



Molecular modeling of a polymer nanocomposite model in water and chloroform solvents



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ABSTRACT

Grafted polymer on nanoparticle is an efficient way to obtain/improve aggregation, solubility, form and size of nanoparticles. In the present work molecular dynamics simulations were carried out to study a polyethylene glycol (PEG) based nanocomposite model in which the polymer is filled with Fe₃O₄ nanoparticle in water and chloroform solvents. Radial distribution function (RDF), dihedral distribution function, end-to-end distance and radius of gyration analysis indicate that the structural properties of the pure polymer is similar when attached to the nanoparticle. Due to the high polymer density a compact shell is formed around the nanoparticle surface in chloroform (poor solvent). Contrary, in water (good solvent), the polymer chains adopt an extended conformation due to entropic effects. Furthermore, the polymer structure in the nanocomposite is similar to that one founded in the solvents considered. Finally, the results corroborate to the hypothesis of the transferability of the polymer properties to the nanoparticle in solution.

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1. Introduction

Nanoparticle (NP) is a class of material characterized by the diameter below 100 nm with a wide range of applications in different areas, i.e. biology and medicine [1,2], and industrial chemistry [3]. The physical and chemical properties of the NP are sensitive to their morphology (size and shape). These characteristics are important to define the thermo-mechanical and electrical properties of the NPs. The use of compounds such as polymers and surfactants filled on the nanoparticle surface can improve the mechanical, thermal and electrical properties of NPs [4]. This new class of nanomaterials, called nanocomposite (NC), inhibits the anisotropic growth of nanocrystals which can controls the size and shape of nanoparticles. Polymers adsorbed on surfaces or polymer nanocomposites (PNC) are important in many phenomena and applications, such as adhesion [5], stabilization of colloidal dispersions [6], flotation of minerals [7], oil recovery [8], smart materials [9], wetting and spreading phenomena [10,11]. In general, polymer matrix composites play a decisive role in optical, magnetic and dielectric properties and also in electrical and thermal conductivity

[12]. On the other hand, for widespread use of nanoparticles generated from the nanocomposites, these must be dispersed in different solvents. For example, for biomedical applications, the ability to solubilize a NP in water is essential for their use. In this way, the understanding of the PNC-solvent interactions is very important to improve their applications. Theoretical methods have been used to understand the structural and energetic properties of polymer brushes in solution, but there is no direct comparison between these data and the system with the pure polymer. Moreover, the nanoparticle is modeled as a single hard sphere, whereas the polymer is represented by a bead-spring [13,14]. Furthermore, in some theoretical studies the solvent molecules are not considered explicitly [15–19], being treated as dielectric constant. The more realistic simulation was reported by Elliott et al. [20], where they simulated polyethylene oxide (PEO), which was represented by the coarse-grained force field [21], filled on a planar surface whereas the solvent was treated as a good solvent. In order to simulate a more realistic nanocomposite, this present work has a purpose to study a grafted polyethylene glycol (PEG) polymer in a nearly spherical nanoparticle in different solvents. The polymer model was parametrized to reproduce experimental data [21,22]. The PNC model studied here can be classified as a spherical polymer brushes [23]. The PEG was chosen due its large applications

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in drug delivery systems such as vesicles, micelles, and nanoparticles [24], motivating several experimental studies [25–29]. The hypothesis of the transferability of solubility related to the adsorbed polymer on the nanoparticle is achieved.

2. Models and methods

2.1. Models

To deal with the length and time scale problems the coarse grained (CG) model was used to study the polymer nanocomposite in different solvents. The MARTINI CG force field developed by Marrink's group [22] was used and the parameters are shown in Table 1. Nonbonded interactions have been represented by a Lennard-Jones potential, Eq. (1).

$$V_{ij}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

where r_{ij} is the particle separation distance, σ_{ij} represents the range of the interaction, and ϵ_{ij} the interaction strength.

