



From atomistic structure to thermodynamics and mechanical properties of epoxy/clay nanocomposites: Investigation by molecular dynamics simulations



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ABSTRACT

Polymer/clay nanocomposites (PCNs) are multi-functional materials that have superior mechanical and thermal properties than polymer-based materials while maintaining their characteristic properties of lightweight and optical clarity. These materials are obtained by adding small amounts of clay nanofillers to a polymer matrix. In this work, we proposed a molecular model to investigate the morphology and thermomechanical properties of thermosetting clay nanocomposites. The epoxy matrix was composed of several representative cross-linked epoxy units, and different structures of PCNs, which correspond to intercalated or exfoliated status, were considered by varying the amount of polymer phase in the inter-layer space. Molecular dynamics simulations of different nanocomposite structures were used to provide atomistic insights into the arrangement of the constitutive components of PCNs, the molecular interactions occurring in the interphase zone, and the influence of silicate layer on the thermodynamic and elastic properties of these multi-functional materials.

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1. Introduction

Polymer/clay nanocomposites (PCNs) materials are obtained by adding small amounts of clay nanofillers that have an extremely high aspect-ratio (up to 0.5 μm in length and width, but only 1 nm in thickness) and great mechanical properties (strength and flexibility) to a polymer matrix. PCNs exhibit significant enhancements in mechanical and thermal properties while maintaining the characteristic of lightweight and optical clarity of polymer-based materials [1–4]. To date, the physical behaviour of PCNs is not yet well understood and to the best of our knowledge, few studies have considered the molecular structures and overall thermomechanical properties of polymers/clay nanocomposites. So, the physical behaviour of this kind of nanomaterial is not yet well understood and still stimulate numerous research activities [5,6].

The molecular structures of intercalated and exfoliated poly ϵ -caprolactone (PCL) nanocomposites have been previously studied by means of the molecular dynamics (MD) technique [7,8]. Gardebien et al. [7] investigated the effect of the number and

length of polymer chains on the structure of intercalated nanocomposites. By examining the interlayer density profiles, the authors found that the interlayer phase organizes into four layers while the charged heads of the surfactants remained at the surface. On the other hand, for the exfoliated nanocomposites it was found a layered structure with high density of organic phase near the clay surface. The different arrangement of poly (ethylene oxide) (PEO) in the intercalated and exfoliated nanocomposites was considered by Suter and Coveney [9] using large-scale MD simulations, where non-modified montmorillonite (MMT-Na) was used to model the inorganic phase. It was found that the PEO chains organize in layers parallel to the clay surface, and because of the sodium ions and the charges within the clay surface the conformation of the polymer in the exfoliated structure was significantly different from the intercalated system.

Elastic coefficients of PCNs are important properties that can be used as parameters in continuum mechanical models to estimate other macroscopic properties of PCNs [10,11]. However, only Xu et al. [12] has used computational methods to predict the longitudinal and lateral Young's moduli of the exfoliated and partially intercalated/exfoliated clay clusters.

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So far, computational models of PCNs were restricted to the cases of clay with pristine surface or chemically modified through cationic exchange with surfactant molecules.

In the works cited above, the pristine clay or organically modified clays with cationic surfactants were modelled. Modification of the clay surface by the covalent grafting was, for the first time, modelled using in the work of Piscitelli et al. [13]. Their MD simulations revealed that an increase of aminosilanes concentration and the use of shorted aminosilane chains contribute to the extent of the d -spacing in the clay.

To the best of our knowledge, there is no computational study where these silanized clays served as fillers in polymer matrix, despite these techniques are extensively used in the synthesis of epoxy/clay nanocomposites [14–18]. Moreover, there is only a single computational study on the structural and thermosetting properties of polymer/clay nanocomposites [14], where Chen and co-workers [14] considered intercalated and exfoliated clay-nanocomposites based on epoxy matrix cross-linked from Diglycidyl ether of bisphenol-A and Diethylmethylbenzenediamine (DGEBA and DETDA). In this study, a series of surfactants with a single ammonium group and one alkyl chain of various length were used and the failure behaviour of the interphase in terms of quantifiable parameters such as peak strength, fracture energy and final separation distance were determined. However, details of the molecular structures and overall thermomechanical properties of these nanocomposites were not investigated.

In the present work, we propose a molecular model based on the epoxy-based nanocomposite and silanized-clay models of Piscitelli et al. [13] to investigate the structural, thermodynamic and mechanical properties of thermosetting clay nanocomposites. The arrangements of the constitutive components of PCNs, and the effect of silicate layer on the thermodynamic and elastic properties of these multifunctional materials are quantified by means of molecular dynamics simulations of three nanocomposite structures consisting of different representative cross-linked epoxy molecules to represent intercalated or exfoliated structures.

