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CLAY-POLYMER NANOCOMPOSITE STRUCTURES FOR FOOD PACKAGING

253.06 Biological and chemical technologies in the food industry

Abstract of the PhD dissertation

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The summary and the PhD dissertation can be consulted at the library of the Technical University of Moldova as well as on the ANACEC website (www.anacip.md).
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CONTENTS

LIST OF ABREVIATIONS

MD	Molecular Dynamics
FF	Force Field
RDF	Radial distribution function
ADP	Atomic density profile
MSD	Mean Square Displacement
TGA	Thermogravimetric analysis
dTG	Negative derivatives of thermogravimetric curves
TGMS	Thermogravimetric mass spectrometric analysis TGMS
XRD	X-ray Diffraction
NaMt	Na^+-montmorillonite
CaMt	Ca^{2+}-montmorillonite
CEC	Cation exchange capacity
Oh	Octahedral charge
Th	Tetrahedral charge
Oh/Th	Mixed octahedral and tetrahedral charge Oh/Th
PEG	Poly(ethylene glycol) PEO Poly(ethylene oxide)
AML	Amylose
1W	Monoslayer hydrate
2W	Bilayer hydrate
3W	Three-layer hydrate
WVTR	Water vapour transmission rate
RH	Relative humidity
PMF	Mean Force Potential

CONCEPTUAL RESEARCH GUIDELINES

The actuality of the investigated topic

In recent decades, the production and use of petroleum-derived plastics has increased enormously, creating both environmental and economic problems. The European packaging industry has a market value of around €80 billion and is growing every year [1]. Food packaging is an important concept for consumer satisfaction and increasing the shelf life of food products. The introduction of new food packaging materials has become an emerging trend in recent years, which may be mainly due to environmental pollution caused by plastic packaging and to reduce food waste. Such notions as biodegradable, biocompatible, eco-friendly packaging are becoming increasingly common in the packaging literature. Strict regulations on waste recycling and material recyclability have led to demands from the food industry for more eco-efficient packaging materials.

The need for renewable biodegradable materials capable of replacing conventional, petroleum-based plastics is a growing area of research, as it offers an important advantage for the sustainable growth of the packaging industry. Of these, starch is one of the most promising biopolymeric materials because it is renewable, has a low price, is fully biodegradable and, most importantly, is permitted for food contact [2-5]. Paper coatings made from starch have demonstrated improved barrier properties, reducing the water vapor transmission rate (WVTR) from 800 g/m^2.day for untreated paper to 400 g/m^2.day [1]. Poly(ethylene glycol) has been used as a plasticizer for starch, which is known to be brittle.

Clays are another promising material. Clay minerals are a family of layered materials. They are a class of anisotropic materials whose intrasphere atoms are fixed by chemical bonds, while atoms in adjacent layers interact by physical forces (Van deer Waals). Clays have a wide range of potential and actual uses, due in part to their ability to intercalate a wide variety of inorganic and organic species. Compared to traditional composite-based fillers, it offers substantial advantages in terms of increased adhesion. Clay-based composites currently have numerous commercial and potential applications in the automotive, health care, coatings and pigments sectors, as well as in other industries [6]. Incorporation of nanoclays into the packaging matrix improves mechanical and barrier properties and at the same time prolongs the biodegradation of the packaging material [7]. The mechanical, barrier and antibacterial characteristics of nanoargil based food packaging materials can be significantly improved [8].

Description of the research situation and identification of research problems

Non-swellable clays are used in traditional paper coating technologies as they exert an insignificant effect on the rheological properties of the formed layers [9]. Analysis of the properties of montmorillonite and starch films and demonstrated by migration tests that they can be satisfactorily used according to current European regulations on biodegradable packaging [3]. The presence of swellable clays within a polymer matrix has been shown to significantly influence the barrier properties of formulated coatings [10]. This approach was further developed by Breen et al [1], who identified a particular combination of clays, starch and plasticizer to form a durable coating. Coatings applied to the paper substrate showed a remarkable WVTR of 10 g/m^2.d [1,5], being competitive with some of the conventional latexes [11].

Current experimental techniques have limited performance for investigating interlayer materials. Only rarely are sufficiently large crystals obtained for complete structural determination by conventional X-ray diffraction [12]. Powder X-ray powder diffraction (PXRD) provides some information on the overall structure of the material (e.g. interlayer spacing), but in general, intercalated clay structures are characterized by the absence of significant long-range order. Interlayer arrangements (e.g. adsorbate orientation) can sometimes be estimated from the interlayer spacing determined by PXRD measurements, but these are usually estimates based on the assumed molecular sizes of the adsorbent [13]. It is also not possible to determine whether starch or plasticizer can effectively compete with water for a place in the primary coordination sphere of cations in the gallery. It is also very difficult or impossible to identify what proportion of starch and plasticizer is present in the gallery of swelling clays [14].

Because of these limitations, there has been increasing interest in using computational methods to study these layered solids and intercalates. The role of this research is to be able to streamline experiments and predict the physical and chemical properties of the nanocomposite structures formed. The development of computer simulation techniques applied to clay materials provides insight into the structure, dynamics and reactivity of polymer clay systems [15, 16].

Aim and objectives of the research

The aim of the work was to develop new biopolymers based on Na^+- and Ca^{2+}-montmorillonite clays, polyethylene glycol and amylose; to elucidate the functions of clay, plasticizer, starch and water in the formation of nanocomposite layers using experimental and computer simulation techniques (molecular dynamics); Investigation of the mutual affinity of the components and structures formed on the barrier properties and water vapour transfer rate in order to determine the scope of application of biopolymers in the field of eco-friendly packaging.

Research objectives

1. Influence of clay layer loading size and its distribution on the hydration dynamics of smectite clay minerals in order to develop and optimize potential biopolymer modes based on polyethylene glycol, amylose and Na^+- and Ca^{2+}-montmorillonite clays.
2. Experimental and computational investigations of the molecular structure of nanocomposites in order to improve the barrier and mechanical properties of layers deposited on the basis of these biodegradable materials.
3. Simultaneous adsorption of three adsorbents - water, plasticiser and starch, determination of the relative affinity of the components and how this is influenced by the size, location and charge density of the layer and the type of exchangeable cations in the clay interlayer.
4. Reducing the rate of water vapour transfer through the interlayer space to create a barrier to reduce water vapour penetration through dry food packaging materials.

Research hypothesis

Dry food packaging made of nanocomposites based on Na^+- and Ca^{2+}-montmorillonite clays, polyethylene glycol and amylose, used as barrier coatings, would contribute to reducing oxygen and moisture permeability, thereby increasing shelf-life of products, and would decrease environmental impact by substituting petroleum-derived packaging materials.

Scientific research methodology

- The theoretical support of the thesis was made based on the analysis of the literature accessed from the electronic libraries of the Technical University of Moldova, as well as by accessing online scientific journals and open access articles.
- In order to achieve the objectives of the thesis the following research methods were used:

- Molecular Dynamics (MD) method. This technique was applied to calculate the equilibrium and transport properties of multicomponent systems using the laws of classical and quantum mechanics, with the integration of these effects.
- The three-dimensional Ewald simulation method applied to calculate Van-deer-Waals interactions and solve the slow convergence problem.
- DL_POLY software, for MD simulations of macromolecules, polymers, ionic systems and solutions on a parallel computer with distributed memory.
- CLAYFF model, which was applied to simulate realistic crystallographic parameters of clay minerals.
- X-ray diffraction method, applied to study the associated swelling behaviour of polymer/clay nanocomposites.
- Thermogravimetric analysis (TGA), which was used to investigate the distribution of water and organic materials in polymer/clay composite samples.
- Thermogravimetric mass spectrometry (TGMS), which was applied to determine the elemental composition of the examined samples.

Scientific novelty and originality

- The PhD thesis focuses on the development of potential models for computer simulation of polymer-clay nanocomposites, which is a relatively new and promising area of research.
- The study explores the effect of different parameters including clay concentration, polymer matrix and processing conditions on the properties of nanocomposites, which provides valuable insights into the behaviour of these materials.
- The thesis investigates the application of nanocomposites as barrier coatings for food packaging applications, which is a relatively new and emerging area of research with the prospect of significantly improving the shelf life of packaged products and reducing food waste.
- The paper uses a combination of theoretical and experimental methods, which presents an innovative approach and enables a more comprehensive understanding of the behaviour of polymer-clay nanocomposites.
- The research results demonstrate the effectiveness of these nanocomposites used as barrier coatings for packaging materials, such as reducing oxygen and moisture permeability, which is a significant contribution to the field of food packaging.În ansamblu, teza oferă o înțelegere cuprinzătoare a comportamentului nanocompozitelor biopolimer-argilă și a potențialelor lor aplicații drept acoperiri de barieră, ceea ce preconizează atât implicații semnificative pentru industria ambalajelor alimentare, cât și pentru domeniile știința materialelor și fizica polimerilor.
- Overall, the thesis provides a comprehensive understanding of the behaviour of biopolymer-clay nanocomposites and their potential applications as barrier coatings, which predicts both significant implications for the food packaging industry and the fields of materials science and polymer physics.

The scientific problem solved consists in developing and optimizing biopolymer models based on polyethylene glycol, amylose and Na^+ and Ca^{2+}-montmorillonite clays, describing the swelling behavior, water and biopolymer affinity for different cations; reducing the permeability and improving the barrier properties of coatings formulated based on these bio-composites.

Main scientific results submitted for support

1. The models were adapted to simulate tertiary clay-PEG-biopolymer-water systems with an optimal amount of materials.
2. Effect of rotational disorder on energetic and structural parameters of clay.
3. Effect of isomorphic substitution of Na^+- and Ca^{2+}-montmorillonite on the adsorption and distribution dynamics of intercalated water and polymer molecules.
4. Effect of exchangeable cations and isomorphic substitution on the formation of clay-biopolymer nanocomposites.
5. Distribution of biopolymers in nanocomposites, influence of mineral surface and clay structure on polymer-clay interface.
6. Formation of barrier structures and reduction of gas and vapour permeability.
7. Affinity of clays towards biopolymers as a function of layer structure and charge.
8. Structure and barrier properties of nanocomposites as a function of molecular weight and nature of biopolymer.

