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Investigating the properties and interaction mechanism of nano-silica in polyvinyl alcohol/polyacrylamide blends at an atomic level

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ABSTRACT

The nano-silica can be incorporated into polymers for improved mechanical properties. Notably, the interaction between nano-silica and polymer is of a microscopic phenomenon and thus, hard to observe and study by using experimental methods. Based on molecular dynamics, this paper presents a study on the properties and the interaction mechanism of nano-silica in the polyvinyl alcohol (PVA)/polyacrylamide (PAM) blends at an atomic level. Specifically, six blends of PVA/PAM with varying concentrations of nano-silica (0–13 wt%) and two interfacial interaction models of polymers on the silica surface were designed and analyzed at an atomic level in terms of concentration profile, mechanical properties, fractional free volume (FFV), dynamic properties of polymers and X-ray diffraction patterns. The concentration profile results and micromorphologies of equilibrium models suggest PAM molecular chains are easier to be adsorbed on the silica surface than PVA molecular chains in blends. The incorporation of nano-silica into the PVA/PAM blends can increase the blend mechanical properties, densities, and semicrystalline character. Meanwhile, the FFV and the mobility of polymer chain decrease with the silica concentration, which agrees with the results of mechanical properties, densities, and semicrystalline character. Our results also illustrate that an analysis of binding energies and pair correlation functions (PCF) allows for the discovery of the interaction mechanism of nano-silica in PVA/PAM blends; and that hydrogen bond interactions between polar functional groups of polymer molecular chains and the hydroxyl groups of the silica surface are involved in adsorption of the polymers on the silica surface, thus affecting the interaction mechanism of nano-silica in PVA/PAM blend systems.

1. Introduction

Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer, which is commercially available in a form of partial or complete hydrolysis of poly(vinyl acetate). Due to its hydrophilicity, biodegradability, biocompatibility, and high mechanical strength, PVA has been widely used in potential drug delivery systems and scaffolds for various tissue engineering applications (Anastasia et al., 2016; Morales-Hurtado et al., 2015; Jiang et al., 2011) PVA, however, has some demerits, such as lack of biological activity, inability to withstand complex loads, and unfavorable properties for cell adhesion and growth (Choi et al., 2012), thus limiting its application to tissue engineering. Polyacrylamide (PAM) is a type of water-soluble polymer formed from acryl amide monomers; and its hydrogel possesses favorable characteristics for tissue engineering, such as three-dimensional network structure, nontoxic side effects, good biocompatibility and biological activity (Leng et al., 2011; Suriano et al., 2014; Labarre et al., 2002). Therefore, PAM has been always used for the modification of PVA (Patel and Sureshkumar, 2014; Wei et al., 2017a) so as to obtain the combined advantages of PVA and PAM. Meanwhile, it is noted that due to the brittleness and poor mechanical properties of PAM, the addition of PAM can weaken the original mechanical properties of PVA hydrogel (Wei et al., 2017a; El-Zawawy et al., 2012), which limits the application of PVA/PAM blends in some tissue engineering application, such as bone and cartilage repair, where the mechanical property is a critical issue (Olubamiji et al., 2016; Chen, 2014; Little et al., 2011).

A large number of studies show that adding the nanoparticles into polymers can significantly improve the mechanical properties (e. g., strength, stiffness, elastic modulus) of polymers (Qiao et al., 2016; Gomez et al., 2016; Zhao et al., 2016). Due to its properties of nontoxicity, nano-silica has been widely used as an inorganic nanomaterial to improve the mechanical properties as well as thermodynamic properties, chemical stability and water resistance (Dil et al., 2016; Zhou et al., 2016; Griffin et al., 2016). Taheri-Behrooz et al. (Taheri-Behrooz et al., 2015) investigated the addition of nano-silica in phenolic resin, with the results illustrating that the resultant Young's modulus and

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hardness steadily increased as the weight percent of silica nanoparticles. Malaki et al. (2016) studied the erosion resistance, adhesive strength, micro-hardness and weathering stability of the acrylic-based polyurethane nano-composites and found that they could be reinforced with the addition of nano-silica particles. Sowjanya et al. (2013) fabricated biocomposite scaffolds from the blends of chitosan, alginate and nano-silica by using a freeze drying method; and they found the scaffolds possessed a well-defined porous architecture with pore sizes varying from 20 to 100 μm suitable for cell infiltration and that the presence of nano-silica in the scaffolds increased the protein adsorption and reduced the swelling occurred. Besides, the silica processed in this scaffold also assisted with osteoblast cell proliferation, and the collagen fiber network interconnecting the ß-TCP/silica granules yielded a rigid, fleece-like mold (Wilmowsky et al., 2008; Ghanaati et al., 2010).

As discussed above, adding nano-silica particles into PVA/PAM blend composite can not only improve mechanical properties, but also promote proliferation of cells in blend. These advantages make PVA/PAM/nano-silica composite suitable for bone tissue engineering. To this end, the knowledge on the micro properties and interaction mechanism of nano-silica in PVA/PAM blend is of importance to prepare the PVA/PAM/nano-silica composites. Notably, the interaction between nano-silica and polymer is of a microscopic phenomenon and thus, is hard to observe and study by using experimental methods. As a result, the interaction mechanism of nano-silica in PVA/PAM blend has been rarely investigated and elucidated.

