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Swelling and dimensional stability of xyloglucan/montmorillonite nanocomposites in moist conditions from molecular dynamics simulations

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ABSTRACT

Nacre-mimetic biocomposites made from the combination of montmorillonite clay and the hemicellulose xyloglucan give materials that retain much of their material properties even at high relative humidity. Here, a model composite system consisting of two clay platelets intercalated by xyloglucan oligomers was studied at different levels of hydration using molecular dynamics simulations, and compared to the pure clay. It was found that xyloglucan inhibits swelling of the clay at low water contents by promoting the formation of nano-sized voids that fill with water without affecting the material's dimensions. At higher water contents the XG itself swells, but at the same time maintaining contact with both platelets across the gallery, thereby acting as a physical cross-linker in a manner similar to the role of XG in the plant cell wall.

1. Introduction

The field of clay-polymer composite materials took a huge leap forward when a new class of nanocomposites emerged in the early 2000s as the group of Kotov et al. conceived the first "nacre-mimetic" material [32,28,29]. They used high volume fraction Mnt clay combined with organic polymers in an intricate, but tedious, layer-by-layer process to mimic the brick-and-mortar structure of natural nacre, thereby achieving extraordinary nanostructural control leading to materials that were unusually strong and stiff. Later, the concept was further developed by Walther et al. who utilized self-assembly of clay nanoparticles and polymers in a process similar to papermaking [33,34].

Moisture is a problem for biocomposites in general [1], and for nacre-mimetics in particular [25,26]. Mnt clay in its pure form is highly hygroscopic, and at elevated relative humidity (RH) the moisture uptake of these materials is significant. This leads loss of mechanical performance [32], presumably by weakening the interactions between the clay and the polymer phase leading to poor stress transfer. One successful solution to this problem has been to use chemical cross-linking between the phases, which greatly improved the mechanical properties at high RH [28,29,33,34,25,26]. It would however turn out that there is a much simpler route to this end.

Hemicelluloses are structural polysaccharides that act as physical cross-linkers of cellulose microfibrils in the plant cell wall [12], helping the organism to maintain structural integrity and mechanical properties even at very high levels of hydration. Inspired by this fact, Kochumalayil et al. [25,26] showed that by using tamarind seed xyloglucan (XG), a hemicellulose found in the primary cell wall of plants, the mechanical properties of a clay-polymer nanocomposite was preserved even at high RH, without the need for chemical modification. This was due to unexpectedly strong interaction between the XG and Mnt, also in the hydrated state, a view that was later supported by molecular dynamics simulations [36–38].

Pure Mnt clay exhibits substantial swelling with increasing RH [17,14,11]. This becomes a huge technical problem for the stability of bore-holes in oil and gas exploration, which has inspired large endeavors in the research for effective swelling-inhibitors to be used in water-based drilling fluids [2]. Here, one important class of inhibitors consists of uncharged, water-soluble polymers of relatively low molecular weight, which inhibits swelling by intercalating between the clay platelets.

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Swelling due to the adsorption of water but is also of considerable concern in composite materials where as little movement as possible with variations in RH is desirable. Based on the experiences from the oil and gas fields, it is likely that the swelling of a clay-polymer nanocomposite can be minimized by using a suitable polymer matrix. Bains et al. [4] used computer simulations of Mnt clay intercalated with a large variety of organic polymers to study swelling as function of water content. They concluded that the best inhibitors were linear organic polymers with both significant hydrophobic and hydrophilic regions, which, incidentally, is a description that fits polysaccharides well.

Atomistic computer simulation has evolved over the last decade to a suitable tool for tackling problems in materials science in general, and in the field of clay-polymer composites in particular, both at atomistic detail [18,13,19,9,8], and, recently, with the use of coarse-grained multiscale models [30,31].

In the present work we use extensive atomistic molecular dynamics simulations, based on our previous work on polysaccharide adsorption to clay [36–38], to look at the dimensional stability of an XG/Na-Mnt nanocomposite by studying the swelling as a function of water content. The model nanocomposite system is characterized with respect to intergallery spacing, distributions of polymer, water and counter ions in the galleries, and polymer conformational properties, at different levels of hydration. Results from the composite system are compared to those for pure Mnt clay.