Approval of work in national and international scientific conferences

The main results of the PhD thesis have been presented at 12 national and international conferences:

International Conference "MTFI", Chisinau (2022); International Symposium "European Kesterite Hybrid Workshop", Copenhagen, Denmark (2022); International Conference "Materials Science and Condensed Matter Physics", Chisinau (2018); International Conference "Clay Science and Technology Euroclay", Edinburgh (2018); Symposium "CCP5 Annual Meeting", Edgmond (2017); Conference of Students, Masters and PhD Students (2020, 2022); International Conference "Nanotechnologies and Biomedical Engineering" (2021, 2023); International Conference "TIM", Timisoara (2021, 2022), Romania; The XXV International Scientific Conference of Young Scientists and Specialists (2021), Almaty, Republic of Kazakhstan.

Publications on the thesis topic

The main results of the research have been published in 12 scientific papers, including 3 articles in international journals, 2 articles in national journals and 7 articles and theses in the proceedings of national and international conferences, the full list of which is presented at the end of this Abstract and in Appendix I of the thesis.

Volume and structure of the work

The thesis consists of an introduction, five chapters, general conclusions and recommendations, a bibliography of 166 titles, 110 pages of basic text, 71 figures and 7 tables.

Keywords: *montmorillonite, biopolymers, polyethylene glycol (PEG), amylose, nanocomposites, biodegradable packaging.*

THESIS CONTENT

In the **first chapter** - ***Clay Minerals and Clay-based Composites*** a comprehensive review of clay mineral materials is presented. Special attention has been paid to the structural features of these minerals that influence the loading state of clay layers. Electric neutrality conditions were elucidated, including the presence of vacancies in tetrahedral or octahedral layers as well as in intercalated structures (smectite and mica). The specific isotherm types of swelling processes and clay-polymer interactions, as well as the preparation methods and characteristic properties of polymer/clay nanocomposites were analysed.

The **second chapter** - ***Analysis methods and computational models*** includes a detailed description of the molecular dynamics (MD) simulation techniques used, together with a comprehensive review of various potential models of water-polymer-clay systems with atomistic resolution. The molecular dynamics (MD) method has been applied to calculate the equilibrium and transport properties of multicomponent systems using the laws of classical and quantum mechanics, with integration of these effects. The three-dimensional Ewald simulation method was selected to calculate Van-deer-Waals interactions and solve the slow convergence problem. For the simulation of realistic crystallographic parameters of clay minerals the CLAYFF model was applied. Molecular dynamics simulations of macromolecules, polymers, ionic systems and solutions were performed using DL_POLY software on a parallel computer with distributed memory. The methods used for the experimental characterization of polymer/clay nanocomposites are presented: the X-ray diffraction method, applied to study the associated swelling behavior of polymer/clay nanocomposites; thermogravimetric analysis (TGA), which was used to investigate the distribution of water and organic materials in polymer/clay composite samples; and thermogravimetric mass spectrometry (TGMS), applied to determine the elemental composition of the examined samples.

The **third chapter** - ***Hydration of Clay Layers*** presents the results of a series of simulations on the swelling behaviour of clay minerals. Specifically, the influence of clay layer loading size and distribution on the hydration dynamics of smectite clay minerals is investigated and the performance of the simulation protocols is presented. Figure 1(a) shows the results of the current series of simulations for NaMt hydration. The calculated basal distance of the clay is plotted as a function of water content along with the experimental data. The results are in very good agreement, both qualitatively and quantitatively, and indicate that the swelling of the clay layers occurs in a stepwise manner, with the formation of plateaus around water contents of 0.1 and 0.2 g_{H2O}/g_{clay}.

For CaMt, comparison with experimental swelling curves is difficult due to the lack of data on swelling behaviour as a function of reported interlayer water content. Therefore, our simulated data for the basal spacing of CaMt are shown in Figure 1(b) together with recent results obtained from MD simulation [17]. The inset axes show the experimental swelling behavior of predominantly octahedral loaded CaMt [18] as a function of relative humidity (RH).

Analogous to the NaMt simulations, CaMt demonstrates a nonlinear increase in d-spacing with increasing water content, although this reveals only a single plateau at about 0.15 g_{H2O}/g_{clay}. Discrepancies between the expansion behaviors of NaMt and CaMt upon hydration have been previously observed through multiple experimental [18, 19] and theoretical studies [18]. This good agreement with experimental results and previous simulations ensured the adequacy of the potential model developed.

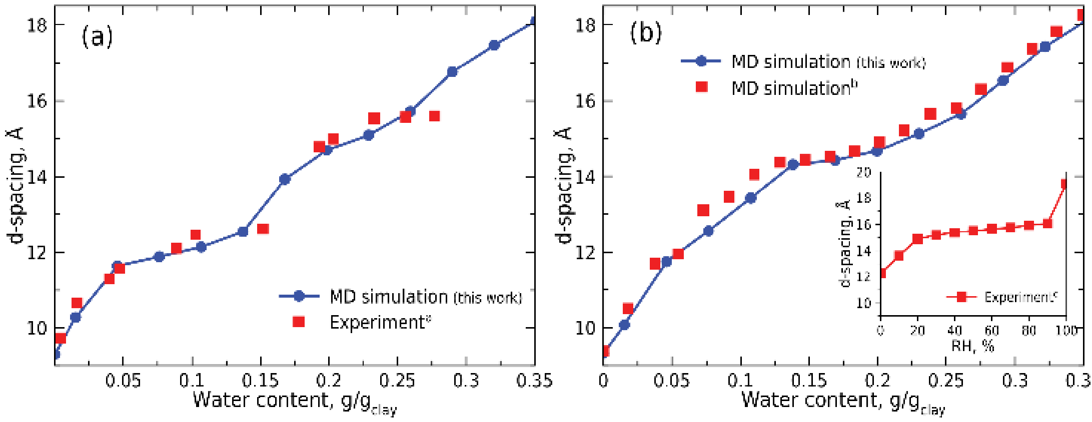


Figure 1. Simulated and experimental basal spacing of (a) NaMt and (b) octahedrally loaded CaMt as a function of increasing water content.

Six simulated swelling curves for NaMt and CaMt models with a range of layer loadings are shown in Figure 2. The general stepwise swelling behaviour of NaMt suggests the potential for the formation of a well-defined monolayer (1W) hydrate with partially and fully filled interlayers, a bistratified (2W) hydrate and a three-layer hydrate. The observed values of basal distances of 9.3-9.7 Å for the anhydrous interlayer, 12.15-12.27 Å for the monostratified hydrate and 14.55-14.92 Å for the bistratified hydrate are in very good agreement with the values reported from experimental observations. The basal distance trends for NaMt with the selected locations and charge sizes are virtually identical (Figure 2a).

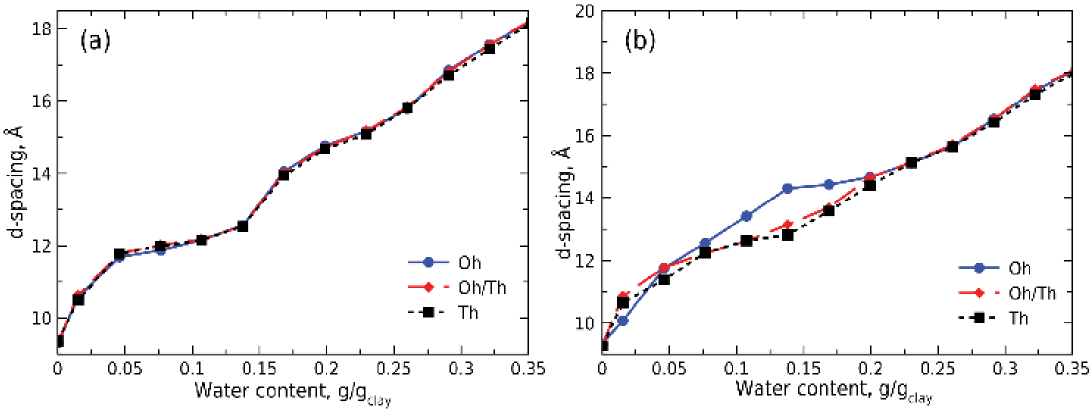


Figure 2. Simulated swelling curves of (a) NaMt and (b) CaMt as a function of water content and clay loading position. MD simulations were performed at 300 K and 1 atm

The d-spacing of the tetrahedral (Th) charged clay is smaller than that of the octahedral (Oh) charged clay by only 0.1 Å at the monolayer hydrate and by 0.3 Å at the water content of the bilayer hydrate. This indicates that neither the magnitude of the clay layer charge nor its location seems to have a significant influence on the swelling behaviour of the montmorillonite Na^+ clay. The siloxanic surface of smectites is predominantly hydrophobic, especially where isomorphic substitutions have not occurred in the octahedral or tetrahedral sheet [1]. Therefore, the main mechanism by which montmorillonites adsorb water is through hydration of exchangeable cations.

Since the ionic radii of Na^+ and Ca^{2+} cations are similar (~1.15 Å [20]), the simulated basal spaces of dehydrated NaMt and CaMt are also very similar (Figure 3b) and equal to 9.3±0.05 Å for all clay types studied. However, experimentally, it is very difficult to obtain completely dry CaMt at room temperature because of the high hydration enthalpy of the divalent cation (1577 kJ-mol-1 for Ca^{2+} and 406 kJ-mol-1 for Na^+ [20]). Under normal conditions, the intermediate layer of octahedrally charged CaMt contains two layers of water [1], which is consistent with the simulated swelling behavior of this mineral. There is no stable plateau corresponding to a monolayer hydrate on the swelling curves of octahedrally charged CaMt (Figure 3b); swelling to the bistrate hydrate with basal spacing of 14.5 Å occurs at ~0.12 g_{H2O}/g_{clay}, much lower than that for NaMt. Most clearly, this difference is related to the hydration energies of the exchangeable cations.

Upon introduction of tetrahedral charge in CaMt systems, the basal distance is reduced to 12.5 Å, which corresponds to a monostate hydrate. The high hydration energy of divalent calcium results in a strong interaction with the substitution sites in the tetrahedral sheet near the clay surface, breaking the cation hydration shell and limiting the basal distance.

From the MD simulations it can be clearly seen that, if a charge deficit occurs in the tetrahedral sheet, cation adsorption is favoured near the tetrahedral sheet and probably the isomorphic substitution sites. On the other hand, the bistratified hydrate is characterized by four layers of water hydrogens located at 1.7 Å and 2.4 Å from both basal surfaces. As in the case of the monolayer hydrate, some hydrogen atoms are oriented towards the basal surface, but due to the larger space available and the complete hydration of the cation, the orientations of the dipole moment of the water are more diverse.