The influence of the silanized clay on the morphology and density of polymers and the molecular interactions occurring at the issue of the resulting interphase region was analysed. In addition, the effect of the end functional groups of the grafted aminosilane molecules, on their interactions with the host epoxy polymer was also discussed by examining the local structure of nanocomposites. The thermodynamics and physical properties, including the glass transition temperature, the time-dependent mean squared displacement (MSD), the elasticity coefficients, and the isothermal bulk modulus of the epoxy matrix and PCNs were also computed.

After this introduction on the rationale for studying the polymer/clay nanocomposites materials, the paper is organized as follows. In Section 2, the methodology adopted to construct the molecular models of sodium montmorillonite and polymer clay nanocomposites, and the force fields used to conduct the molecular dynamics simulations are discussed in detail. The methods adopted to determine the glass transition temperature and the mechanical properties of the PCN models are also discussed in this section. The results of our simulations are presented in Section 3, where the effect of different cross-linked epoxy-units is discussed by comparing radial distribution function, glass transition temperatures, translational dynamics of the polymer and elastic properties. Finally, in Section 4, we draw the conclusion of this work.

2. Computational methods

It is also important to point out that the molecular models used in this manuscript are “clay clusters” and not true PCNs. Real PCNs

should be the mixture of clay clusters with polymer matrix, and they have a very complex structure [9,19]. Therefore, a comparison with the real PCNs in the experimental part will be not appropriate. Moreover, it should be noted that, in the experimental part, it is impossible to make the nanocomposites with a specific controlled interlayer distance. Thus, the molecular dynamics simulation has been used to investigate the properties of the nanocomposites.

2.1. Molecular model of polymer/clay nanocomposites

2.1.1. Pristine and silanized clay

Let us consider a sodium montmorillonite (MMT- Na^+) which has the chemical structure $\text{Na}_x(\text{Si}_8)(\text{Al}_{4-x}\text{Mg}_x)\text{O}_{20}(\text{OH})_4$ where $x = 0.67$ presents a cation exchange capacity of 91 meq/100 g. This structure corresponds to the sodium montmorillonite provided by Southern Clay Products. Starting from the crystallographic unit cell [20], an orthogonal basis was defined with the Z-axis being perpendicular to the clay surface of the cell. Next, the unit cell was replicated 4 times according to the X-axis and 3 times according to the Y-axis. Then, 8 atoms of Al^{3+} were randomly chosen and replaced by Mg^{2+} in the octahedral layer, which resulted in a charge deficiency of -8 for the clay layer. Finally, 8 sodium ions Na^+ were added in the interlayer space to obtain the complete MMT- Na^+ cell. The size of the MMT- Na^+ cell were $21.12 \times 27.42 \times 6.56 \text{ \AA}^3$.

For the silanized clay, the size along the Z-axis of the MMT- Na^+ cell was fixed at 18 \AA , which corresponds to the bilayer organization of aminosilanes within the clay interlayer space [21,16,17,13,22]. Grafting of aminosilanes onto the clay surface was carried out following the procedure proposed by Piscitelli et al. [13]. Herein, it is assumed that the silane molecules can be grafted covalently with the oxygen atoms on the surface of clay [13]. We only considered the case where the 3-aminopropyltrimethoxysilane molecules were linked with clay surface through three covalent bonds [13]. The molecular structure of this aminosilane molecule is shown in Fig. 1(a). In this model, 8 aminosilanes were grafted on each clay surface. This corresponds to the number of monocationic surfactant needed to obtain a fully treated clay surface based on its cation-exchange capacity.

2.1.2. Polymer clay nanocomposites

In our PCN model, the polymer matrix consists of representative cross-linked molecules as shown in Fig. 1(d). This type of cross-linked molecules has been previously used for simulating thermoset polymers [23–26]. The use of these representative cross-linked molecules was also shown to be suitable for estimating thermodynamic and mechanical properties of thermoset polymer [27]. Fig. 2 reports the curing reaction mechanism between the epoxy group and the primary amine group. The carbon-oxygen bond in the epoxy monomers is broken through opening of the epoxy ring. The oxygen-end of the opened epoxy ring takes over the hydrogen atom from a nearby amine group in the hardener molecule and leaves a dangling nitrogen in the hardener molecule, which forms a covalent bond with the carbon-end of the opened epoxy ring. This process allows the epoxy monomer to link to an amine based hardener.

The structures of the epoxy monomer and of the hardener used in this work are reported in Fig. 1(b) and (c), respectively. Each epoxy monomer has two reactive epoxy groups and the hardener has six reactive amine groups. The representative cross-linked molecule was build from the cross-link process between three linear epoxy monomers and one chain of curing agent. Therefore, as suggested in the work of Yu et al. [27], a cross-linking ratio of 50% is used for this representative molecule based on the consumption of the reactive functions on both epoxy monomers and hardener molecule. Fig. 1(d) shows the configuration of the representative cross-linked molecule.

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