CLAY-STARCH NANOCOMPOSITE COATINGS ON PAPER SUBSTRATE - A PROMISING FRONTIER IN ENVIRONMENTALLY FRIENDLY PACKAGING MATERIAL

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Abstract. The growing concern for environmental sustainability has created an urgent need for the development of innovative and environmentally friendly packaging materials. Among the various options available, clay-starch nanocomposites have emerged as a promising avenue for improving the barrier properties and mechanical strength of paper substrates. In this scientific paper the importance of clay-starch nanocomposite coatings on paper substrate and highlight the role of computer simulations, especially molecular dynamics, in elucidating their structural and functional properties. It has been shown that phyllosilicates with a layer charge < 0.4 electrons per stoichiometric unit can intercalate starch in the interlayer space, forming a barrier for water vapor in the covering layer. Phyllosilicates with a shell charge of > 0.4 electrons per stoichiometric unit were not able to intercalate starch. Thus, clay-starch nanocomposites can provide limited water vapor transfer rates and can be recommended as a promising material for dry food packaging.

Keywords: *Molecular dynamics, montmorillonite, clay, water, diffusion, clay-coatings.*

Rezumat. Preocuparea tot mai mare pentru sustenabilitatea mediului a creat necesitatea urgentă de dezvoltare a materialelor de ambalare inovatoare şi ecologice. Printre diferitele opţiuni disponibile, nanocompozitele argilă-amidon prezintă o cale promiţătoare pentru îmbunătăţirea proprietăţilor de barieră şi a rezistenţei mecanice a substraturilor de hârtie. În această lucrare se evidenţiază importanţa acoperirilor nanocompozite argilo-amidon pe substrat de hârtie şi rolul simulărilor pe computer, în special a dinamicii moleculare în elucidarea proprietăţilor structurale şi funcţionale ale acestora. S-a demonstrat, că filosilicaţii cu o sarcină a stratului < 0,4 electroni pe unitate stoechiometrică pot intercala amidonul în spaţiul interstrat, formând o barieră pentru vaporii de apă în stratul de acoperire. Filosilicaţii cu o sarcină de înveliş > 0,4 electroni per unitate stoechiometrică nu au fost capabili să intercaleze amidonul. Astfel, nanocompozitele argilă-amidon pot asigura viteze limitate de transfer al vaporilor de apă şi pot fi recomandate ca material de perspectivă pentru ambalarea produselor alimentare uscate.

Cuvinte cheie: *dinamică moleculară, montmorillonit, argilă, apă, difuzie, acoperiri cu argilă.*

Abbreviations;

   MD – Molecular Dynamics;
   NaMt – Na^+-Montmorillonite;
   CaMt – Ca^{2+}-Montmorillonite;
   Th – Tetrahedral clay sheet;
   Oh – Octahedral clay sheet;
   AML – Amylose;
   PEG200 – Poly(ethylene) glycol, MW = 200 g/mol
   ADP – Atomic density profile.

1. Introduction

The ever-increasing demand for packaging materials, driven by the global rise in consumption and e-commerce, has led to the accumulation of vast amounts of non-biodegradable waste, causing significant environmental concerns. Addressing this issue necessitates the development of sustainable packaging solutions that minimize environmental impact while maintaining the required mechanical and barrier properties [1]. In this context, clay-starch nanocomposites have garnered substantial attention due to their unique combination of renewable and abundant components, as well as their potential to improve the performance of traditional paper-based packaging materials.

In the domain of packaging applications, starch is one of the promising biopolymer materials, because it is renewable, low in price, fully biodegradable and rather importantly, approved for food contact [2-5]. Starch based paper coatings improved barrier to water vapour, reducing water vapour transmission rate (WVTR) from 800 g/m^2.day for untreated paper down to 400 g/m^2.day for paper coated with starch and poly(ethylene glycol) [6]. The incorporation of clay minerals into different polymeric matrices has drawn a particular interest due to their potential to improve the barrier properties of formulated coatings. When montmorillonite clay was added to starch polymer matrix, the barrier properties were significantly improved, reducing the WVTR to lower than 200 g/m^2.d [7]. Furthermore, adding PEG to the starch/clay nanocomposite plummet the WVTR to remarkable 10 g/m^2.d [5, 6], which is competitive with some of the conventional latexes.