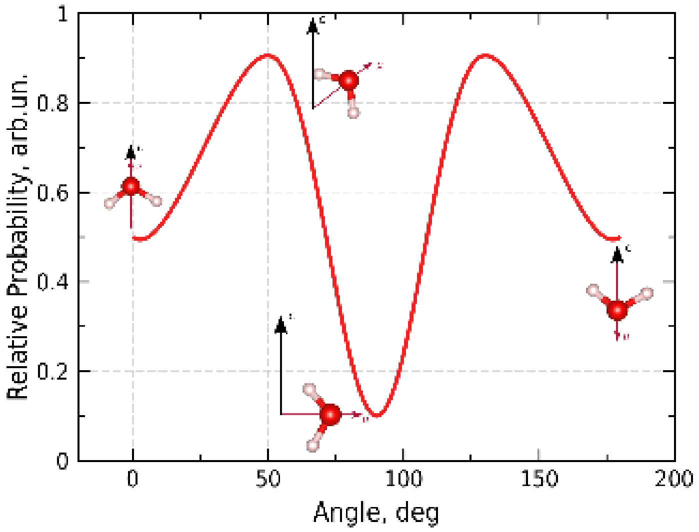


Figure 3. Water dipole distribution in the intermediate layer of the bilayer hydrate

To quantify this, Figure 3 shows the distribution of the dipole moments of the water molecules forming the hydration shell of each cation as a function of the angle between the dipole moment vector and the c-axis. The angle is relative to the c-axis vector, perpendicular to the clay layer. Water orientations in which one of the OH - bonds faces the clay surface and the other is almost parallel to it were the most common. These are followed by the configuration in which both hydrogen atoms are oriented towards the basal surface of the clay. An NMR spectroscopy investigation of water dynamics at the smectite/water interface suggested similar water orientations in bistratified hydrates [21].

Species dynamics in the interlayer were analysed by superimposing 500 ps trajectory maps of NaMt and CaMt with different interlayer water contents and shown in Figure 4. These illustrate both the mobility and hydration of interlayer cations and water. It can be seen that the overlapping trajectories of Ca^{2+} and the accompanying coordinated water molecules are much denser than in the case of Na^{+}.

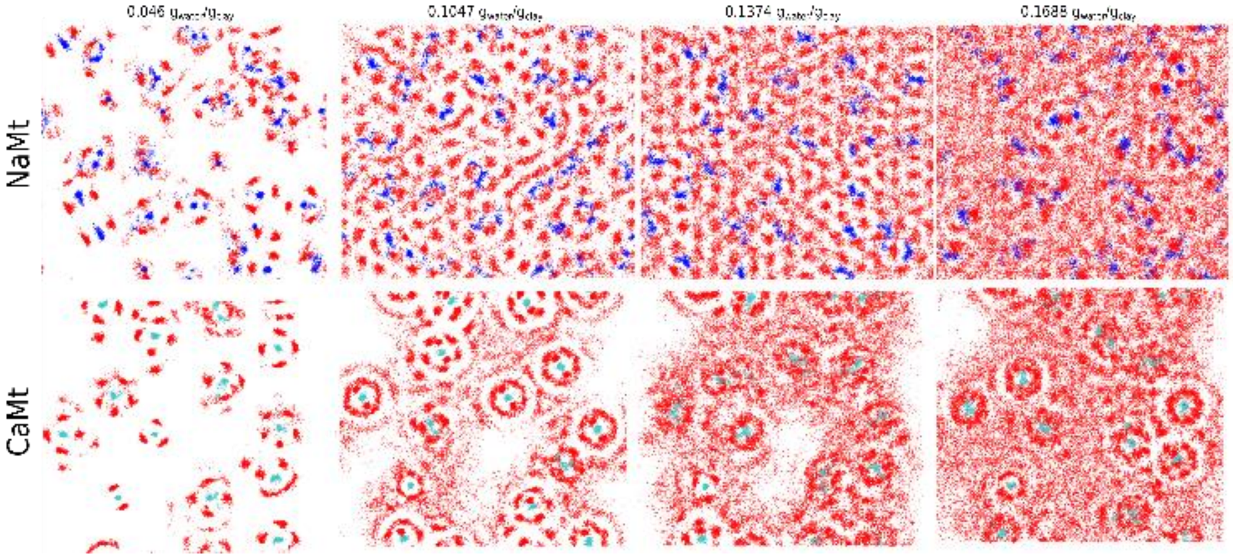


Figure 4. Final 500 ps overlapping snapshots from MD simulations at 300 K and 1 atm of octahedrally loaded NaMt and CaMt
Colors: Na^+ blue, Ca^{2+} light blue, H_2O - red.

The obtained models clearly indicate that water adsorption by montmorillonite clays occurs in two steps. First, solvation of interchangeable cations occurs either with three (in the case of monovalent Na^+ cations) or with several water molecules (in the case of divalent Ca2+ cations) (Figure 5, 0.046 g_{H2O}/g_{clay}). At this stage, water is predominantly located around the cations or near the substitution sites that are the focus of the net negative charge of the clay layers. Secondly, as the amount of water in the interlayer increases, full hydration shells form around the cations. Monovalent sodium cations develop an octahedral solvation complex, while divalent calcium forms a second solvation shell (Figure 5, 0.1047 g_{H2O}/g_{clay}). Since this hydration process depends only on the hydration capacity of the exchangeable cations, the formation of complete water monolayers is not required, as indicated by the "unoccupied" region between the hydrated Ca^{2+} cations.

The more negative hydration enthalpy of Ca^{2+} produces a water coordination sphere around it that is much more stable than that of Na^+. Because of this, Ca^{2+} mobility is limited, unlike Na+ cations, which remain mobile even at low water contents. Ca^{2+} diffusion is further inhibited by a second coordinating water shell, which may be complete or may share some parts with those of neighbouring cations. The diffusion coefficient values obtained for water and exchangeable cations in Mt are summarized in Table 1.

Table 1. Diffusion coefficients of cations and water (OW) (10^{-10} m^2s^{-1}) from MD and experimental simulations.

	D_{OW} (NaMt)	D_{OW} (CaMt)	D_{Na+}	D_{Ca2+}
1W	2,4-2,8 (1-3)	1,7-4,2	0,2-1,6 (0.1)	0,02-0,03 (0,06)
2W	7,5-9,7 (5-10)	3,5-6,7	0,9-2,9 (1)	0,02-0,5
3W	13,9-15,4	7,6-9,5	2,6-5,2 (2)	0,2-1,2

Experimental values are shown in brackets [22].

Thus, the simulation was able to reproduce the behaviour of water in the interlayer. The polarization effects are due to the cation and are highly sensitive to its nature. Also, the experiment deduced an extremely low DCa coefficient for octahedrally charged CaMt at 1W hydrate. This is due to the isolation of the Ca^{2+} cation in the ditrigonal cavity of the clay surface. However, upon introduction of -0.3 e-uc-1 tetrahedral charge into the clay model, the cations rearrange into two distinct layers that fix a single layer of water. This leads to a significant reduction in the basal distance of the clay, the driving force behind this process being the interaction between the cation exchanger and the charged sites in the tetrahedral clay layer.

The *fourth chapter* - ***Adsorption of Polyethylene glycol onto Montmorillonite***, combines experimental and computational investigations of polyethylene glycol/clay nanocomposites. The swelling behavior of selected clay minerals in the presence of plasticizer and the relative affinity of water and polymer for different exchange cations are explored.

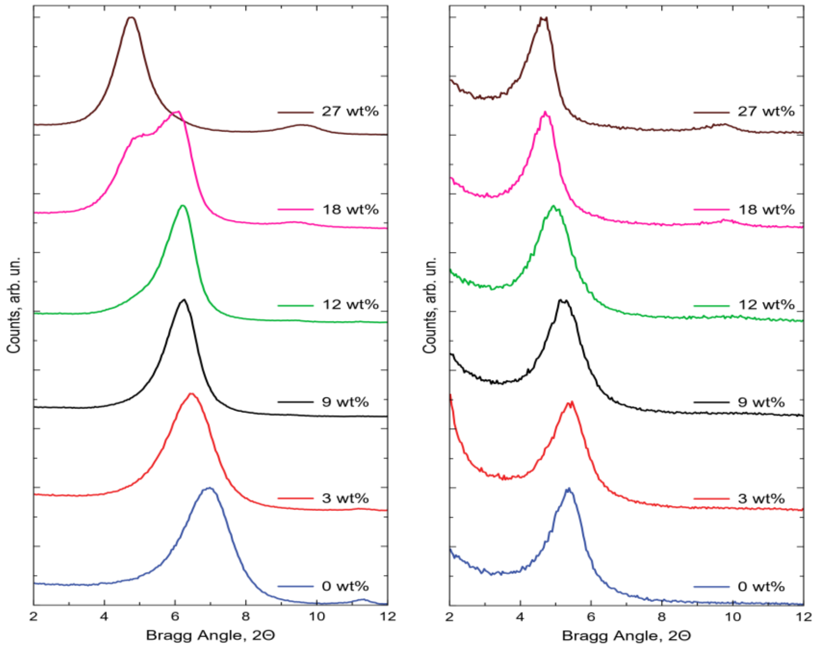
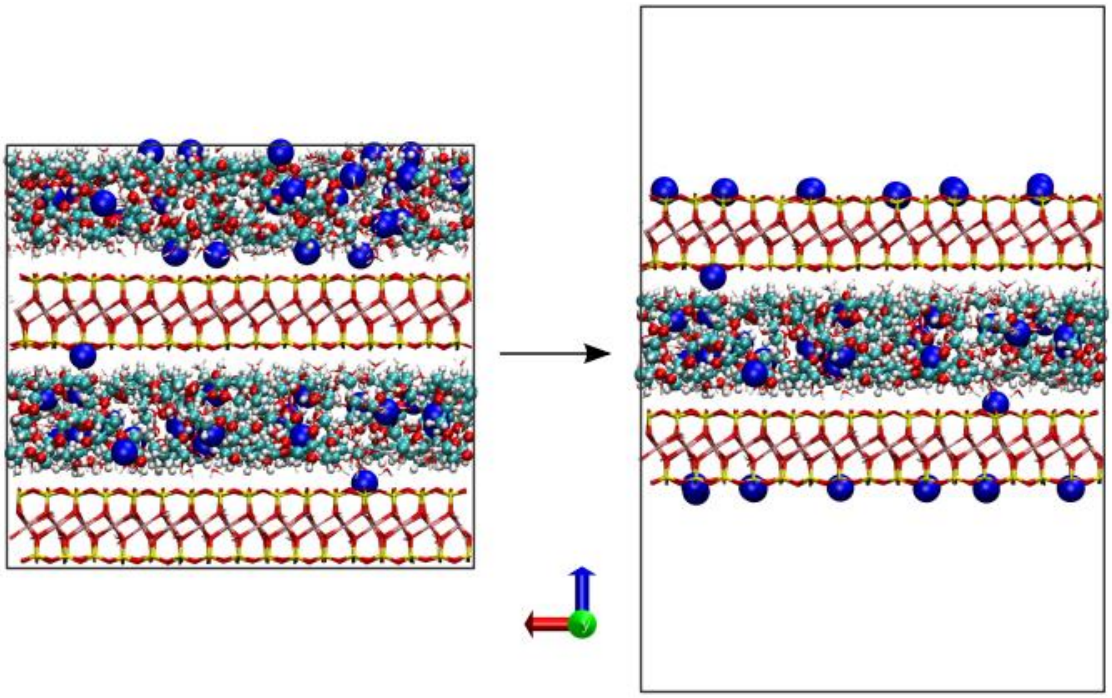


Figure 5. XRD plots of PEG/Mt with 0-27% by mass of PEG200 for a) Na^{+}-cloisite and b) Ca^{2+}-cloisite.

