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Structural and thermodynamics properties of organo-modified montmorillonite clay

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HIGHLIGHTS

- We used molecular dynamics simulation based on two force fields (CLAYFF and CHARMM).
- We have evaluated the thermodynamics and structural properties of organoclay.
- The basal spacing and density are in good agreement with available experimental data.
- The effect of the cation exchange capacity (CEC) on the basal spacing and the thermodynamics properties was considered.
- The calculated isothermal bulk modulus agrees well with the density value of organoclays with two different CEC.

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ABSTRACT

Polymer clay nanocomposites (PCNs) have been seen as the most novel materials in engineering applications since they exhibit significant improvement in mechanical and physical properties. Indeed, with few amount of organoclay, PCNs exhibit enhanced mechanical, optical, thermal and liquid or gas barrier properties compared to pure polymers and to their counterpart microcomposites. Thus, organoclays are extensively used as precursors in the preparation of PCNs. They are the best candidate in reinforcing PCNs because of the lightweight and the high availability of clay minerals in the nature. However, structure and physical phenomena arising at molecular level in organoclays, and subsequently in PCNs, are not completely or difficultly accessible with existing experimental techniques. In this work, molecular dynamics (MD) simulation was conducted using the combination of two force fields (CLAYFF and CHARMM) to evaluate the thermodynamics and structural properties of organoclay such as heat capacities, isothermal bulk modulus, density, basal spacing and chains arrangement in the interlayer spacing. Our results regarding the basal spacing and density are in fairly good agreement with available experimental data. This allows us to validate the use of the two force fields to represent interactions in organoclays. The effect of the cation exchange capacity (CEC) on the basal spacing and the thermodynamics properties is assessed. We found, through our MD simulation, that the calculated isothermal bulk modulus is in good agreement with the density value of organoclays with two different CEC.

1. Introduction

During the past few years, academic and industrial researchers have expressed great interest to nanomaterials; this to master technological innovation by infinitesimal. Since the precursor work of Kojima et al. [1] and Usuki et al. [2] in Toyota Research Laboratory (Japan), polymer clay nanocomposites (PCNs) have been seen as the most novel materials in nanotechnology, and the most promising research area of the 21st century, because of their significant improvement in physical properties. Indeed, with few amount of organoclay, PCNs exhibit enhanced mechanical, optical, thermal and liquid or gas barrier properties [3–5] compared to pure polymers and to their counterpart microcomposites. The lightweight and the high availability of the clay minerals in the nature, make this new class of nanomaterials as a perfect candidate in several engineering applications. However, the mechanisms of properties improvement at atomistic scale are not well understood to date. Their development

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for specific applications, via effective characterization technique, is a challenge that seeks to address the experiment; and the prediction of their physical properties is not an easy task, especially as we are dealing with finer scale modeling and new physical phenomena. The knowledge and the quantification of these physical phenomena such as molecular interactions among PCNs constituents are important to better devise PCNs with tailored properties for well defined applications.

Montmorillonite (MMT) clay, with periodic layered structure such as 2:1 phyllosilicates minerals, is widely used as nanoparticles in the synthesis of PCNs because of its good swelling property in presence of water. The hydrophilic nature of MMT clay leads to an incompatibility with the majority of organophilic polymers generally hydrophobic. Thus, to promote the miscibility of polymer with MMT clay, the latter is treated with organic modifiers such as quaternary alkylammonium salts or aminoacids. Organophilization of clays affects considerably the microstructure and thus the physical properties of PCNs. Molecular dynamics (MD) studies of interactions among constituents of PCNs, structural properties as well as interlayer spacing, arrangement and conformation of organic modifiers and polymer chains in the interlayer gallery, and physical properties of PCNs are a useful research way to provide a better understanding the mechanisms of properties improvement and a help for design PCNs.

Some of our previous works have been devoted to clay systems in order to understand the swelling and shrinking behaviors [6,7], the diffusion of cations in interlayer space [8,9], the thermodynamics and mechanical properties of clays [10–13], the interaction between radionucleides and clay surface [14,15] and pressure effect on the clay portions [16]. More recent studies have addressed the mechanical properties of nanocomposites using experimental and micromechanics-based approaches [17,18] as well as MD simulations [19].