Clay minerals, such as montmorillonite, possess layered structures consisting of stacked silicate sheets, with exchangeable cations in the interlayer spaces [8]. The incorporation of clay nanoparticles into starch matrices creates a synergistic effect, resulting in nanocomposites with enhanced mechanical strength, gas barrier properties, and thermal stability. These characteristics make clay-starch nanocomposites highly suitable for coating applications on paper substrates, imparting them with improved functionalities. The clay type and, in particular, layer charge distribution, however, has significant effect on the barrier properties of formulated coatings. In some studies addition of montmorillonite (Mt) sometimes had no effect or even a slight negative effect on the resultant barrier properties [9-11]. One explanation of that has been difference in the polymer intercalation dynamics for various Mts [5, 6]. It was concluded that starch-PEG/clay based coatings would have good barrier properties only when both starch and plasticiser coexist in the interlayer of clay. Adsorbed PEG onto the Mt surfaces forms a strongly constrained layer with very low oxygen permeability [6]. The organisation of plasticiser and bio-polymer in the clay interlayer, however, is not accessible through experimental techniques. Therefore, molecular simulation of PEG-starch/clay nanocomposites may provide insight on the nanocomposite interlayer

structure in relation to the clay type, and, as a result on the mechanism of the formation of coatings with high barrier properties.

Computer simulations, particularly molecular dynamics (MD), have emerged as indispensable tools for investigating the behavior and properties of materials at the atomic and molecular scales. By simulating the interactions between clay nanoparticles, starch molecules, and the paper matrix, MD simulations enable researchers to gain valuable insights into the structural organization, interfacial interactions, and mechanical behavior of clay-starch nanocomposite coatings [3, 4, 12, 13]. Furthermore, MD simulations facilitate the exploration of the effects of various processing parameters, such as temperature, humidity, and nanoparticle concentration, on the overall performance of the coating material.

In this paper, we present a comprehensive study on the computational modeling of clay-starch nanocomposite coatings. Our work aims to elucidate the mechanisms underlying the improved barrier properties and mechanical strength exhibited by these coatings. Through systematic molecular dynamics simulations, we investigate the nanoscale interactions between clay nanoparticles, starch molecules, and the paper matrix, considering different clay loadings and coating architectures. Additionally, we explore the influence of processing conditions on the structural arrangement and properties of the nanocomposite coatings.

The findings of this research will provide critical insights into the design and optimization of clay-starch nanocomposite coatings for environmentally friendly packaging materials. By harnessing the advantages of computer simulations, we can accelerate the development of novel coatings with enhanced performance, reduced environmental impact, and improved recyclability.

2. Materials and Methods

The model framework for Montmorillonite (Mt) was generated from a pyrophyllite crystal structure. A number of Mt models were investigated with a selection of charge locations and two exchange cations (Na^+, Ca^{2+}). Starch is one popular natural polymer material due to the fact that it can be easily produced from plants, e.g. potato, corn, cassava etc. [14]. Starch consists of two types of molecules; amylose (AML) and amylopectin. It it generally accepted that amylose is amorphous polymer whereas amylopectin has semicrystalline structure [14]. Through analysis of the XRD traces of the thermoplastic starch plasticised with urea, it was shown that freshly prepared nanocomposite contained starch in its amorphous form [15]. Therefore, for our computer simulations we created a model of amorphous amylose to represent starch/clay interactions. Amylose is a spiral polymer made up of D-glucose units. Each molecule of amylose in the developed model consisted of five D-glucose units resulting in total molecular weight of 828.7 g·mol^{-1}. The initial binary and tri-systems were constructed by randomly distributed Amylose (AML) or AML and Poly(ethylene) glycol (PEG200) molecules with pre-equilibrated water molecules at desired ratios. Starting amylose and water content for AML/Mt system was 0.7 g_{AML}/g_{clay} and 0.07 $gH_2O/gclay$ respectively. Water content of 7 wt% is reported from experimental observation of starch based clay nanocomposites [16]. For AML-PEG/Mt system, a broad range of PEG200 and H_2O concentrations, ranging from 0 to 0.35 g_{PEG200}/g_{clay} (0 to ~7.1 PEG200·uc-1) and 0 to 0.2 $gH_2O/gclay$ (0 to ~16.5 $H_2O·uc^{-1}$) respectively were used (Figure 1).