XRD patterns for PEG/NaMt and PEG/CaMt with a range of PEG200 loadings are shown in Figure 5. The diffraction profiles obtained are in very good agreement with many previous investigations of PEG intercalation into NaMt [13, 17, 18]. The shift in the positions of the XRD peaks for the Na^{+} clay (Figure 5(a)) indicates the presence of intercalated structures for the entire range of PEG loadings.

Even a very small amount of PEG200 (3 mass %) forces the clay layers to extend from 12.7 Å to 13.6 Å (6.98° 2Θ and 6.46° 2Θ, respectively) (Figure 6).

This continues with higher PEG loadings, which gradually fills the interlayer until a complete PEG200 monolayer is apparently formed in the interlayer at 12 wt% (6.22° 2Θ) with a distance d of ~14.4 Å (Figure 7(a)). Additional PEG200 loading (18 wt%) results in the formation of two coexisting structures - monostrate (14.4 Å) and bistrate (16.7 Å), which are evident from the two peaks in the XRD trace at 6.1° 2Θ and 5.1° 2Θ, respectively. The bistratified polymer structure is fully formed when the PEG200 loading reaches 27 mass %, as evidenced by the narrow d-spacing distribution and the high intensity of the XRD peak, corresponding to a d-spacing of 18.5 Å.



NPT equilibrated configuration

NVT production runs
with vacuum gap

Figure 6. Simulation flow of interleaved PEG200/Mt systems. The NaMt cell containing 34 PEG200 molecules (0.28 g_{PEG}/g_{clay}) and 180 H_2O molecules are shown molecules in each interlayer.

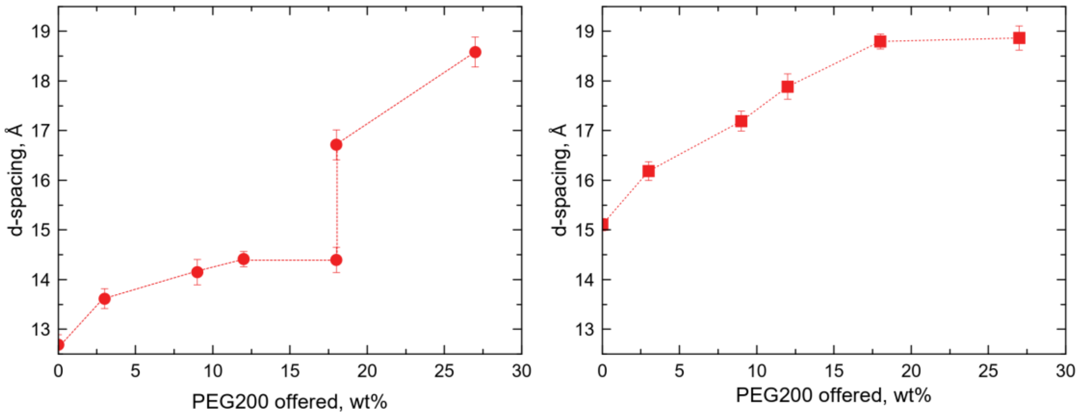


Figure 7. Summary of d-spacing observed in the XRD patterns of PEG200/Mt for a) Na^+-cloisite and b) Ca^{2+}-cloisite.

XRD traces suggest a completely different behaviour for Ca^{2+}-exchanged clay following PEG200 intercalation (Figure 1(b)). The XRD peak for the 0 mass % PEG200 sample is located at 5.68° 2Θ, corresponding to a d-spacing of 15.1 Å (Figure 2(b)). At this point, only water and hydrated Ca^{2+} cations are present in the interlayer. The calculated d-spacing is in agreement with that of simulated clay and water systems, where it was concluded that CaMt always forms an intermediate layer of bilayer hydrates under ambient conditions, due to the high hydration capacity of the bivalent exchange cation. Upon introduction of PEG200 into this system, the d-spacing of PEG/CaMt increases almost linearly until it reaches a spacing of 18.8 Å at 18 mass %. It then stabilizes, probably showing the limit of Ca^{2+}-cloisite intercalation capacity at room temperature and normal pressure.

Thermal decomposition of polyethylene glycol into nanocomposites

The thermal stability of the formulated samples was investigated using the TGA technique. Thermograms (TG) and corresponding negative derivatives (dTG) for PEG/Mt nanocomposites are shown in Figures 7 and 8 and were used to quantify the amount of intercalated PEG and water present in the nanocomposites. The thermal decomposition of PEG/Mt nanocomposites proceeds as a multi-step process, (i) mass loss due to water release at a temperature below 225°C; (ii) polymer decomposition at 250-400°C, forming monomers, small oligomers and other decomposition products [13]; (iii) dehydroxylation of the Mt layer at ~ 700°C. These three processes are intrinsic to both Na^+-exchanged and Ca^{2+}-exchanged montmorillonites, as shown by the TG curves shown in Figures 7(a) and 7(b), respectively.

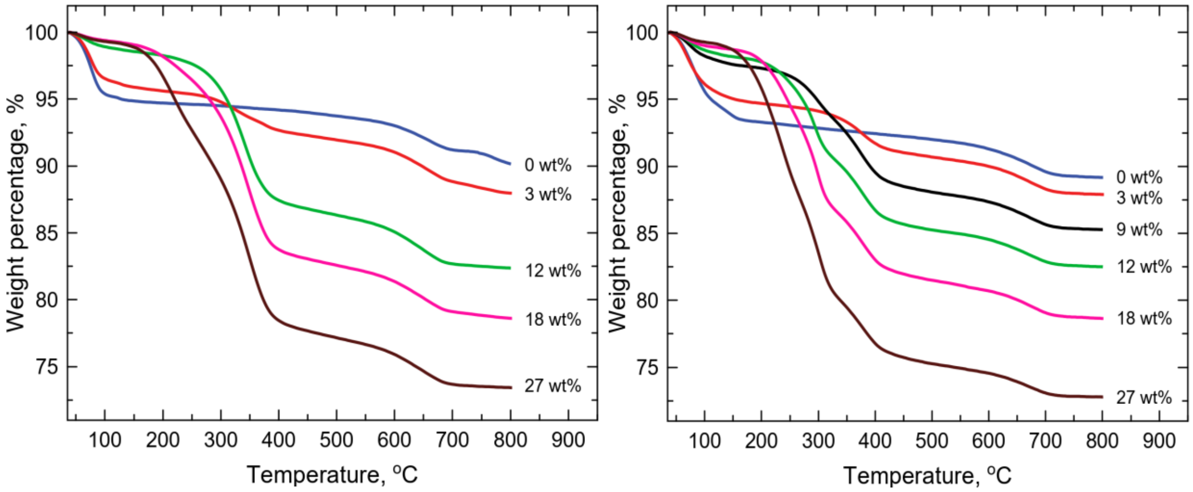


Figure 7. Thermograms of PEG200/Mt with different percentages by mass of PEG200 for a) Na^+-cloisite and b) Ca^{2+}-cloisite.

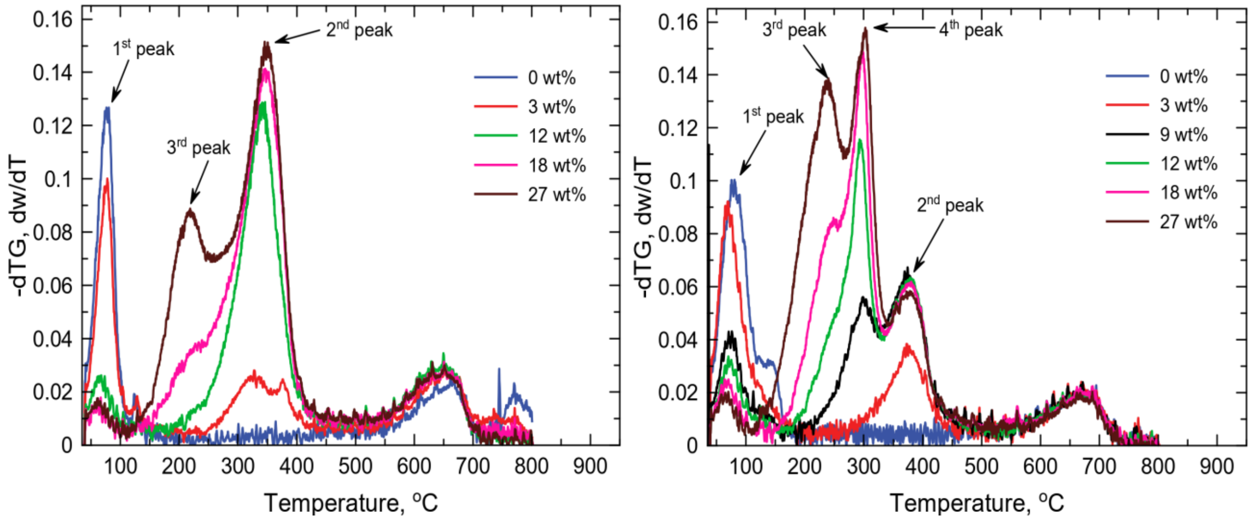


Figure 8. Negative TGA derivatives of PEG200/Mt with different percentages by mass of PEG200 for a) Na^+-cloisite and b) Ca^{2+}-cloisite.