Except for the PEG-NP and for the solvents-NP, all parameters indicated in Table 1 were parametrized to reproduce the experimental data. The high grafting densities for the PNC model are in good agreement with the experimental data reported by Gonçalves et al. [30]. An initial nanoparticle with 7.0 nm of diameter and nearly spherical form was built from the crystallographic octahedral structure of a Fe_3O_4 at an atomistic level. To describe the CG model, each Fe_3O_4 unit of this nanoparticle was replaced by one interaction site being connected with another one using a constant force of the $10,000 \text{ kJ mol}^{-1} \text{ nm}^2$. Using this procedure, the number of particles was reduced considerably. The interaction strength of each CG site with the polymer was considered attractive (in the MARTINI definition, Qd) with $\sigma = 0.47 \text{ nm}$ and $\epsilon = 5.0 \text{ kJ/mol}$. These Lennard-Jones parameters were chosen because the experimental data shows that the polymers are filled on the nanoparticle [30] and, as a consequence, there is a strong interaction between the polymer and nanoparticle. The CG force field developed by Lee et al. [21] was used to describe the structural and energetic prop-

erties of the polyethylene glycol. This force field was developed within the framework of the MARTINI CG force field where each monomer of the ethylene glycol is represented by one site. The nanocomposite was built filling covalently 188 chains of polymers composed by 24 monomers (molecular weight ~ 1000). The initial conformation of polymer chains was considered as extended, see Fig. 1. Fig. 1 shows the procedure to elaborate the nanocomposite model.

We have considered two systems. (i) Pure polymer: characterization of the pure polyethylene glycol in water and chloroform (CLF) solvents. These initial systems were constructed inserting 75 polymers with nearly extended conformation into a box of size $11 \times 16 \times 11 \text{ nm}$ with 19,399 solvent sites. (ii) PNC: characterization of a single polymer nanocomposite in water and CLF solvents. These initial systems were built by the insertion of a nanocomposite into a cubic box of $25 \times 25 \times 25 \text{ nm}$ edge and 127,128 solvents sites were added, see Fig. 1. This system is composed by 135,206 CG particles, which correspond an atomistic system with $\sim 1,600,000$ atoms.

2.2. Molecular dynamics simulations

All systems were initially minimized in terms of the energy using the steepest descent followed by the conjugated gradient algorithms to obtain an energy gradient lower than 200 kJ mol^{-1} . The solvent molecules were allowed to relax for 1.0 ns, while the nanocomposite was kept rigid using a restraint potential with a force constant of the $1000 \text{ kJ mol}^{-1} \text{ nm}^2$. The simulations were conducted at NpT ensemble using the Berendsen thermostat and barostat [31], with a temperature of 300 K and a coupling time of 0.1 ps. The pressure was of 1 bar with the compressibility of 4.5×10^{-5} and coupling time of 1 ps. Periodic boundary conditions were used with 1.2 nm as cutoff for the non-bonded interactions (Lennard-Jones). The equations of motion were integrated using the leapfrog algorithm [32] with 10.0 fs as an integration time step. The production runs were 100 and 200 ns for the pure polymers and PNC systems, respectively. All simulations and analysis were performed using GROMACS 4.0.4 package [33,34] with support of homemade programs.

3. Results and discussion

To our best knowledge, the advantage of the present work compared to the others is the reliable of the force field parameters used. We considered the MD simulations for pure polymer in water and chloroform to understand the polymer dynamics behavior in these solvents. This knowledge is very important for understanding the nanocomposite properties and the effect of the polymer filled on the nanoparticle as well.

Table 1
Lennard-Jones parameters used to describe the nonbonded interactions.