Molecular Dynamics simulation is a technique used to compute the equilibrium and transport properties of a classical many-body system by using essential information about a

system's dynamics, usually resolved at atomistic detail. Molecular dynamics simulations were performed using the Nosé-Hoover thermostat and DL_POLY simulation package [17] with a 1.0 ps relaxation time. For the NPT simulations, a Nosé-Hoover barostat was utilised to control the pressure. Interatomic interactions were evaluated using a time step of 0.001 ps, and three-dimensional periodic boundary conditions were employed with a cutoff of 15 Å for short-range interactions. Interatomic potentials for the clay and interlayer ions were obtained from the CLAYFF force field developed by Cygan et al. [18]. Each atom in CLAYFF force field has an assigned partial charge derived from DFT calculations, and the flexible TIP3P/Fs water model [19] is incorporated to describe water.

3. Results and Discussion

A. Adsorption Thermodynamics

The adsorption analysis employs a simple model of montmorillonite – amylose interface, containing one layer of Mt and one single chain of AML. MD simulations were used in order to investigate the adsorption process of AML on hydrated clays and influence of clay charge location on this process. The simulation cell of this model is shown in Figure 1. The free energy of adsorption was calculated from potentials of mean force (PMF).
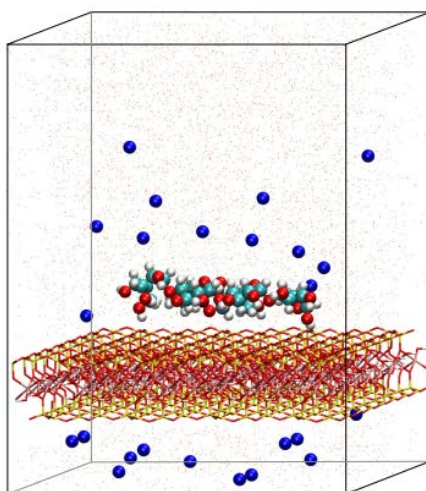
Figure 1. Starting structure of the AML/Mt adsorption model. The centre of mass of single amylose molecule in aqueous environment is positioned at 3.5 Å above the clay surface.

Each AML was placed parallel to the selected Mt surface with its centre of mass at a distance of 3.5 Å above the surface. Two main orientations of amylose molecule were considered – parallel to (100) direction (Fig. 2(a)) and parallel to (010) direction (Fig. 2(b)). Thereafter, into each system 2400 of pre-equilibrated H_2O molecules were added.

(a)   (b)
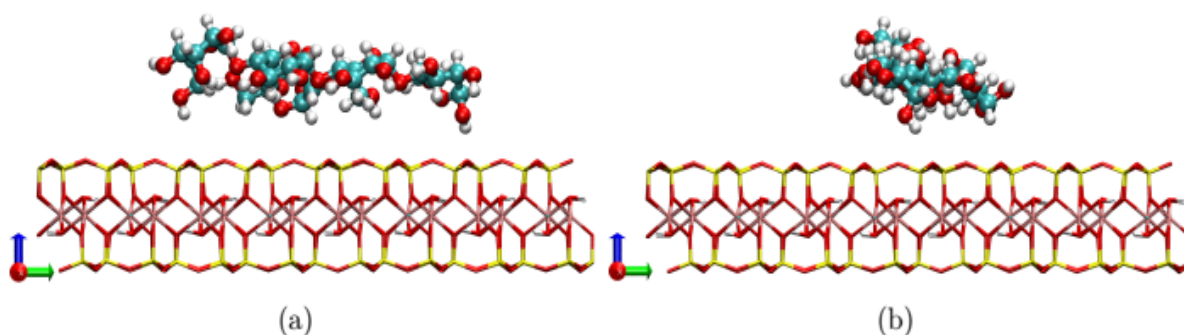
Figure 2. Definition of the AML orientations of te AML/Mt adsorption model. The amylose molecule is oriented along (a) (010) and (b) (100).

