramolecular segment-segment distribution function $\omega_{ij}(r) = \rho_{i,j}^{(C,D)}(r)$, where $\rho_{i,j}^{(C,D)}(r)$ is the density profile of segment i on the tethered chain (C or D) around the fixed segment j . There is only one tethered chain and therefore the normalization condition is $\int 4\pi r^2 \omega_{ij}(r) dr = 1$. From the different segment-

segment distribution functions, we can calculate the average intermolecular distribution function of polymer with

$$g_{pp}(r) = \frac{1}{m_F^2} \sum_{i=1}^{m_F} \sum_{j=1}^{m_F} g_{ij}(r), \text{ and the average intramolecular}$$

distribution function of polymer with $\omega_{pp}(r) =$

$$\frac{1}{m_F} \sum_{i=1}^{m_F} \sum_{j=1}^{m_F} \omega_{ij}(r).$$

As the essential criterion to evaluate microscopic conformation of polymer chain, form factor is particularly useful for studying the scaling behavior. Generally, the form factor is derived from light scattering experiments. However, in a theoretical model, it can be calculated directly from the Fourier transform of the average intramolecular distribution function^[51]

$$P(q) = \left\langle \frac{1}{m_F^2} \sum_{i=1}^{m_F} \sum_{j=1}^{m_F} \frac{\sin(qr_{ij})}{qr_{ij}} \right\rangle = \left\langle \frac{1}{m_F^2} \sum_{i=1}^{m_F} \sum_{j=1}^{m_F} \omega_{ij}(q) \right\rangle = \left\langle \frac{1}{m_F} \omega_{pp}(q) \right\rangle \quad (13)$$

where r_{ij} is the distance between segments i and j , q denotes the magnitude of the scattering wave vector.

Radius of gyration R_g is another important parameter for the overall chain configuration. In the theoretical model, it is a version of the average intramolecular distribution function^[52, 53]

$$R_g^2 = \frac{2\pi}{m_F} \int_0^\infty r^4 \omega_{pp}(r) dr \quad (14)$$

A standard way to examine the structure of a polymeric chain at all length scales is *via* the structure factor $S_{pp}(q)$, which is defined as^[52]

$$S_{pp}(q) = \omega_{pp}(q) + \rho_p h_{pp}(q) = \omega_{pp}(q) + \rho_p [g_{pp}(q) - 1] \quad (15)$$

RESULTS AND DISCUSSION

We first present the structure of neat PDMS in the absence of nanoparticles, which can be used as the reference. Figure 2(a) shows a Kratky plot of experimental^[54] and theoretical $q^2 P(q)$ versus q for PDMS with molecular weight of 2.13×10^4 g/mol. In order to mimic the polymer system, the coarse-grained chain length and packing fraction are 60

and 0.4, respectively. The experimental curves are evaluated in terms of $u^2 I(u)$. We transform the data to obtain $q^2 P(q)$ with $u = q \cdot R_g$ and divide by a constant factor of 2.6 which is equal to the ratio of the experimental value of $u^2 I(u)$ at high u for linear PDMS to the Gaussian asymptotic value of 2.0. The Kratky plots show a monotonically increasing function of the wave vector with a near plateau in the intermediate wave vector regime, clearly demonstrating that PDMS chains always remain Gaussian. Figure 2(b) shows the values of R_g as a function of molecular weight for PDMS, which are obtained from the theoretical calculations and experimental measurements^[55]. From the two subfigures, one sees a good agreement between the DFT calculations and experimental values for both the local chain structure and overall chain dimensions, suggesting that the current theory is suitable for describing PDMS conformation.