Interaction	σ (nm)	ϵ (kJ mol ⁻¹)
PEG-PEG	0.43	3.375
PEG-water	0.47	4.0
PEG-CLF	0.47	3.0
PEG-NP	0.47	5.0
Water-water	0.47	5.0
CLF-CLF	0.47	3.5

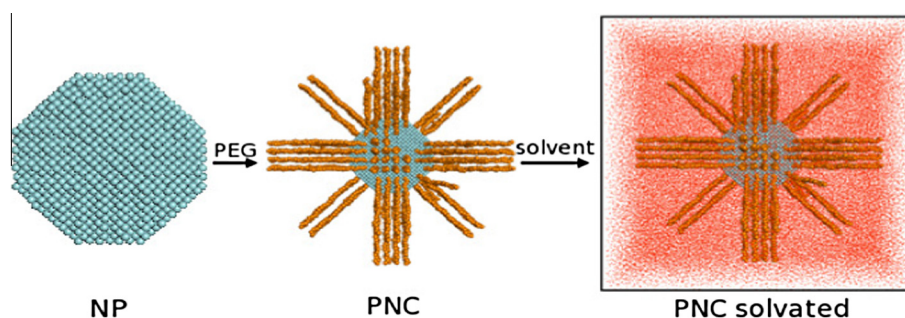


Fig. 1. Systematic construction of the polymer nanocomposite. Nanoparticle in cyan color, polymer chains in orange color and solvent in red color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

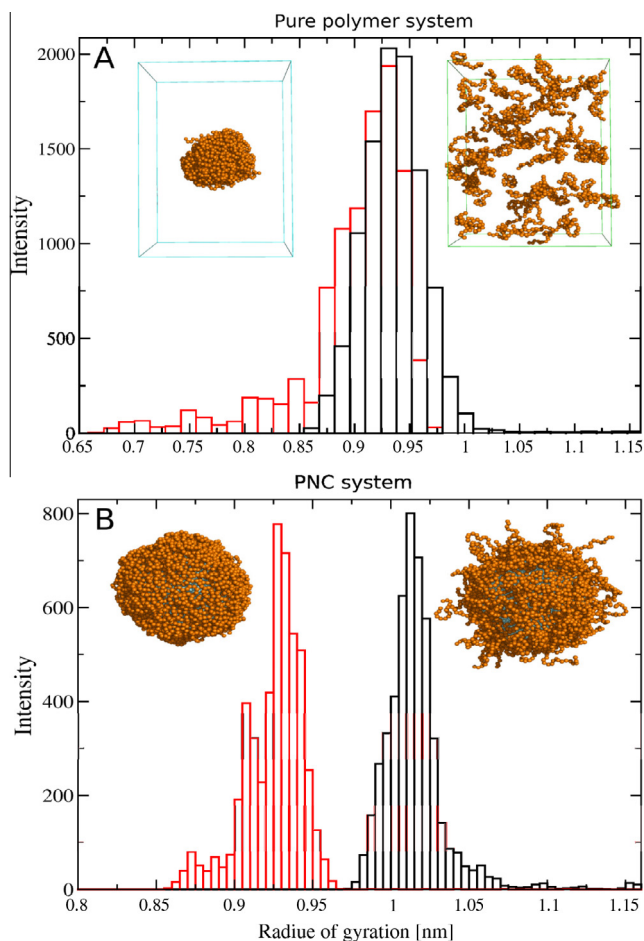


Fig. 2. Mean of radius of gyration: (A) for all pure polymer chains in solution and (B) for polymer chains filled with nanoparticle in chloroform (left side and in red color) and in water (right side and in black color) solvents. Inset, the snapshot without solvents obtained at the end of MD simulation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.1. Radius of gyration (R_g)

In order to understand the structural behavior of the polymer in the solvents, we calculated the radius of gyration (R_g) using the following equation,

$$R_g = \left(\frac{\sum_i ||r_i||^2 m_i}{\sum_i m_i} \right)^{1/2} \quad (2)$$

where m_i is the mass of site i and r_i is the position of site i with respect to the center of mass of the molecule. For instance, the R_g analysis is an important property to measure the effective size of a polymer. Therefore, it was used to quantify the degree of folding process of the PEG polymer. Hence, Fig. 2 shows the radius of gyration of the pure polymer in solution and its filled with the nanoparticle in both solvents considered here.