The first major loss of mass occurs between 35 and 150°C. The reciprocal dTG peak, noted as the first peak in Figures 8(a) and 8(b), corresponds to the removal of water from the samples. The amount of water released decreases as the PEG concentration increases from 0 to 27 mass % (Figure 8(a) and 8(b)). This indicates that either some of the water present in the clay is replaced by PEG200 [17] or that more compact water aggregates are created that remain in place up to ~ 150°C [18]. A shoulder at ~ 140°C in the dTG curve of pure Ca^{2+}-cloisite (Figure 8(b)) is due to the decomposition of relatively strong Ca^{2+} hydration shells [13].

The addition of only 3 mass % PEG200 to both clays reveals a second mass loss peak between 300°C and 400°C (Figure 8). The intensity of this peak increases as the amount of PEG in the nanocomposite increases - significantly, up to 7-fold for NaMt, but to a much lesser extent for CaMt (up to 1.5-fold). The mass loss curves associated with the second dTG peak (Figure 8) clearly correlate with the shapes and progression of the corresponding XRD swelling curves (Figure 6). In particular, the mass loss curves of the PEG/NaMt nanocomposites stabilize between 12 and 18% by mass of PEG200 content, which corresponds to a monolayer polymer organization within the interlayer. Further increase in PEG content leads to a significant increase in the associated mass loss. On the other hand, the corresponding mass loss of CaMt-based nanocomposites reaches a plateau at lower PEG200 content, which corresponds to the formation of a PEG200 bilayer in the interlayer. Similar to the swelling curve, a further increase in PEG200 content does not influence the observed mass loss.

The third peak (Figure 8(a)) becomes noticeable at PEG200 contents of 18 mass % for NaMt and 12 mass % for CaMt. These loadings correspond to the formation of the bistratified interlayer structure for clays of both exchanged forms (Figure 6(a)). The mass losses at these corresponding temperatures are almost linear, especially at high PEG content. An explanation for the 3rd mass loss peak could be the completely unintercalated PEG, where only a few polymer chain segments are bypassed by the gallery and most of each molecule remains in solution [16].

The amounts of water and PEG200 for all studied samples, calculated from TG curves and TGMS analysis, are shown in Table 2. Here only mass loss peaks 1, 2 and 3 were considered (Fig. 8).

Table 2. Amounts of PEG and water adsorbed from water solution on NaMt and CaMt determined by thermogravimetry.

PEG200 offered (wt%)	NaMt			CaMt	
	H_2O amount (%)	PEG amount (%)		H_2O amount (%)	PEG amount (%)
0	5,0	-		7,3	-
3	4,1	3,8		5,4	2,7
12	1,2	10,2		2,2	9,1
18	0,5	17,3		1,5	15,8
27	0,4	23,6		1,1	21,0

It is important that these values do not refer exclusively to intercalated media, as there is no direct way to distinguish intercalated from supernatant adsorption configurations. CaMt retained more water for all samples studied, as expected from the hydration analysis. For example, pure NaMt and CaMt contained 5.0% and 7.3% water, respectively. NaMt, on the other hand, adsorbed larger amounts of polymer, giving adsorbed PEG loadings very close to the percentages of polymer provided. As the PEG content of the nanocomposite increased, the amount of water decreased for both forms of clay exchanged. This suggests that PEG intercalates by replacing the free water molecules in the gallery as well as some of the water that is directly coordinated to the exchangeable cations.

Computational simulation of polymer/clay nanocomposite

Figure 9 shows the results of a series of simulations for PEG200 intercalation into montmorillonite exchanged with Na$^+$ and Ca^{2+} cations. The calculated basal space of the clay complex is plotted as a function of polymer content, together with the experimental data presented earlier in this chapter. The carefully selected variable amounts of water in the interlayer were based on experimental data obtained from TGA and TGMS calculations (Table 2).

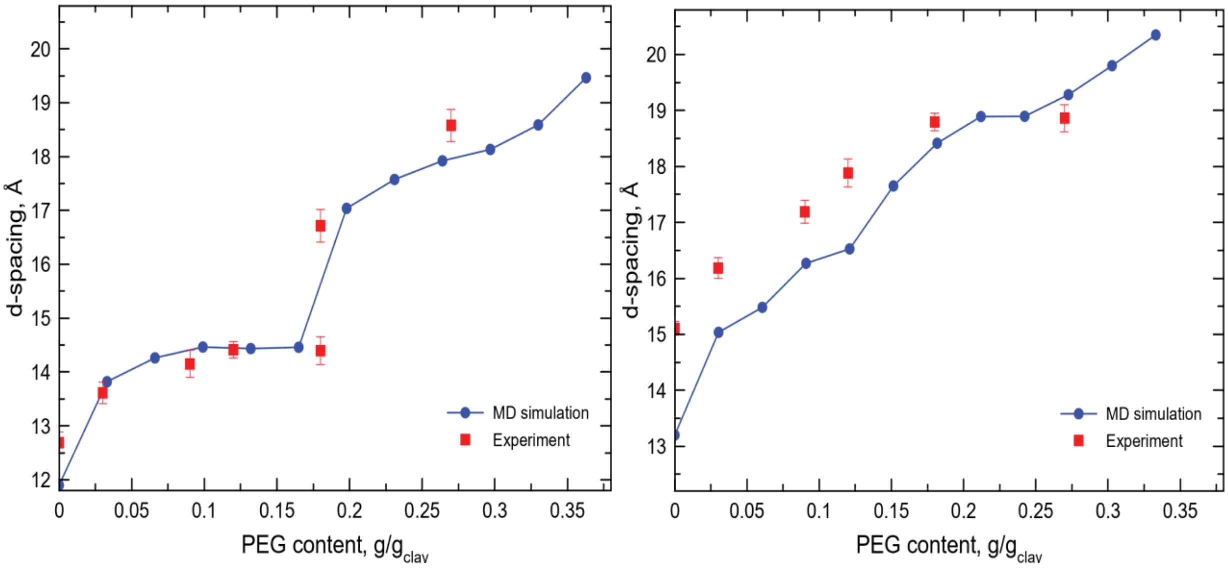


Figure 9. Simulated and experimental basal distance of NaMt (a) and CaMt (b) as a function of increasing poly(ethylene glycol) (PEG200) content in the interlayer. The amount of water in the interlayer was selected according to the experimental results shown in Table 2.

The simulations correctly predict a stepwise swelling behaviour for NaMt. Two plateaus are observed around PEG200 contents of 0.10 and 0.25 g_{PEG200}/g_{clay} (Fig. 9(a)), which supports the organization of the interlayer polymer into two extensive layers parallel to the clay surfaces - monolayer and bilayer. More importantly, for the first time, we obtained realistic basal spaces for these two polymer arrangements from simulation. The first plateau on the swelling curve corresponds to a monostrate polymer organization with a d-spacing of 14.5 Å. This is an excellent match with the experimental observations presented in the previous section as well as with previous experimental investigations [9, 13, 16]. The simulated spacing corresponding to the bicameral structure of the polymer is about 0.5 Å smaller than that obtained experimentally.

As in the case of the clay hydration process, the interchangeable cation significantly affects the PEG intercalation (Fig. 9(b)). CaMt shows an almost linear increase in d-spacing with PEG200 adsorption until a plateau is reached at about 0.2-0.25 g_{PEG200}/g_{clay} with a spacing of 18.8 Å. This plateau corresponds to the formation of a polymeric bichamer structure and is again consistent with experimental observations. At lower polymer content, the swelling curve for CaMt is less accurate than for NaMt, but the almost linear swelling trend is similar to that observed experimentally. The absence of a stable monolayer polymer structure in the interlayer suggests that the level of PEG200 uptake by CaMt is lower compared to that of NaMt. Similar behavior was observed experimentally, where the ratio of PEG1500 uptake by NaMt to that by CaMt was found to be about 2.3 [22].

Polymer/clay-based clay nanocomposites with low charge are characterized by predominant polymer conformations in the form of "Saturn ring" and "Crown", with the latter occurring more often in tetrahedrally charged clays, due to partial coordination of the cation exchanger by oxygen on the mineral surface (Fig. 10).

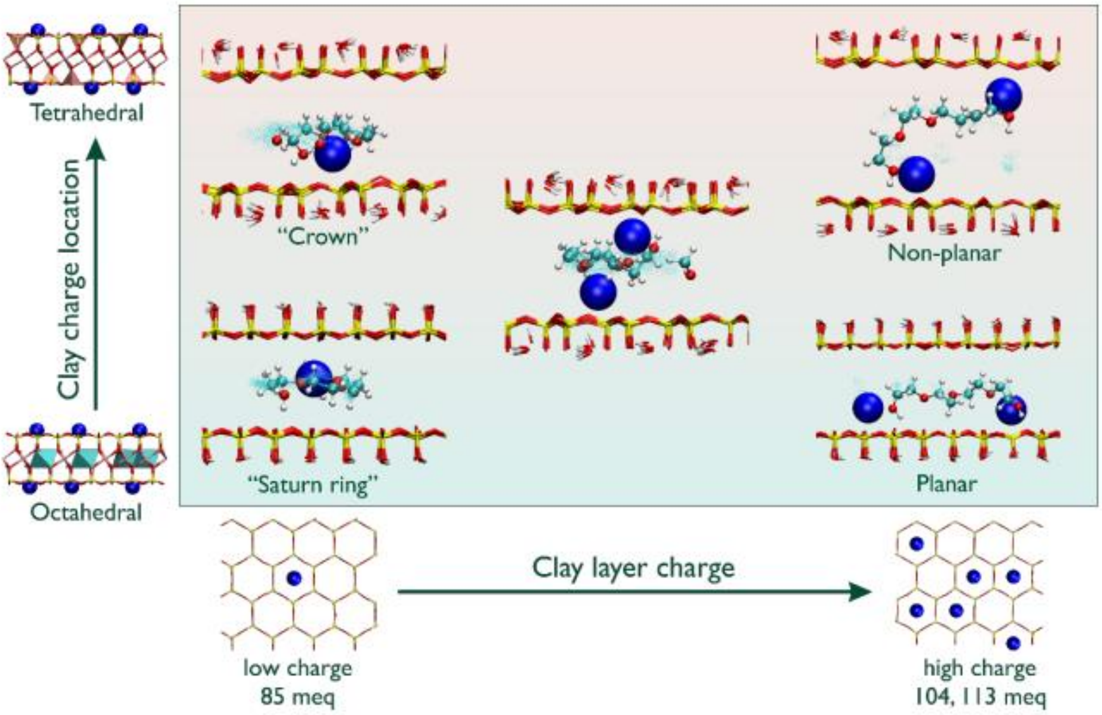


Figure 10. Influence of the size and location of the clay layer load on the conformations of PEG 200 interlayers.