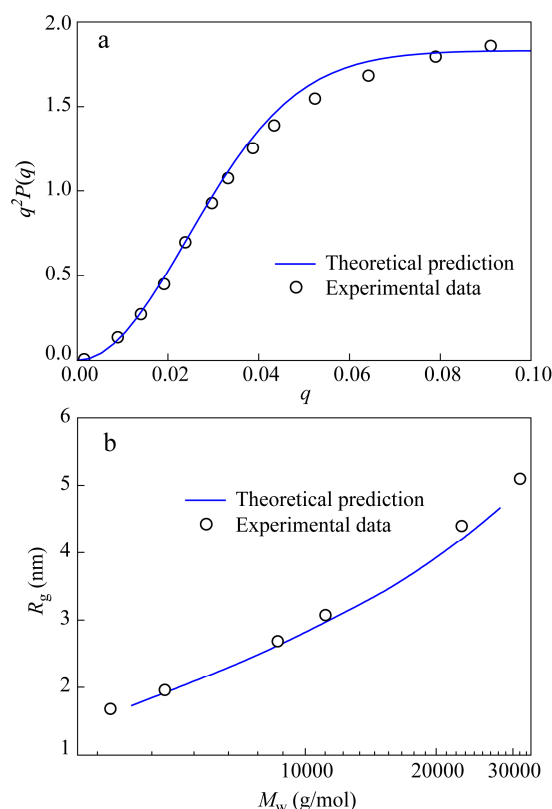


Fig. 2 Comparison of (a) form factors and (b) gyration radii of PDMS obtained from the theory and experiment

In the theoretical calculations, the actual packing fraction of polymer/particle blend should be determined with consideration of the asymmetric interactions of particle-polymer. In general, the ideal packing fraction can be given by $\eta_{id} = \phi \eta_n + (1 - \phi) \eta_p$, in which ϕ is particle concentration, η_n and η_p are the independent packing fractions of particles and polymer. On the other hand, the actual packing fraction in the system can be given by

$$\eta_t = (1/r_{c,n}) \cdot \int_0^{r_{c,n}} g_{nn}(r) \rho_n \sigma_n^3 dr + (1/r_{c,p}) \cdot \int_0^{r_{c,p}} g_{np}(r) \rho_p \sigma_p^3 dr \quad (16)$$

where the two terms on the right hand side represent respectively the actual packing fractions of particles and polymer chains, and can be calculated by integrating their

local density distributions. $g_{nn}(r)$ and $g_{np}(r)$ are obtained from an independent DFT calculation of particle and polymer distributions around particles for polymer/particle blend. The ideal densities of $\rho_n = 6\phi\eta_n/\pi\sigma_n^3$ and $\rho_p = 6(1-\phi)\eta_p/\pi\sigma_p^3$ are used as the initial inputs for calculation of $g_{nn}(r)$ and $g_{np}(r)$, respectively. The cutoff distance $r_{c,n} = 3.5\sigma_n$ and $r_{c,p} = 3.5\sigma_p$, $\sigma_{np} = (\sigma_p + \sigma_n)/2$ is the interaction diameter of two species.

As a test of the actual packing fraction concept and demonstration of its importance at asymmetric interactions of particle-polymer, we present theoretical calculations about the single chain dimensions of polystyrene (PS) containing nanometric crosslinked PS particles and compare these results with experimental measurements^[9]. For the considered systems, the independent packing fractions of pure PS chains and PS particles are 0.4 and 0.52. The particle diameter is 4 nm and the 65 KD d-PS chain has been chosen. The corresponding coarse-grained chain length for DFT calculation is 90. The coarse-grained parameters for PS are taken from our earlier work^[56]. In Fig. 3(a), one sees that both the ideal and actual packing fractions increase with the particle concentration. More importantly, the actual packing fraction deviates from the ideal packing fraction. As the particle concentration increases, the deviation first increases ($\phi \leq 0.3$), and then decreases. Figure 3(b) shows the values of R_g/R_{g0} for PS nanocomposites at different particle concentrations with actual and ideal packing fraction. One