Significant investigations, using MD and density functional theory (DFT) simulations, have been done by several authors to probe the structure and chains arrangement, and to evaluate molecular interactions involving in organoclay and PCNs [19–38]. The influence of cation exchange capacity (CEC), chain length and functional head group of organic modifiers on the structural properties and arrangement of molecular chains and layering behavior in organo-modified MMT clay and PCNs has been recently studied independently by Katti et al. [23], Sikdar et al. [26–30] and Zeng et al. [32–36] to name a few. Zeng et al. [32–36] have shown that the arrangement of organic modifier chains in the clay galleries is flat and parallel to the interlayer clay surface. They have proved that the basal spacing of organoclay increases when chains length and the value of CEC increase. Tanaka and Goettler [31] have used MD simulation to estimate the binding energy between the constituents of exfoliated nylon 6,6 clay nanocomposites with 12 different quaternary alkylammonium salts modified clay. Sikdar et al. [27–29] have demonstrated that, in organo-modified MMT clay and PCN, organic modifiers and polymer exhibit strong nonbonded attractive interactions with clay, and repulsive–attractive significant interactions between themselves. The organic modifiers acting as conductive medium for polymer interactions with clay, disturb significantly the semi-crystalline polymer matrix in PCNs and hence the physical properties due to the differences in interactions between constituents [27,29,30]. By MD simulation, the effect of CEC, chain length and heat group on the cleavage energy of organo-modified MMT clay has been assessed by Fu and Heinz [37] using 50 different quaternary alkylammonium salts. Total cleavage energy is high when CEC and chain length increase. Recently, Xu et al. [38] have calculated Young's modulus of exfoliated clay and partially intercalated clay clusters in PCNs via MD technique. However, the physical and mechanical properties of organoclay and PCNs have been, in our knowledge, little or not fully investigated to date.

In this work, MD simulation is used to predict the structural and thermodynamics properties of organoclay with two different CEC; the influence of the value of CEC on these properties is estimated.

2. Construction of organoclay systems

We use here sodium montmorillonite (Na-MMT) in which the sodium cations Na^+ are the only chemical species present in the interlayer space. This clay is usually used in the synthesis of PCNs because of its swelling property, its large specific surface and its CEC with ionic species in solution. MMT is a smectite clay mineral, which belongs to the family of phyllosilicates with 2:1 structure [39] in which alumina (Al_2O_3) octahedral layer is sandwiched between two silica (SiO_4) tetrahedral layers. Isomorphic substitutions occur in the octahedral and tetrahedral layers of MMT sheets. However, the charge of MMT sheets mainly depends on octahedral substitutions where aluminum cation (Al^{3+}) is replaced by magnesium cation (Mg^{2+}). Chemical species are naturally captured by clay to balance charges deficit to the isomorphic substitutions. The chemical composition of a dried Na-MMT unit cell, depending on these isomorphic substitutions and deposit extraction, used in this work is given by

$$Na_{\alpha}Al_{4-\alpha}Mg_{\alpha}Si_8O_{20}(OH)_4 \quad (1)$$

where α represents the charge of the MMT sheet arising from the isomorphic substitutions. The atoms positions in the MMT sheet of dimensions $5.28 \times 9.14 \times 6.56$ are extracted from the work of Skipper et al. [40]. Two kinds of organoclay systems are constructed based on the value of the parameter α

- $Na_{0.5}Al_{3.5}Mg_{0.5}Si_8O_{20}(OH)_4$ (CEC=68 meq/100 g)
- $Na_{0.67}Al_{3.33}Mg_{0.67}Si_8O_{20}(OH)_4$ (CEC=91 meq/100 g)

The initial configuration of Na-MMT unit cell is $a = 5.28$ Å, $b = 9.14$ Å, $c = 19.6$ Å and $\alpha = \beta = \gamma = 90^\circ$. The third dimension c is chosen arbitrary close to the maximum basal spacing d_{001} of hydrated MMT clay to avoid any critical assumption on this value. Indeed, for an amount of water molecules ranging from 0 to 30%, clay swells from 9.6 to 19.6 Å [26]. Zeng et al. [34] choose this value close to the experimental results available in the literature. The sodium atoms are inserted at the middle of the interlayer space of the Na-MMT clay unit cell. The organic modifier chains (MT2EtOH) are sketched and used to build the initial configuration of the organoclay systems by substituting sodium cations. The construction of the aliphatic chain named tallow, connected to the amine functional group in Fig. 1, depends on its composition of carbon atoms ($\approx 65\%$ C_{18}, $\approx 30\%$ C_{16}, $\approx 5\%$ C_{14}). For simplicity, the tallow was constructed with an assumption that all the chains in this molecule are composed with 100% C_{18}.

The periodic MD simulation supercell of each organoclay system contains 18 unit cells of MMT sheet i.e. 6 in X-direction and 3 in Y-direction, resulting in dimensions of a=31.68 Å, b=27.42 Å and c=19.6 Å; and consequently producing a charge deficiency of -9 and -12 in each MMT clay sheet respectively for CEC = 68 meq/100 g and CEC = 91 meq/100 g. Thus, 9 and 12 sodium cations are replaced respectively with equivalent numbers of the organic modifiers to conserve the electroneutrality. The initial configurations of organoclay systems are shown in Fig. 2. MD simulation cell is marked with dotted box.

3. Simulation details

In this study, MD simulation as implemented in DL_POLY code [41] is conducted using the combination of two force fields to