Molecular dynamics (MD) simulations has been illustrated promising for investigating material properties and interfacial interactions of inorganic fillers and polymer matrix in an atomic scale (Lammers et al., 2017; Roussou and Karatasos, 2016; Hagita et al., 2016), thus providing the microscopic information or details of molecular interactions inside materials. Base on MD simulations, Lai et al. (2014) investigated the mechanical characteristics of the interfaces between osteopontin and hydroxyapatite and they found that the interfacial mechanical behavior was governed by the electrostatic attraction between acidic amino acid residues in OPN and calcium in HA. Boulet and Coveney (2004) and Gardebien et al. (2005) also employed the experimental and MD methods to study the properties of the montmorillonite polymer nanocomposite, which helped understand different aspects of structures and properties of polymer nanocomposite. Sahu and Anup (2016) applied MD simulations to investigate the effect of the structural arrangement of reinforcements on the mechanical properties of a nano-composite under transverse loading. In this regard, we have also successfully employed MD simulations to investigate the properties of biopolymer blends (Wei et al., 2016a, 2016b, 2017a; Wang et al., 2017) and interfacial interaction (Wei et al., 2016c, 2017b).

Inspired by the above studies, we employed the MD simulation method to investigate into the micro structures and properties of PVA/PAM/nano-silica blend composites, as presented in this paper. We also present the discovery of interaction mechanism between nano-silica and polymers in blend system from the perspective of molecular interaction. This work not only elucidates the reinforcing mechanism of nano-silica in polymeric matrix, but also provides theoretical basis for synthesizing nano-silica/polymers composites for various applications.

2. Materials models and simulation methods

2.1. Polymer model

An appropriate molecular chain length in polymers is critically important to the model development, thus contributing the accuracy of the simulation results. A short molecular chain length may not represent the real polymers appropriately, while a long molecular chain length may lead to difficulties for computer simulations. In the present study, each polymer molecular chain with the same molecular weight was constructed, so that the results of models in simulations can compare with each other. In this study a PVA molecular chain with 50 repeat units and a PAM molecular chain with 31 repeat units were constructed according to the molecular structural formula (Fig. S1) as per our previous study (Wei et al., 2016b, 2016c). The all simulation models were constructed by using the Materials Studio software (Accelrys Inc., 2010).

2.2. Nano-silica model

The crystal structure of a-quartz (silica, space group P3321) was adopted from the Cambridge Structural Database with the lattice parameters as follows: a = b = 0.491 nm, c = 0.5402 nm, α = β = 90°, γ = 120°, and its density is 2.648 g/cm^3 (Fig. S2a). Considering the computer efficiency and the specific surface area, a spherical silica nanoparticle with a radius of 6 Å was constructed, without consideration of surface functionalization or covalent grafting (Fig. S2b). The unsaturated boundary effect was avoided by adding hydrogen atoms to the unsaturated oxygen atoms and hydroxyl groups to the unsaturated silicon atoms of the silica particle surface (Fig. S2c).

2.3. PVA/PAM/silica blend models

Before constructing the blend models, the PVA chain, PAM chain and the spherical silica nanoparticle were all optimized by using the geometry optimization method (as detailed below), to ensure the energies of the models built were minimized and following the stable configurations of PVA, PAM and silica nanoparticle were obtained. To eliminate the effects of polymer composition ratio on calculation results, the amount ratio of PVA and PAM chains in each model was 1:1. Furthermore, to purely study the interaction mechanism of nano-silica and polymers and prevent any finite size effect of nanocomposites and account for any particle effect at the bulk level, only one silica nanoparticle was embedded at the center of the blend unit cell and the periodic boundary condition was used. Thus, all the simulation models used here were constructed under an ideal condition without considering the agglomeration of nano-silica, and the blends with different silica contents were constructed by changing the number of polymer chains in the models. In our research, six blend models with different compositions of PVA/PAM/silica were constructed, and the ratios of molecular number in models were 7/7/0, 7/7/1, 6/6/1, 5/5/1, 4/4/1,

Table 1
Parameters of simulated blend models.

Cell component	Weight fraction (wt%)			Cell after refinement			
	PVA	PAM	Silica	Cell length (nm)	Density (g/cm^3)	2θ (°)	d-spacing (nm)
7PVA/7PAM/0silica	50.0	50.0	0.0	3.412	1.295	18.65	0.476
7PVA/7PAM/1silica	47.0	47.0	6.0	3.459	1.317	18.95	0.468
6PVA/6PAM/1silica	46.5	46.5	7.0	3.288	1.329	19.15	0.463
5PVA/5PAM/1silica	45.9	45.9	8.2	3.091	1.350	19.35	0.459
4PVA/4PAM/1silica	45.0	45.0	10.0	2.876	1.368	19.45	0.456
3PVA/3PAM/1silica	43.5	43.5	13.0	2.624	1.397	19.65	0.452