All simulations were performed in NPT ensemble at 300 K and 1 atm. The simulation timestep was 1 fs. Simulation lasted for 10 ns. The data from final 5 ns was used for analysis. All bonds were constrained. The equilibration was established through monitoring two parameters – structural and energetical stability. Structural stability of a molecule was assessed by calculating the root-mean-square deviation (RMSD) of AML molecule. Energy stability was judged by the total instantaneous interaction energy between the AML and Mt, which is defined as;

$$E_{int}(t) = E_{AML+Mt}(t) - E_{AML}(t) - E_{Mt}(t),$$ (1)

where E_{int} refers to the interaction energy between the AML and Mt, E_{AML+Mt} is the total energy of the AML and Mt, and E_{AML} and E_{Mt} are the internal energies of AML and Mt, respectively. The instantaneous RMSD of the AML and interaction energy between the AML and Mt are presented in Figures 3(a) and 3(b), respectively. All twelve studied models reached equilibration at around 4 ns of the MD simulation. Therefore, the data from final 5 ns was used for analyses.
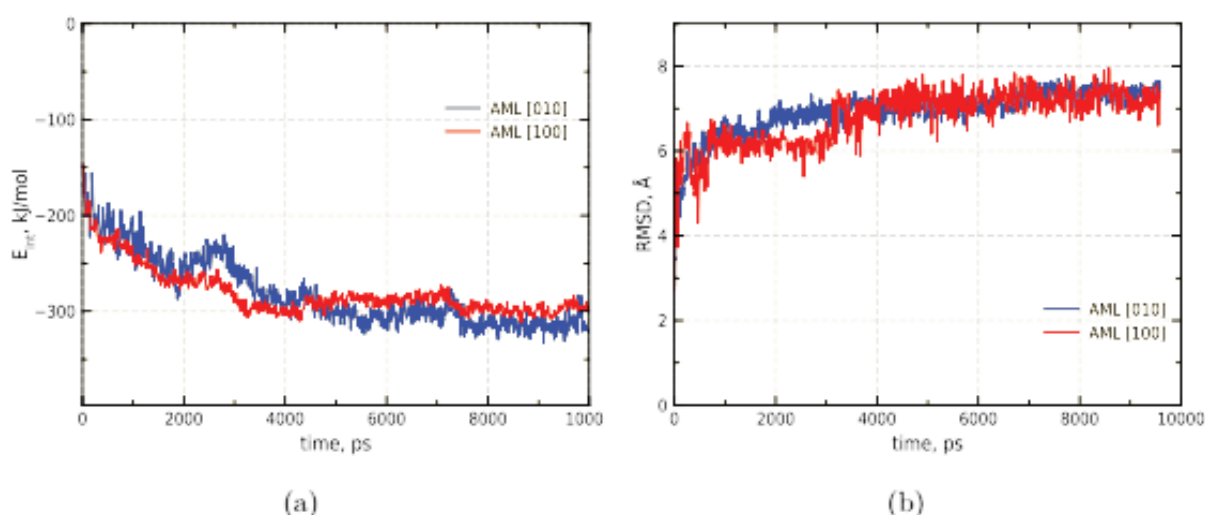

Figure 3. Variation of (a) E_{int} and (b) RMSD of amylose molecules adsorbed onto NaMt in different adsorption configurations with simulation time.

B. Swelling Dynamics and Interlayer Structure

A total of 12 simulated swelling curves for NaMt and CaMt models are shown in Figures 4 and 5, respectively. Error bars based on standard deviation calculated from block averaging over the last 1 ns of simulations are less than data symbol, therefore are not visible on the plots.