The first attempt to this result is that the average of the radius of gyration for the polymer in water is around 0.93 nm, which is in good agreement with a recent work developed by Mondal and co-workers [35]. They used an united-atom model for the poly(ethylene oxide) and investigated the conformational properties of the polymer in water and in ionic liquid. These authors varied the number of monomeric unit and found an average value for the radius of gyration of (0.933 ± 0.046) nm for the system with $N = 27$ [35].

On the other hand, it is important to highlight that the vibrational spectroscopic study showed that the PEO chains present

an ordered structure quite similar to the helix, found in the solid state, where the *trans-gauche-trans* conformation occur as a pattern for the O-C-C-O dihedral [36]. Even with the simplicity of CG model, it is possible to observe in Fig. 2A (inset) the presence of helical-like structure for the polymer dispersed in water, while it was observed the polymer chains aggregation in chloroform, forming a drop. Consequently, there is a polymer self-interaction preference in chloroform with the water acting as a good solvent for polymer at 298 K. According to the Flory-Huggins theory, the solvent quality is characterized by the parameter χ , in which $\chi < 0.5$ and $\chi > 0.5$ corresponds to poor and to good solvents, respectively [37]. In this way, our results are in agreement with the Flory-Huggins theory, where a polymer in a good and poor solvents adopt an unfolding and folding configurations, respectively [37]. In addition, the Lo Verso et al. [38] has observed the same trends in polymer brush-coated spherical nanoparticles in a good solvent. As a result, the polymer chains developed a more coil conformation in chloroform than in water solvent. These observations are quantified by the radius of gyration, in which the R_g value of ~ 0.94 nm with similar maximum intensity (~ 2000) for both model solvents was observed in the pure polymer system. This means that in water and chloroform the polymer chains adopt a similar nearly folding conformation. However the narrow of the curve of the polymer in water shows that their structure tends to spend most of the simulation time in the extended or unfolded conformation (Fig. 2(a)), implying that this configuration is stabilized by the water-polymer interactions. The R_g value of 0.94 nm for the polymer in water is in agreement with previous MD simulations [21,39]. At interval 0.7–0.9 nm (Fig. 2A), the R_g values indicate a folding structure with low intensity for pure polymer chains in chloroform solvent. These results are corroborating with the mean end-to-end distance, $\langle r \rangle$, obtained along the 100 ns of the MD trajectory. The $\langle r \rangle$ calculated for the pure polymer chains in water and in chloroform were $2.34 (\pm 0.16)$ nm and $2.19 (\pm 0.21)$ nm, respectively. The difference for the starting configuration was around of 2.2 nm in the chloroform solvent. Therefore, the resulting polymer structure was slight more collapsed in chloroform than in water solvent. Comparing these results with the polymer filled on the nanoparticle, the same trend is observed. This implies that the knowledge of the polymer structure in solution can be used to predict the local environment behavior of polymers filled on nanocomposites. The maximum intensity of R_g values (Fig. 2B) were 1.01 and 0.93 in water and CLF, respectively. These values show that the pure polymer chains are more compact in CLF than in water, in agreement with the $\langle r \rangle$. The $\langle r \rangle$ calculated along the simulation was $2.53 (\pm 0.23)$ nm, indicating that the polymer spend much more time in an extended configuration in the pure polymer than in the NPC. For CLF solvent was not observed significant difference between the $\langle r \rangle$ of pure polymer ($2.19 (\pm 0.21)$ nm) and NPC ($2.01 (\pm 0.12)$ nm).

3.2. Radial distribution function (RDF)

In order to characterize the structure of the system, we carried out RDF analysis for the solvated polymer and for the nanocomposite polymer systems. This approach is useful to describe how the solvent molecules are organized around the solute. Fig. 3 shows the RDF for the polymer-polymer and polymer-solvent pair interactions in both systems (pure polymer and PNC).