Increasing the layer loading leads to an increase in the fraction of both planar and non-planar linear extended conformation of polymer chains absorbed parallel to the basal surface and of non-planar conformation to chains joining silicate layers. When the polymer creates a bridge between adjacent clay layers, the result is the release of more space for the PEG content of the interlayer. This illustrates the preferential adsorption mechanisms of higher molecular weight polymers when it is easier to bridge clay layers with a long polymer chain. The lower polymer mass fraction predisposes towards "Saturn ring" conformations in clays with positive charge deficit in the octahedral structure, which is due to the position of exchangeable cations in the dodecahedral cavities of the mineral surface.

In **chapter five** - ***Synergistic Adsorption of Polyethylene glycol and Amylose*** onto Montmorillonite, the model is put into question by the simultaneous introduction of three adsorbents - water, plasticizer and starch in proportions that can be directly correlated with those used previously. Once again, the relative affinity of each component is investigated and how this is influenced by the size, location and charge density of the layer and the type of exchangeable cation in the clay interlayer.

The adsorption analysis uses a simple montmorillonite-amylose (AML) interface model, which contains a Mt layer and a single AML chain. MD simulations were used to investigate the adsorption process of AML on hydrated clays and the influence of clay loading position on this process. The simulation cell of this model is shown in Figure 11. The adsorption free energy was calculated from the mean force potentials (PMF). Each AML was placed parallel to the selected Mt surface, with its center of mass at a distance of 3.5 Å above the surface. Two main orientations of the amylose molecule were considered - parallel to the [100] direction (Fig. 12(a)) and parallel to the [010] direction (Fig. 12(b)). Subsequently, 2400 pre-equilibrated H_2O molecules were added to each system.

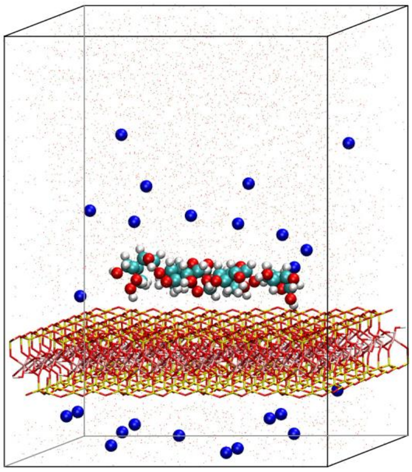


Figure 11. Starting structure of the AML/Mt adsorption model. The centre of mass of a single amylose molecule in aqueous medium is positioned 3.5 Å above the clay surface.

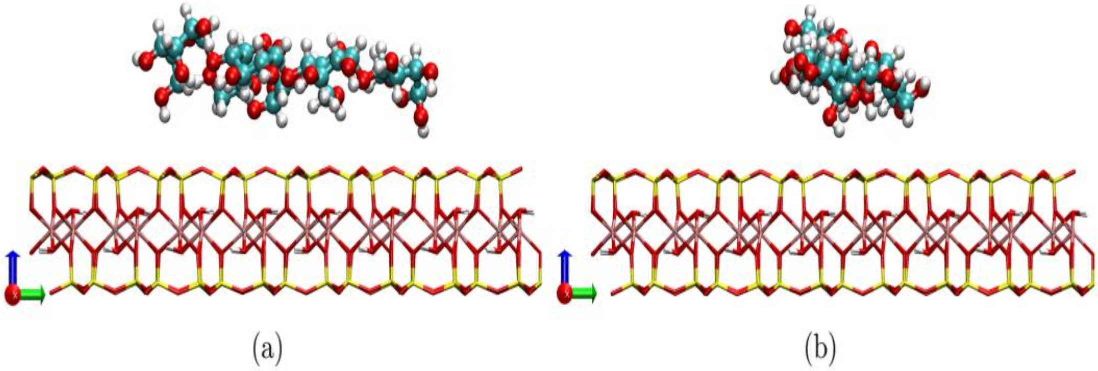


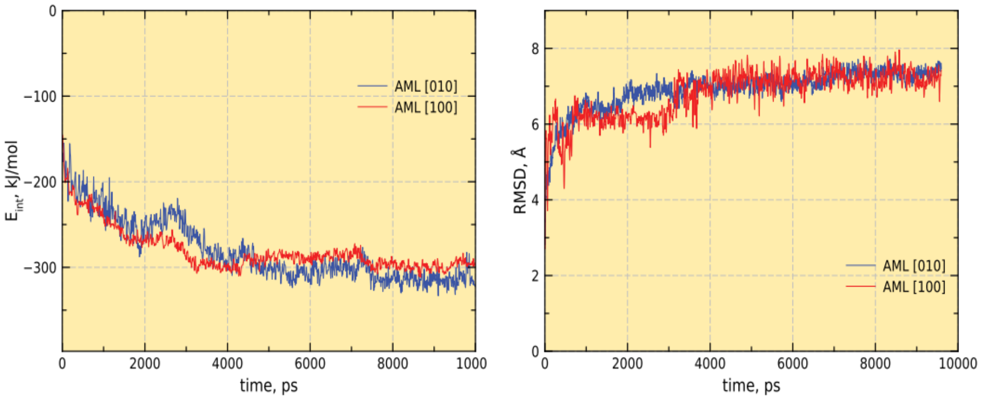
Figure 12. Definition of AML orientations from the AML/Mt adsorption model. The amylose molecule is oriented along (a) [010] and (b) [100].

All simulations were performed in the NPT assembly at 300 K and 1 atm. The time step was 1 fs. The simulation lasted 10 ns. Data from the last 5 ns were used for analysis. All links were constrained. The equilibrium was established by monitoring two parameters - structural and energetic stability. The structural stability of a molecule was assessed by calculating the root mean square deviation (RMSD) of the AML molecule. Energetic stability was judged by the total instantaneous interaction energy between AML and Mt, which is defined as:

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

where E_{int} refers to the interaction energy between AML and Mt; E_{AML+Mt} is the total energy of AML and Mt; E_{AML} and E_{Mt} are the internal energies of AML and Mt, respectively.

The instantaneous RMSDs of AML and the interaction energy between AML and Mt are shown in Figures 13(a) and 13(b), respectively. Data for 104.4 meq NaMt with octahedral charge are shown. All twelve models studied reached equilibrium at about 4 ns of MD simulation. Therefore, data from the last 5 ns were used for the analyses.



(a) (b)

Figure 13. Variation of (a) Eint and (b) RMSD of amylose molecules adsorbed on 104.4 meq NaMt with octahedral charge in different adsorptions with simulation time.

Similar to the series of simulations presented in Chapters 3 and 4, the investigation of the effect of clay layer loading on the amylose intercalation process is presented. A total of 12 simulated swelling curves for the NaMt and CaMt models are shown in Figures 14 and 15, respectively. Error bars based on the standard deviation calculated from the mean of the blocks over the last 1 ns of simulations are smaller than the data symbol and therefore not visible on the plots.

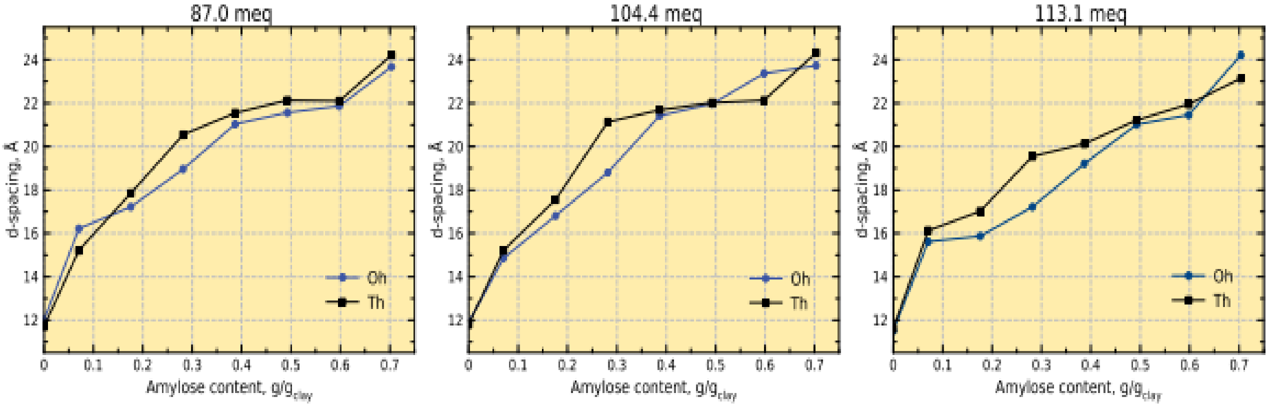


Figure 14. Swelling curves of NaMt as a function of the amylose content in the interlayer according to MD simulations at 300 K and 1 atm. Swelling curves are shown for clays with different net load distributions.

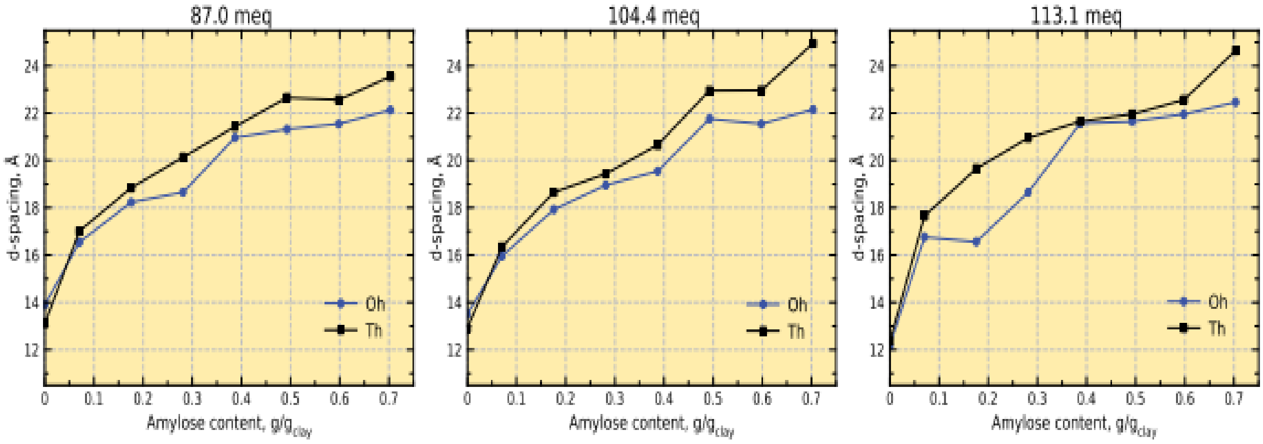


Figure 15. CaMt swelling curves as a function of interlayer amylose content from MD simulations at 300 K and 1 atm. Swelling curves are shown for clays with different net load distributions.