2. Methods

2.1. Model

A two-sheet Na-Mnt clay model was built by replicating a crystal super-cell ($1.036 \times 1.796 \times 0.662\ nm^3$) six times in the *x* direction, 4 times in *y*, and 2 times in the *z* direction. The supercell was comprised of four Mnt unit cells and had chemical formula $Na_3[(Si_{31}Al)](Al_{14}Mg_2)O_{80}(OH)_{16}{\cdot}16H_2O$, which was overall neutral due to the presence of Na+ counter ions. The initial interlayer spacing d_{001} was set to 2.26 nm. Four XG chains were placed in each interlayer (eight chains in total) between the two Mnt sheets as shown in Fig. 1. Each XG chain consisted of nine β1-4 linked glucose units with side chains according to the sequence GXXLGXXXG, where G stands for unsubstituted β-D-glucose, X stands for β-D-glucose with a β-1-6 linked xylose, and L stands for an X unit with an additional galactose α-1-2 linked to the xylose. This composition is representative of native xyloglucan found in, e.g., Tamarind seeds [25,26]. The initial placement of XG is in a sense highly superficial, since it is not likely that the oligomers would be so perfectly oriented in a real composite material. However, this configuration can be viewed as a representation of the most compact structure attainable, giving the smallest possible *d* spacing at low water contents. The long equilibration runs ensures that the XG adopt its most favorable conformation, within the constraints imposed by the confinement.

In the hydrated Mnt and XG-Mnt systems, water molecules were placed randomly in the free space between the sheets, to reach a water content of 0.42 g/g (grams of water per 1 g of Mnt clay). This number is representative of the water content in the pure clay when the relative humidity approaches 100% [17] and was thus used as the maximum water content in the present study. Consequently, all simulations correspond to a specific water content found along the Mnt-vapor adsorption/desorption isotherm.

2.2. Computational details

All simulations were performed using the GROMACS/4.6.5 package [21]. VMD/1.9.1 [22] was employed for trajectory visualization and analysis. A combined force field, CLAYFF [14] and GLYCAM06 [24] was used to model the inorganic Na-Mnt clay mineral and the organic polysaccharide XG, respectively. Both force fields use the same protocol for defining partial charges, and can therefor be expected to give reasonable electrostatic energies when mixed. This particular combination has also been used before in our previous studies [38,36,37]. Finally, the SPC model [6] was used for the water.

A completely dry model consisting of the clay sheets with intercalated XG was studied. First, energy minimization was carried out for 50,000 steps. Next, the system was equilibrated in the *NVT* (constant number of atoms, volume and temperature) ensemble for 500 ps, at 298 K, followed by a 5 ns production run in the *NpT* (constant number of atoms, pressure and temperature) ensemble with $T = 298$ K and $p = 1$ bar. The time step was set to 2 fs and data were saved every 2 ps.

For the hydrated systems, both the XG-Mnt and the pure clay were equilibrated at a water content of 0.42 g/g. Next, 96 water molecules at a time were removed to reduce the hydration level in the XG-Mnt system, while 48 water molecules at a time were removed in the pure Mnt clay system. The resulting system after each removal was subjected to energy minimization and *NVT* equilibration, followed by an initial 20 ns simulation under *NpT* conditions where the first 3 ns were subject an annealing process with a linearly increasing temperature from $T = 298$ K to $T = 450$ K. The high temperature simulations was performed in an attempt to speed the sampling of the XG conformational space, which in this case is even slower than for XG in solution due to effects of the

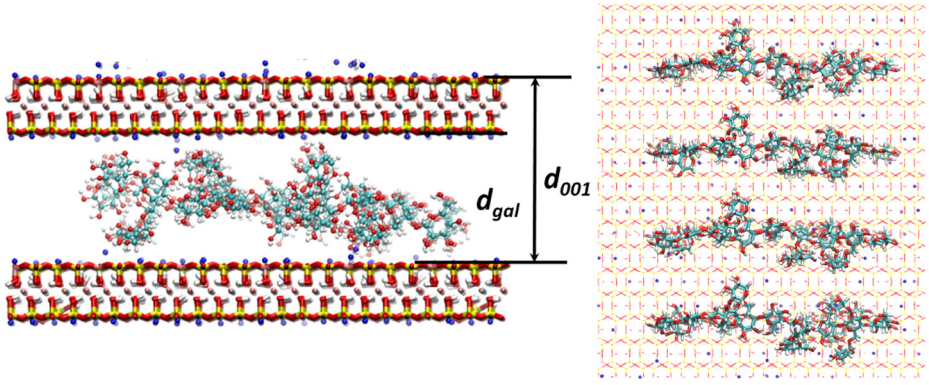

Fig. 1. Molecular model of XG/Na-Mnt intercalated system. Note that due to periodic boundary conditions there is actually another layer of four XG oligomers included in the computational box. This is not shown for clarity. Left: front view of the molecular system; right: the top view of the molecular model. Color scheme: hydrogen: white; oxygen: red; sodium: blue; carbon: cyan; aluminum: pink; magnesium: light blue; silicon: yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)