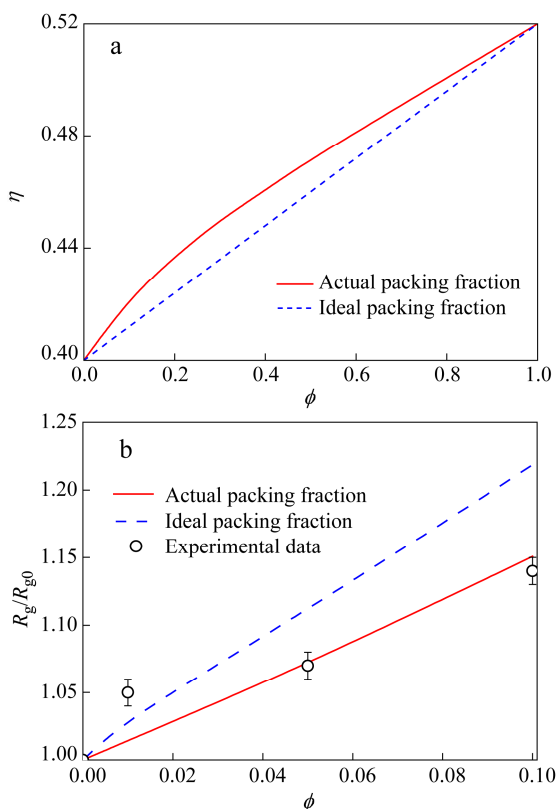


Fig. 3 (a) Actual and ideal packing fractions for PS nanocomposites as a function of particle concentration; (b) Normalized radii of gyration of PS with the addition of crosslinked PS particles at different particle concentrations (Solid lines and dash lines correspond to DFT calculations with actual and ideal packing fraction, respectively. Symbols show the experimental data^[9].)

sees that the theoretical predictions for ideal packing fraction tend to overestimate the expanding effect in the concentration region. The actual packing fraction model is more appropriate to describe the experimental data. The results provide motivation for use of the actual packing fraction model.

Recall that our primary aim is to analyze the influence of POSS nanoparticles on the conformations of PDMS chains. For PDMS with a molecular weight of 2.13×10^4 g/mol, the theoretical prediction of R_g is 4.22 nm, which is used as the reference below. The corresponding coarse-grained chain length for DFT calculation is 60. The actual packing fraction has been included in the process of the subsequent research. Figure 4 shows the values of R_g/R_{g0} for PDMS/POSS nanocomposites at different particle sizes and concentrations. As shown in Fig. 4, it is clearly apparent that the increase magnitude of R_g/R_{g0} is strongly correlated to the concentration and/or particle size. In particular, R_g/R_{g0} shows a maximum at $\sigma_n = 2$ nm with $\phi = 0.15$. In the case of low particle concentration, particles behave as a solvent swelling PDMS chains; the increase of R_g with ϕ can be explained by the dilution effect. As the particle concentration increases, the nanoscopic inclusions could certainly aggregate and interconnect, such that the effective free volume accessible to chain trajectories between the particles decreases drastically and more compact configurations have been formed. Thus we conclude that the particle concentration plays an important role in controlling chain dimension. On the other hand, there is a region where R_g decreases with increasing particle diameter. When the particles have small size, there is considerable free volume available among particles for the chain trajectory. In contrast, large particles provide large obstacles, which restrict chains accessible to the free region; thereby polymer configurations are more compact.

A common material science motivation for creating a PNC is to dramatically modify the properties of the polymer matrix, which are determined by the microstructure. The structural consequences are statistically characterized in real space by intermolecular distribution functions $g_{pp}(r)$. Figure 5 presents the corresponding intermolecular distribution functions of PDMS with different particle sizes and concentrations. One sees that a universal long-range correlation hole exists due to shielding of intermolecular chain contacts *via* intramolecular chain connectivity, *i.e.*, $g_{pp}(r) < 1$ for $r < R_g$. When particles

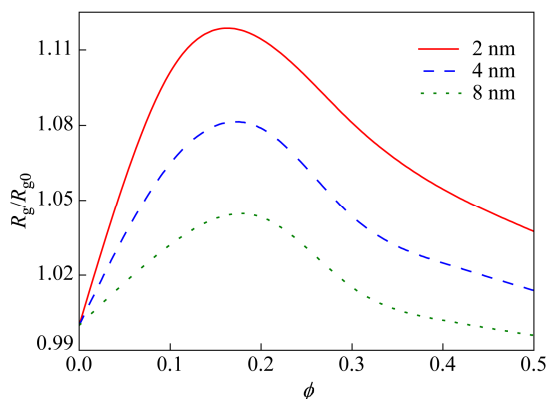


Fig. 4 Normalized radii of gyration of PDMS with the addition of POSS particles of diameter $\sigma_n = 2, 4$, and 8 nm