Unlike the swelling curves of hydrated montmorillonite or PEG/Mt systems, the intercalation of amylose into Mt does not suggest the formation of highly ordered polymeric structures in the interlayer. Most simulated clays swell gradually with increasing polymer content in the interlayer until a "balanced" basal spacing of ∼21-22 Å is reached. Similar d-spacings have been observed by many experimentalists investigating starch intercalation into montmorillonites under ambient conditions [23, 24]. This is revealed as a plateau at higher AML content on all simulated swelling curves (Fig. 13 and 14). This is a very important result obtained from the simulation and indicates the preferential organization of amylose between layers, evidence for which will be provided throughout this chapter.

Another particular conclusion that can be drawn from the simulated swelling curves is that the gaps between AML/Mt nanocomposites based on low charge clays are generally larger by about 0.9-1.2 Å in the 0.3 g_{AML}/g_{clay} region than those based on high charge clays. A similar conclusion was drawn from the investigation of the barrier properties of starch-clay nanocomposites based on different types of clays [24]. There is evidence that high loading clays do not absorb starch at all in the interlayer [25]. However, it is impossible to investigate directly by the methods presented here because the content of ogranic material in the intermediate layer is fixed and cannot escape from the clay gallery.

Clays with isomorphic substitutions occurring in the tetrahedral sheet (Th charge) produce a larger basal distance compared to charge-deficient clays in the octahedral sheet (Oh charge). The reason is primarily due to the distribution of exchangeable cations in the intermediate layer of the AML/Mt nanocomposite, which is illustrated in Figure 16 as the atomic density profile along the c-axis normal to the basal surface of the clay. The strong association between exchangeable cations and substitution sites in the tetrahedral clay sheet, as well as the low diffusivity of cations and amylose, result in the majority of them being located between the clay layer and the amylose molecules. In addition, the interchangeable cations in the highly charged and charge-deficient clay in the octahedral sheet more readily form an anhydrous adsorption complex. This opens up space for organic material, leading to a smaller basal distance overall.

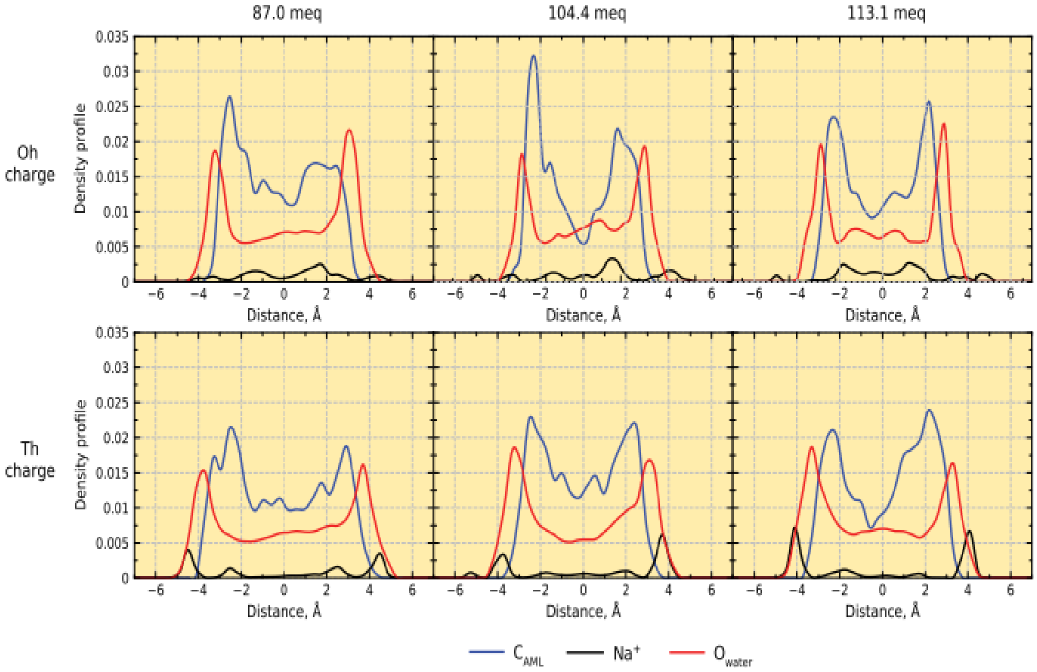


Figure 16. Atomic density profiles from MD simulations at 300 K and 1 atm for the AML/NaMt nanocomposite.

The distribution of carbon atoms for all systems studied suggests the formation of a starch pseudobinder in the interlayer. Amylose can produce a larger number of conformations than PEG, which is why its ADPs are so distorted (Fig. 16). Interestingly, even at a relatively low water concentration (~0.07 g_{H2O}/g_{clay}), a water bilayer is found in the interlayers of all samples. This is expelled from the middle of the interlayer and distinct sharp OW peaks are positioned between the basal clay surface and the AML layer, indicating the hydrophilic nature of amylose and the formation of a hydrogen bonding network. A similar behavior is correct for divalent exchangeable cations.

Thermodynamics of intercalation

The thermodynamics of intercalation of amylose into clay was investigated and the change in potential energy during this process was calculated. Being a multicomponent system, the relationship between reactants and intercalation products AML/Mt-H_2O was expressed by the following equation:

$$Mt - H_2O + AML \longrightarrow AML/Mt - H_2O,$$

The reaction energy for amylose-clay intercalation was calculated according to Eqs:

$$\Delta E = \sum E_{products} - \sum E_{reactants}$$

$$\Delta E = E_{AML/Mt-H_2O} - E_{Mt-H_2O} - E_{AML}$$

The potential energy of hydrated montmorillonite was taken from the simulations of montmorillonite hydration. To obtain the potential energy of AML, simulation cells consisting of 100 randomly distributed AML molecules were constructed, equilibrated and simulated in NPT assembly at 300 K and 1 atm. The resulting density of pure AML was calculated as 1.41 g/cm^3, which is very close to the experimental value of 1.43 g/cm^3 and corresponds exactly to the simulated AML density parameterized by the COMPASS force field [26], confirming the reproduction of the structural parameters of the real amylose system.

The interaction energies between AML and Mt for different clays with different AML orientations - (a) [010] and (b) [100] are shown in Figure 17. The variation of intercalation energy δE as a function of AML content for clays with different loadings confirms the experimental observations of balanced basal distance of ~21 Å for AML/Mt intercalated nanocomposites. The minima indicate a strong preponderance of the formation of these structures.

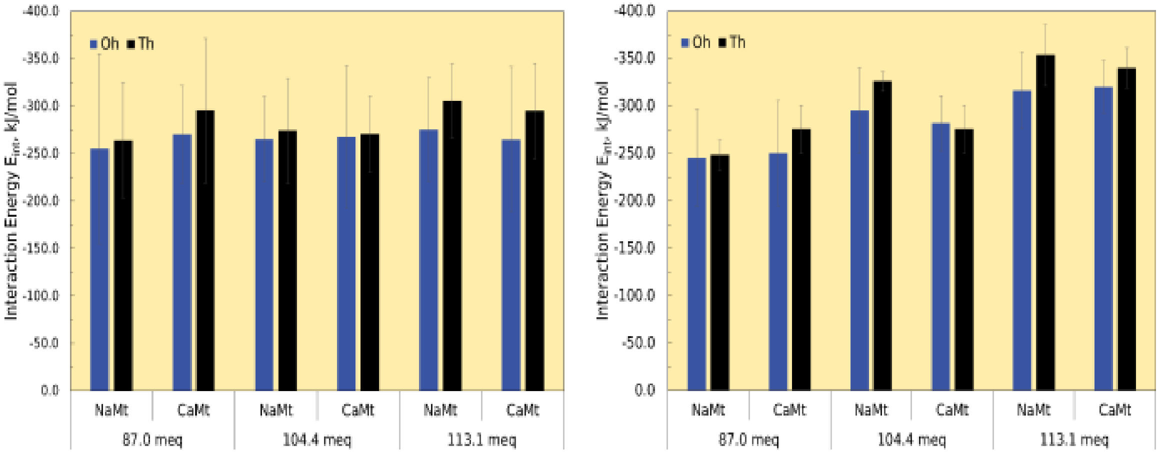


Figure 17. Interaction energies between AML and Mt for different clays with different AML orientations - (a) [010] and (b) [100].

GENERAL CONCLUSIONS

The theoretical and experimental research carried out in the PhD thesis led to the following considerations:

1. New scientific results of theoretical and applied importance in the field of biopolymer technology for food packaging have been obtained. Potential biopolymer models based on polyethylene glycol, amylose and Na^+- and Ca^{2+}-montmorillonite clays were developed and optimised. The research carried out allowed to describe the molecular structure of the composites in order to improve the barrier properties of the layers deposited on the basis of these biodegradable bio-composites, subchapters 3.2.1-3.2.2 [27].

2. Based on the analysis of the main simulation techniques applied to the polymer/clay composites model, the molecular simulation method of the intermediate layer (MS) was selected, which is justified by creating a reliable barrier that can be applied to a wide range of interfaces. Model validation was performed by applying the experimental techniques of conventional X-ray diffraction (XRD), thermogravimetric analysis (TGA) and thermogravimetry coupled with mass spectrometry (TGMS), subsections 2.1-2.3 [28].

3. Experimental and computational investigations of polyethylene glycol/clay nanocomposites allowed to describe the swelling behavior of selected clay minerals in the presence of plasticizer and the relative affinity of water and polymer for different cations. The experimental results corresponded to the model both qualitatively and quantitatively, demonstrating that the swelling of the clay layers occurs gradually, with the formation of plateaus around water contents of 0.1 and 0.2 g_{H2O}/g_{clay} (NaMt). For CaMt only one plateau was found at 0.15 g_{H2O}/g_{clay}, subchapters 4.2.1-4.2.2 [29].