Unlike swelling curves of hydrated montmorillonite or PEG/Mt systems, intercalation of amylose in the Mt do not suggest formation of highly ordered polymer structures within the interlayer. Most simulated clays swell gradually with increase of polymer content in the interlayer until reaching an "equilibrated" basal spacing of ~21-22 Å. Similar d-spacings were observed by many experimentalists who were investigating intercalation of starch in montmorillonites under ambient conditions [6-9]. This is revealed as a plateau at higher AML content on all simulated swelling curves (Figures 4 and 5). It is very important result obtained from simulation and indicates the preferable interlayer organisation of amylose.

Distribution of carbon atoms for all studied systems suggests formation of pseudo bilayer of starch in the interlayer. Amylose can produce larger number of conformations than PEG, therefore its ADPs are so distorted (Fig. 6).
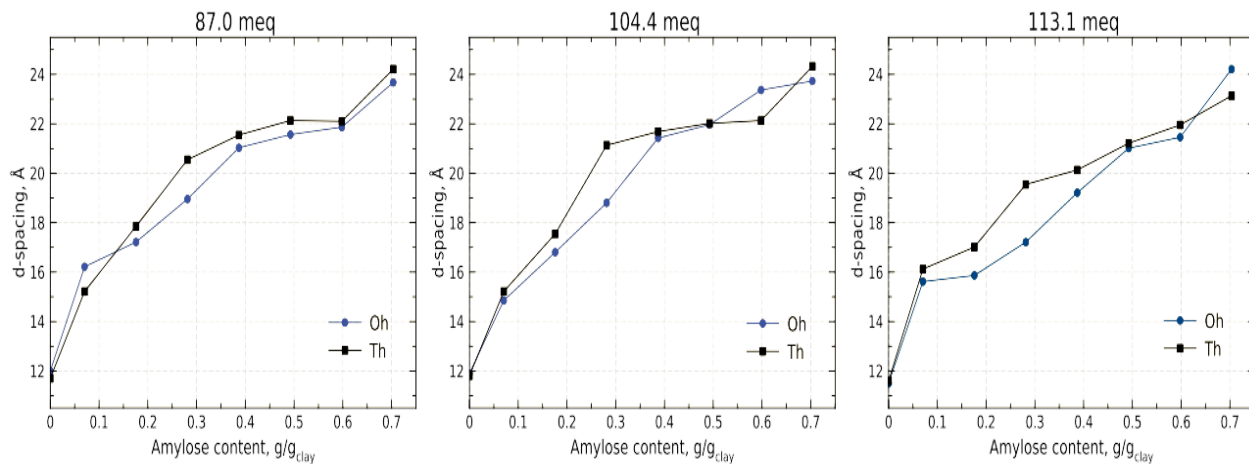
Figure 4. Swelling curves of NaMt as a function of amylose content in the interlayer from MD simulations at 300 K and 1 atm. Swelling curves are shown for clays with various net charge distribution.
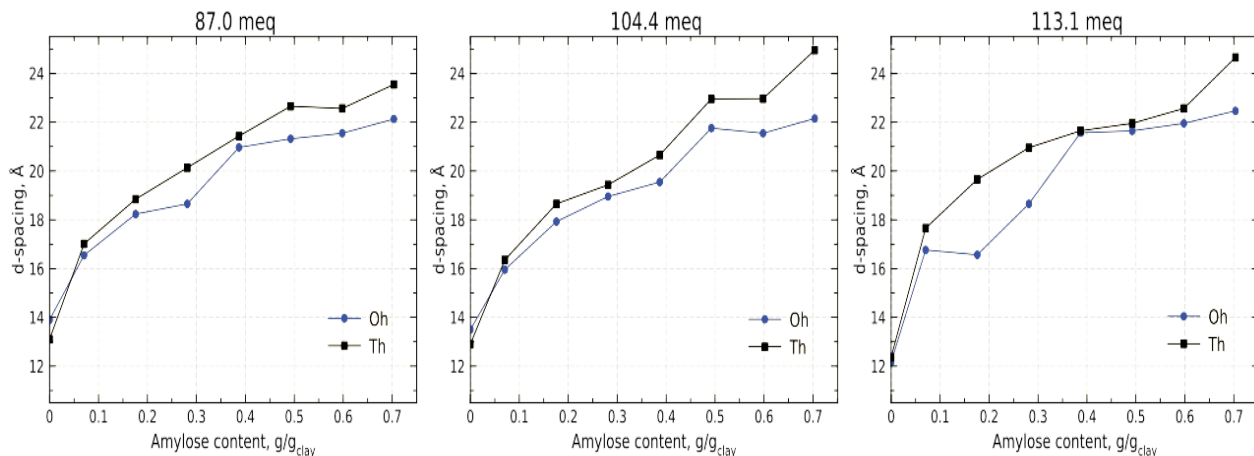