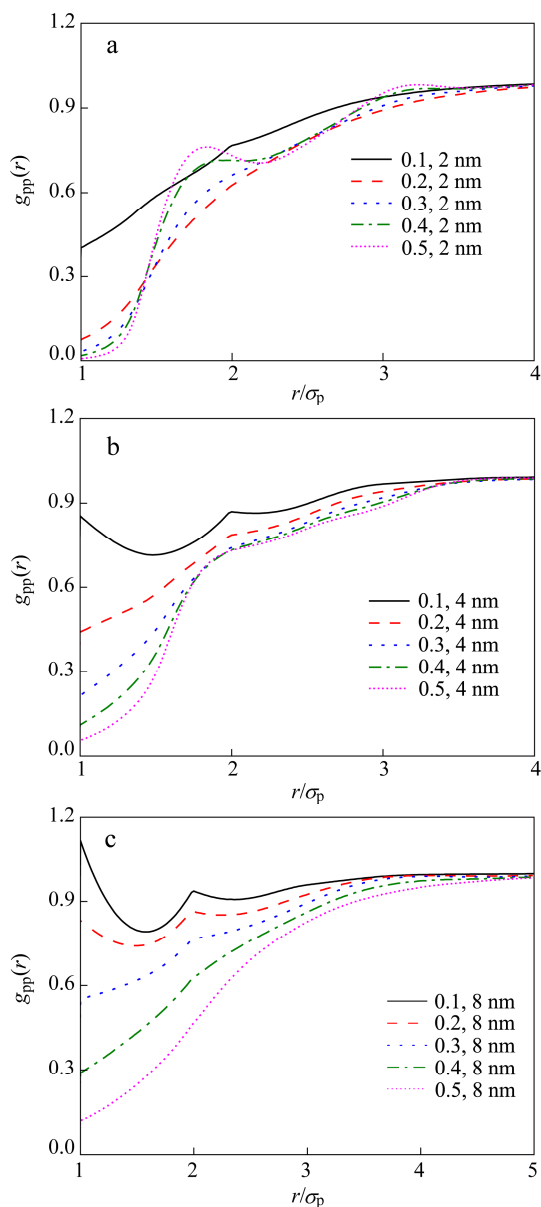


Fig. 5 Intermolecular distribution functions of PDMS with various POSS concentrations and sizes: (a) $\sigma_n = 2$ nm, (b) $\sigma_n = 4$ nm and (c) $\sigma_n = 8$ nm

are added into a PDMS matrix, the reorganization of the monomer necessary to accommodate the particles perturbs the normal PDMS packing features. Therefore, the local PDMS packing correlations dramatically decrease as ϕ increases. The reduction in contact value primarily reflects that, as particle concentration increases, the average density of bulk PDMS declines. Figure 5(a) shows a new peak with high particle concentration, corresponding to the “bound polymer layer”. This peak is associated with the layer of highly intermolecular correlated adsorbed PDMS which is organized in a manner distinct from the PDMS matrix. However, such peak cannot be seen in Figs. 5(b) and 5(c). Besides, the increase of particle size can improve the contact value and decrease the bound polymer layer. As the particle size increases, surface curvature decreases and therefore hinders the polymer segments to be efficiently adsorbed on

the particle surface, thus able to more efficiently stabilize tighter PDMS-PDMS packing.

An examination of the correlation functions reveals further insight into the chain expansion. A standard way to examine the structure of a polymeric chain at all distances is through the structure factor $S_{pp}(q)$, and the results for the PDMS with different particle sizes and concentrations are presented in Fig. 6. It clearly reveals the length scales over which concentration fluctuations are most strongly correlated. The structure factor of PDMS has a notable feature: the monomer scale “local cage” peak emerges at $q\sigma_p \sim 2\pi$, the location and intensity of which quantify the characteristic length scale and coherence of monomer packing. Specifically, a set of peaks appear at $q\sigma_p \sim 2$, which are related to excluded volume correlations due to adsorption of the monomers on the surface of a particle. These aspects of $S_{pp}(q)$ are expected to be modified by the particle-induced reorganization of PDMS. As