It is interesting to observe that the shape of the RDF curves for PEG-water interactions (Fig. 3A (pure polymer) and (PNC)) has the same form, except for the RDF intensity. This indicates that the pure polymer and its filled on the NP have similar solvation process. In the pure polymer system, the most intense peak at 0.52 nm indicates the highest interaction between polymer and water compared to the polymer-chloroform interactions (Fig. 3A).

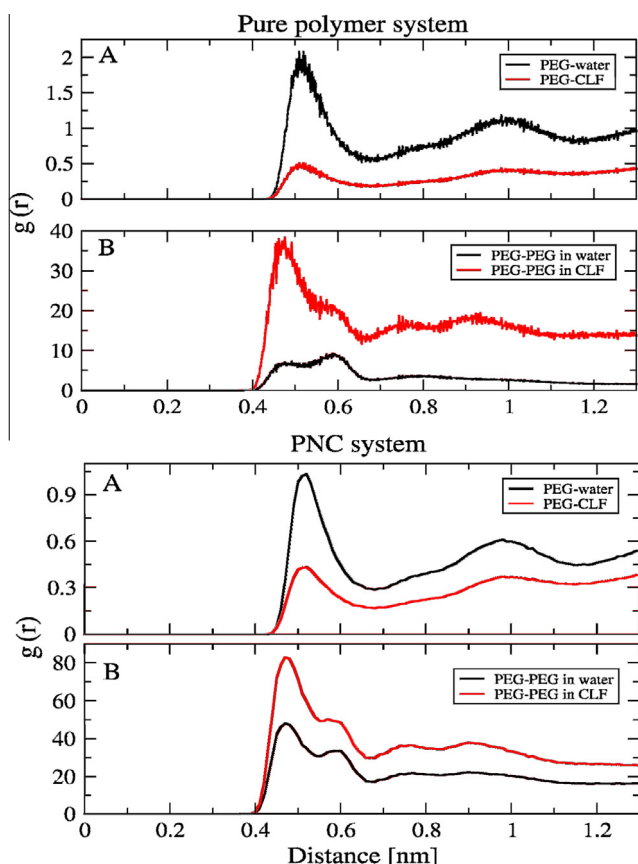


Fig. 3. Radial distribution functions for pure polymer system in the solvents (PEG-solvents (A) and PEG-PEG interactions (B)), and for PNC system (PEG-solvents (A) and PEG-PEG interactions (B)).

In this system, for both solvents, the first solvation shell is characterized by the minimum at 0.68 nm. The coordination number (CN), calculated by the integral of the RDF up to the first minimum, indicates that there are 7 water and 2 CLF around the polymer chains. This implies that the PEG is more solvated by water than CLF. Contrary to the polymer in CLF, a second well defined solvation shell is observed with minimum at 1.15 nm for pure polymer in water with intensity equal to 1.2 (Fig. 3A). For PEG-PEG interactions (Fig. 3B), the RDF shows an intense peak at 0.45, indicating the preference of the PEG to interact with itself than with CLF solvent. Contrary, the lowest $g(r)$ for PEG-PEG in water (Fig. 3B) and the highest $g(r)$ in PEG-water (Fig. 3A) reflect the preference of PEG to interact with this solvent than with itself. Fig. 3B shows that, in water, there are two bands, one centered at 0.48 nm (with $g(r)$ value of ~ 7), which correspond to the direct PEG-PEG interactions and another one at 0.59 nm (with $g(r)$ value of ~ 10), indicating the existence of water sites intercalated between the PEG chains, consequently, the swelling effect is observed. For PNC system, it was not observed significant change in the solvation process of the polymer. The main difference was observed in the CN of the first solvation shell for the PNC in water, with a value of 4 neighbors. This decreases compared to the pure polymer in water (CN is equal 7), indicating that the grafted polymer in the nanoparticle is less exposed to the water solvent. This should be expected because the water cannot access the PEG site located near of the nanoparticle.