Figure 5. Swelling curves of CaMt as a function of amylose content in the interlayer from MD simulations at 300 K and 1 atm. Swelling curves are shown for clays with various net charge distribution.

Interestingly, even at relatively low water concentration ($\sim$0.07 g_{H2O}/g_{clay}), a water bilayer is found in the interlayers of all samples. It is expelled from the middle of the interlayer and distinct, sharp OW peaks are positioned between the basal surface of clay and layer of AML indicating hydrophilic nature of amylose and formation of a network of hydrogen bonds. Similar behaviour is right for the divalent exchangeable cations.

Another peculiar conclusion that can be drawn from the simulated swelling curves is that spacings of AML/Mt nanocomposites based on the low charge clays are overall higher by approximately 0.9-1.2 Å in the region of 0.3 g_{AML}/g_{clay} than those that are based on the high charge clays. Similar conclusion was drawn from investigation of barrier properties of starch-clay nanocomposites based on various clay types [4, 20, 21]. There are evidences that high charge clay do not uptake starch in the interlayer at all [8]. It is, however impossible to investigate directly by the methods presented here, as content of organic material in the interlayer is fixed and cannot escape from the clay gallery.

Clays with isomorphous substitutions occurring in tetrahedral sheet (Th charge) produce higher basal spacing compared to those with charge deficit in the octahedral sheet (Oh charge).
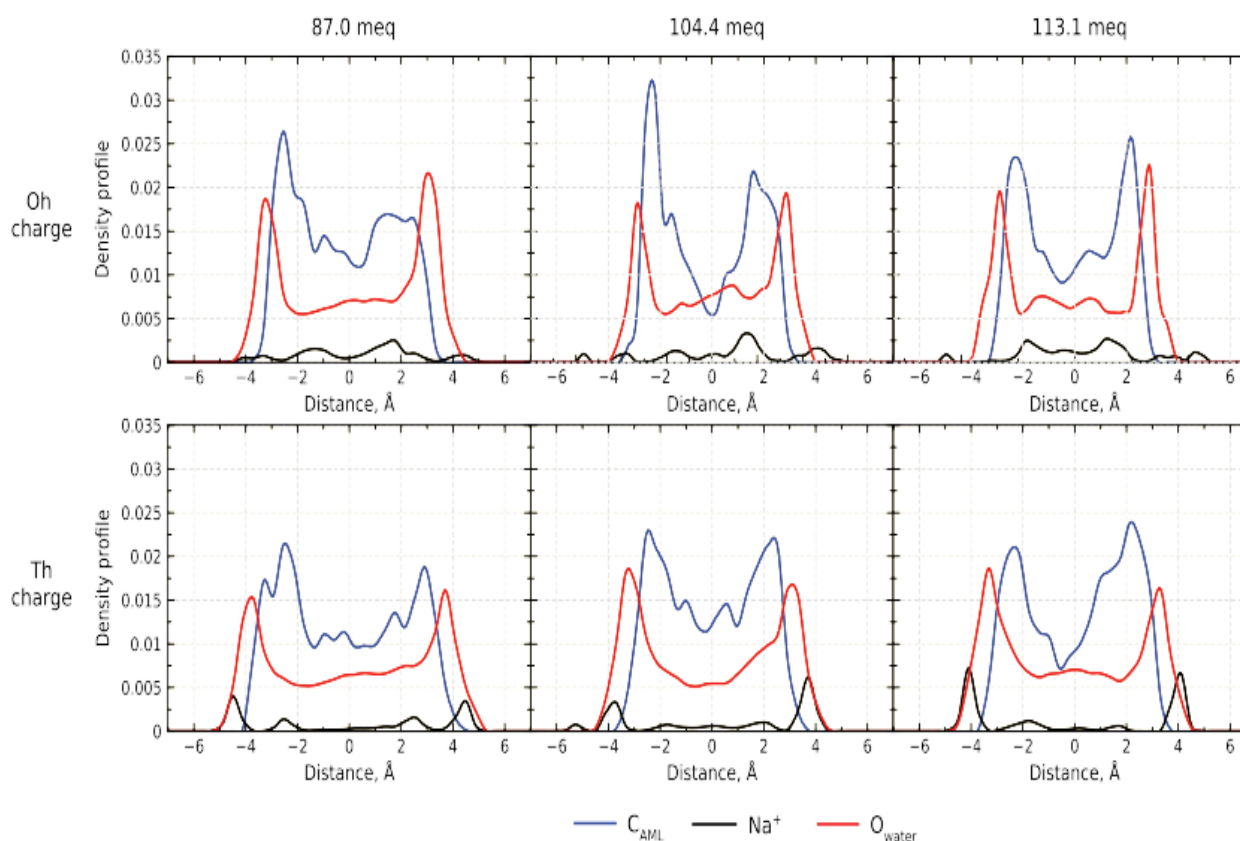
Figure 6. Atomic density profiles from MD simulations at 300 K and 1 atm for AML/NaMt nanocomposite. Amylose backbone carbon atom (C_{AML} – blue curve), sodium (Na^+ - black curve) and water (O_{water} - red curve). Left to right increases clay layer charge.