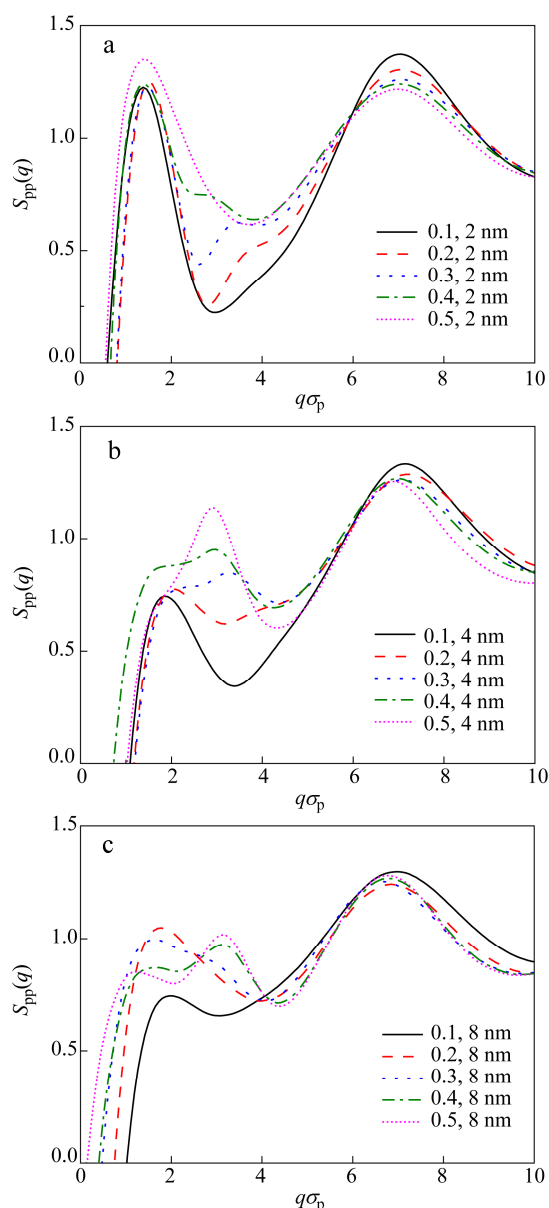


Fig. 6 Structure factors of PDMS with various POSS concentrations and sizes: (a) $\sigma_n = 2$ nm, (b) $\sigma_n = 4$ nm, (c) $\sigma_n = 8$ nm

shown in Fig. 6(a), the local cage peak shifts to lower wavevector and decreases in intensity with increasing ϕ . Unlike the local cage peak, these “excluded volume” peaks relatively increase with the particle concentration. This indicates that the polymer scale cage modestly expands and disorders due to the incorporation of particles in the polymer melt. However, the local cage peaks are insensitive to changes in particle diameter, which are shown in Figs. 6(b) and 6(c). For the excluded volume peak, those large particles no longer efficiently organize the adsorption of monomers on the surface. Such tendency is the Fourier space analogue of the filler-induced suppression of local oscillatory packing correlations in $g_{pp}(r)$, as shown in Fig. 5.

Apart from the structure analysis, a general theoretical model also provides a simple, fast, and flexible way to derive various properties that are difficult to measure from experiments. To make the effect of chemical attributes of polymer and particles on the chain swelling behavior clear, we consider particles with different compatibility with the same PDMS. The chemical properties of POSS can be further modified *via* substituting the functional group, which offers strong or weak interactions.

When particle-polymer interactions double the original ones, the ability of increased interfacial cohesion to enhance R_g/R_{g0} is clearly visible in the range of $\phi \leq 0.1$ in Fig. 7(a). As more particles are introduced, the magnitude of R_g/R_{g0} reduces dramatically. The concentration of particles increases