3.3. Dihedral analysis

The process of unfolding-folding transition was monitored from the probability density of the backbone torsional angles (Fig. 4).

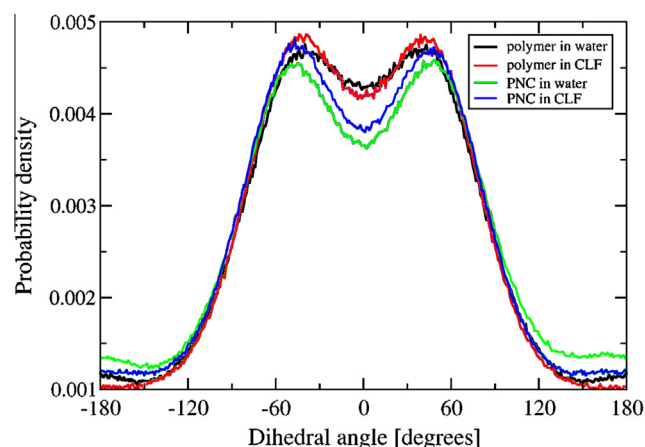


Fig. 4. Probability density function for all dihedral angle of the polymer pure (black and red curves) and polymer in the NCP (green and blue curves). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

This measure is very important to quantify and to characterize the local conformation of the polymer chains in the system.

The highly symmetrical angle distribution (Fig. 4) and its smooth at the local maxima indicate the local conformation relaxation of the polymer chain along the simulations. For the pure polymer, a gauche⁺ at $\sim +40^\circ$ and a gauche⁻ at $\sim -40^\circ$ in both solvents were observed, while for polymer filled on the nanoparticle there is a gauche⁺ at $\sim +46^\circ$ and a gauche⁻ at $\sim -46^\circ$ in the solvents. The highest intensity at 0° and at gauche \pm showed that the pure PEG is more flexible than attached in the nanoparticle. The increase of the $\sim 6^\circ$ of the dihedral angle in the transition PEG pure to the PEG filled on the nanoparticle can be attributed to the steric effect due to the proximity of the chains located at the nanoparticle surface. However, in general the torsional angles of the polymer chains are similar as well in the pure state and grafted on the nanoparticle.

Overall our results show that the presence of the nanoparticle does not affect the structural properties of the polymer in agreement with the Lin et al. [40]. According to these authors, the polymer chains grafted in the nanoparticle have the same or a compatible chemistry with the polymeric matrix. Finally, our theoretical results are in agreement with the experimental data from Dalmascio et al. [41]. In other words, the present results support the hypothesis of the transferability the solubility of the adsorbed polymer to the nanoparticle.

4. Conclusions

In the present work, molecular dynamics technique was used to study a pure polymer and an isolated nanocomposite model in water and chloroform solvents. The knowledge of the structural behavior of polymer grafted in the nanoparticle is very important to clarify the interaction them. For pure polymer, our simulations show that the polymer chains are dispersed in water, while in chloroform there is formation of aggregation. The analysis of the radial distribution functions indicate that the pure polymer is more solvated in water than in nanocomposite. This is attributed to the difficult of water site to access the polymer monomers located near of the nanoparticle surface. On the other hand, in the chloroform solvent was not observed significant difference between the solvation of pure polymer and the polymer filled on the nanoparticle. The mean of radius of gyration indicate the formation of a compact polymer shell in CLF, while in water it was observed an extended conformation around the nanoparticle. In the dihedral analysis, a

slight difference in the torsional angles in the unfolding–folding process of the PEG was observed. Overall, comparing the structural data of the pure polymer and its grafted on the nanoparticle, there is not observed significant change indicating that the nanoparticle does not alters the characteristics of the polymer. Finally, we concluded that the knowledge of the polymer in solution can be used to the nanocomposite design at theoretical and experimental level.

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