The reason for that is primarily due to the distribution of exchangeable cation within the interlayer of AML/Mt nanocomposite which is illustrated in Figure 6 as atomic density profile along the *c*-axis normal to the basal surface of clay. Strong association between exchangeable cations and substitution sites in the tetrahedral sheet of clay, and low diffusivity of cations and amylose, results in most of them being located between the clay layer and amylose molecules. Additionally, exchangeable cations in the high charge clay with charge deficit in the octahedral sheet form anhydrous adsorption complex more readily. This opens up space for organic material, leading to overall smaller basal spacing.

Conclusions

In this study, we employed molecular dynamics simulations to investigate the intercalation process and predict the structure of clay-starch nanocomposite coatings, with the aim of developing sustainable barrier materials for the packaging industry. We observed that the intercalation process occurs in distinct stages. Initially, the clay nanoparticles disperse in the starch matrix, forming stable nanocomposite structures. As the intercalation progresses, the clay particles gradually penetrate the spaces between the starch molecules, resulting in an intercalated structure. The interlayer spacing and interfacial interactions play crucial roles in determining the mechanical strength and barrier properties of the resulting coating material.

Based on our simulations, we can confidently predict the structure of the formulated clay-starch nanocomposite coatings. The intercalated structure exhibits an ordered arrangement of clay layers within the starch matrix, providing enhanced barrier properties

against gas permeation. The formulated clay-starch nanocomposite coatings hold great promise as sustainable barrier materials in the packaging industry. In conclusion, our molecular dynamics simulations have provided valuable insights into the intercalation process and predicted the structure of clay-starch nanocomposite coatings. These coatings demonstrate immense potential as sustainable barrier materials in the packaging industry, offering enhanced gas barrier properties and mechanical strength. This research paves the way for the design and optimization of environmentally friendly packaging materials, contributing to a greener and more sustainable future.

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