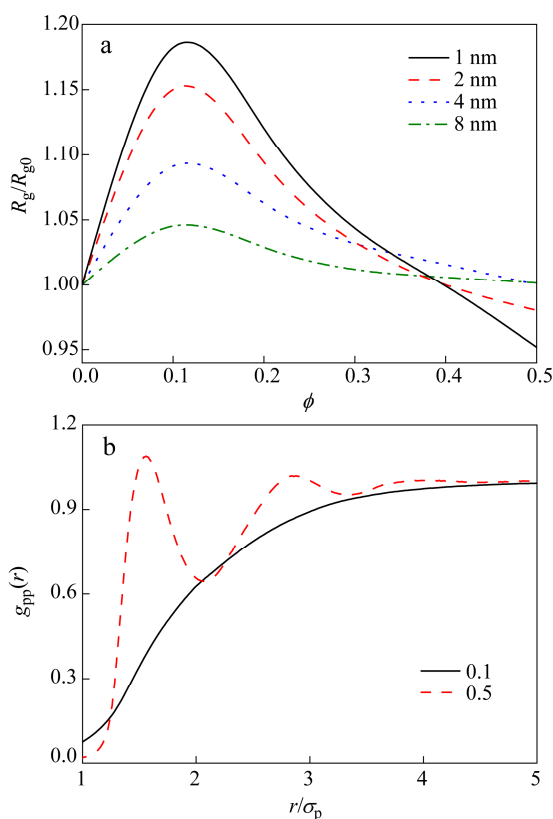


Fig. 7 (a) Normalized radii of gyration of PDMS with the addition of particles of diameter $\sigma_n = 1, 2, 4$, and 8 nm with strong particle-polymer interactions; (b) Intermolecular distribution functions of PDMS with two different particle concentrations at $\sigma_n = 1$ nm

to the point where they begin to touch and interconnect, and the PDMS coil transfers from an expanded state to a collapsed state. To interpret this phenomenon, we present the structure analysis in Fig. 7(b) for the two systems with different concentrations of small particles ($\sigma_n = 1$ nm). At 10% particle concentration, it shows an extremely low density distribution of PDMS chains, corresponding to the expanded correlation hole. On the contrary, the local structure of PDMS chains at 50% particle concentration shows multiple peaks. The first layer of the peaks suggests a local bridging of PDMS chains, such that the particle-induced perturbation effect decreases, and the bulk PDMS chains turn into effective attraction. In addition, larger particles have relatively lower surface and thereby little influence on R_g/R_{g0} .

Figure 8 shows a representative example for the systems with weak interactions of particle-polymer (10% of the original ones). As the particle concentration increases, the values of R_g/R_{g0} relative to Fig. 7(a) follow the same variation tendency. In particular, both positive and negative PDMS expansions can be seen once again when relatively small particles are added. A major result is that the fluctuation amplitude in averaged chain dimension is in the order of 0.5%, since the chains are not strongly perturbed at weak interactions.

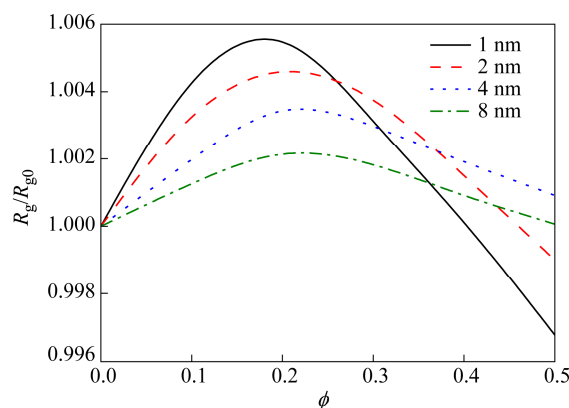


Fig. 8 Normalized radii of gyration of PDMS with the addition of particles of diameter $\sigma_n = 1, 2, 4$, and 8 nm with weak particle-polymer interactions

CONCLUSIONS

In summary, the conformations of PDMS containing various POSS nanoparticles have been investigated with a DFT approach to evaluate the effect of POSS nanoparticles on PDMS conformation. We have found that, with the addition of POSS particles, the radius of gyration of PDMS first increases and reaches its maximum, then declines gradually as more particles are introduced, and the fluctuation amplitude is coherently related to the geometric and chemical properties of particles. In the cases of small POSS particles with strong interactions of POSS-PDMS, PDMS displays obviously positive and negative expansions at low and high particle concentrations, respectively. If the particle radius approaches the radius of gyration of bulk PDMS, the fluctuation amplitude of R_g/R_{g0} dramatically declines, and the contraction phenomenon no longer occurs. Under a weak

interaction, both the positive and negative polymer expansions can also be found but the fluctuation amplitudes have been largely suppressed.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2019-9>.

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