4. It was found, that rotational disorder influences both the internal energy of the clay layers and the basal distance. Hydrated clay and clay with water and PEG intercalated showed rotational resistance by increasing potential energy and extending basal distance (0.1-0.2 Å). Disorder was energetically favorable in the case of dry clay, but involved decreasing internal energy and interlayer distance (about 0.1 Å). Mutual rotation of basal surfaces generates a configurational pattern. The distribution of interlayer molecules (water and PEG) and counterions corresponds to the Moire model, subsection 4.3.1 [30].

5. It was found that the Mg^{2+}/Al^{3+} substitution occurs in the octahedral substrate of the clay and the Al^{3+}/Si^{4+} substitution occurs in the tetrahedral substrate, leading to two different swelling profiles. The substitution site influences the distribution of intercalated water and polymer molecules as well as counterions. In the Na-MMT system the PEG conglomerates are disordered in the interlayer space. In the ternary Ca-MMT system, they are organised and PEG conglomerates avoid isomorphic substitution centres, while cation-water complexes are positioned near these centres. Phyllosilicates with a higher number of tetrahedral substitutions have a higher capacity to retain PEG molecules, subsection 4.3.3 [31].

6. The polymer layer adjacent to the basal clay surface shows minimal translational motion and tendency to concretization with the clay surface, especially NaMt-based nanocomposites with charge deficit in the octahedral substrate. Immobilization of adsorbed polymer chains and formation of complexes with exchangeable cations contribute to reduced gas and vapour permeability by creating a more convoluted pathway for permeable molecules. PEG/Mt nanocomposites with a molecular mass of 100 - 450 $g \cdot mol^{-1}$ and intercalated PEG content from 0 to 40% are bistratal, with d_{001} distances of 16.5 Å, subsection 3.2.3 [32].

7. It was found, that the mineral montmorillonite preferentially adsorbs PEG fractions with high molecular mass. Clay with higher molecular weight PEG content also showed higher stability towards water. From an engineering point of view, these results suggest, that nanocomposites with better barrier and mechanical properties could be obtained by controlling the molecular mass distribution to avoid small polymer fractions, subsection 4.3.2 [33].

8. It has been shown, that phyllosilicates with a layer charge < 0.4 electrons per stoichiometric unit can intercalate starch into the interlayer space, forming a barrier for water vapour in the coating layer. Phyllosilicates with a layer charge of > 0.4 electrons per stoichiometric unit were not able to intercalate starch. The water vapour transfer rate (WVTR) for similar coatings prepared from higher charge bentonites was 3-4 times higher (35 ± 7 $g \cdot m^2 \cdot day^{-1}$) than for phyllosilicates with a layer charge < 0.4 electrons per stoichiometric unit. Thus, a dry food packaging material has been proposed, which provides limited water vapour transfer rates of 8 ± 2 $g \cdot m^2 \cdot zi^{-1}$, subsections 5.2-5.3 [29, 34].

RECOMMENDATIONS

The research carried out in the framework of the PhD thesis allowed to recommend the optimal methodology for planning and obtaining nanocomposites based on polyethylene glycol, amylose and Na^+- and Ca^{2+}-montmorillonite clays for the manufacture of coatings for food packaging. Recommended:

1. Coarse-grained model. Model for clay minerals and polymer molecules.

A big problem in modeling physical material processes is the time scale and length scale. In this context, simulations of PEG molecule interaction using Coarse-Grained potentials are recommended, which are more than 5 times faster than when using fully atomistic potential models. This can provide a significant performance gain in simulating large-scale systems.

To parameterize the CG model of the clay, the use of the VOTCA potential is recommended. In this model, the interface clay layer fragments do not differ from the internal ones. This is the point where the model is to be improved. CG models for clay and PEG - to observe the intercalation process such as Coveney with CG model have been recently developed. The wetting properties of the interfaces should be analysed.

2. Starch intercalation and open surface enhancement in water and carbon dioxide adsorption

In experiments it was found that smectite layers are not purely continuous, but naturally include discontinuities and breaks due to cracks and defects. Therefore, it is also recommended to investigate surfaces in other geometrical directions; such as 010 and 100; which include reactive sites. In the case of exposure to interbedded species, these may have an impact on the behavioural response of the clay. Therefore, in future research discontinuous layers should be considered to study different reactive clay surfaces and to find out if they can enhance swelling or could favour shrinkage.

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31. Siminel, N.; Cleaver, D.; Computer Simulation of Clay-Polymer Nanocomposites. How can Modelling Improve the Barrier Properties of Sustainable Coatings, CCP5 Annual Meeting, 2017, Harper Adams University, Edgmond, Edgmond, United Kingdom
32. Siminel, N. Investigation into interlayer water structure in Na^+- and Ca^{2+}- Montmorillonite: A Molecular Dynamics Study, 4th International Conference on Nanotechnologies and Biomedical Engineering, ICNBME 2019, IFMBE Proceedings, vol. 77, Springer, Cham, pp. 761-76.
33. Lascova-Baciu, R.; Loșmanschii, C.; Siminel, N.; Micu, A.; Nedelea, V.; Kulyuk, L. Synthesis and characterization of nanosheets, 9th International Conference on Materials Science and Condensed Matter Physics, 25-28 September 2018, Chisinau, Republic of Moldova, p. 324
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PUBLICATION LIST

1. ARTICLES IN SCIENTIFIC JOURNALS

1. LOZOVAN, V.; KRAVTSOV, V.; GORINCIOI, E.; ROTARU A.; COROPCEANU, E.; **SIMINEL, N.;** FONARI, M.. Chromism, positional, conformational and structural isomerism in a series of Zn(II) and Cd(II) coordination polymers based on methylated azine N,N′-donor linkers, *Polyhedron*, 2020, 180. doi: 10.1016/j.poly.2020.114411.
2. LOZOVAN, V.; KRAVTSOV, V.; COROPCEANU, E.; **SIMINEL, N.;** KULIKOVA, O.; COSTRIUCOVA, N.; FONARI, M.. Seven Zn(II) and Cd(II) 1D coordination polymers based on azine donor linkers and decorated with 2-thiophenecarboxylate: Syntheses, structural parallels, Hirshfeld surface analysis, and spectroscopic and inclusion properties, *Polyhedron*, 2020, 188. doi: 10.1016/j.poly.2020.114702.
3. GURIEVA, G.; NIEDENZU, S.; **SIMINEL, N.;** SCHOR, S.. The kesterite–stannite structural transition as a way to avoid Cu/Zn disorder in kesterites: the exemplary case of the $Cu_2(Zn,Mn)SnSe_4$, *Faraday Discussions*, 2022, 51(239), pp. 51-69. doi: 10.1039/d2fd00042c.
4. **SIMINEL, N.** Structure Of Polymer/Clay Nanocomposites, A Molecular Modelling Perspective, *Journal of Engineering Sciences*, 2023, 1 2023 (Capitolul 3, p. 3.2.3. 3.2.4)
5. **SIMINEL, N.** Synergistic adsorption of amylose and water onto phyllosilicate surface, *Journal of Engineering Sciences*, 2023, 2, 2023.

2. ARTICLES IN THE PROCEEDINGS OF CONFERENCES

2.1. în culegeri de lucrări ale conferinţelor internaţionale peste hotare

1. **SIMINEL, N.;** STURZA, R. Understanding the barrier properties of clay-based food packaging. A contribution from computational modelling, *MTFI-2022 International Conference*, TUM, Chisinau, 2022, p. 104.
2. **SIMINEL, N.** Computational models of amylose and amilopectin, *12th European Kesterite Hybrid Workshop*, 10-11 February 2022, Copenhagen, Denmark
3. LASCOVA-BACIU, R.; LOȘMANSCHII, C.; **SIMINEL, N.;** MICU, A.; NEDELEA, V.; KULYUK, L. Synthesis And Characterization Of MoS_2 Nanosheets, *9th International Conference on Materials Science and Condensed Matter Physics*, 25-28 September 2018, Chisinau, Republic of Moldova, p. 324.
4. **SIMINEL, N.;** BREEN, C.; CLEAVER, D.; CLEGG, F. Understanding the Barrier Properties of Dry, Clay-Based Coatings, *International Conference on Clay Science and Technology Euroclay*, 5th-10th July 2018, Edinburgh, United Kingdom.
5. **SIMINEL, N.;** CLEAVER, D.; Computer Simulation of Clay-Polymer Nanocomposites. How can Modelling Improve the Barrier Properties of Sustainable Coatings, *CCP5 Annual Meeting*, 4-7 September 2017, Harper Adams University, Edgmond, Edgmond, United Kingdom

2.2. în culegeri de lucrări ale conferinţelor internaționale/naționale în țară

1. **SIMINEL, N.** Computational models for clay minerals, *Conferința Studenților, Masteranzilor și Doctoranzilor*, Volum I, UTM, Chișinău, 1-3 aprilie 2020, pp. 423-426.
2. **SIMINEL, N.** Investigation into interlayer water structure in Na^+- and Ca^{2+}-Montmorillonite: A Molecular Dynamics Study, *4th International Conference on Nanotechnologies and Biomedical Engineering, ICNBME 2019*, IFMBE Proceedings, vol. 77, Springer, Cham, pp. 761-76. DOI: 10.1007/978-3-030-31866-6_135

3. PATENTS AND OTHER INTELLECTUAL PROPERTY OBJECTS (IPO)

1. LOZOVAN, V.; FONARI, M.; KRAVŢOV, V.; SIMINEL, N.; COROPCEANU, E.; KULIKOVA, O.; COSTRIUCOVA, N. Polimer coordinativ unidimensional al cadmiului (II) în baza liganzilor 1,2-bis(piridin-4-ilmetilen)hidrazină şi acid 2-aminobenzoic, care manifestă activitate fotoluminescentă şi capacitate de schimb al moleculelor de solvent. *Brevet de inventie, 4776, 30.06.2022*

ADNOTARE

Siminel Nikita: Structuri clay-polymer nanocompozite pentru ambalaje alimentare, teză de doctor în științe inginerești, Chișinău, 2023.

Structura tezei: Teza inaintată spre sustinere a fost elaborată în cadrul Universitații Tehnice a Moldovei, Chisinau 2023, este scrisa in limba engleza și constituită din introducere, cinci capitole, concluzii generale și recomandări, bibliografie din 166 titluri, 110 pagini de text de bază, 71 figuri și 7 tabele. Rezultatele obtinute au fost publicate in 12 lucrări științifice, dintre care 3 articole în reviste internaționale, 2 articole în reviste naționale și 7 articole în lucrările unor conferințe naționale și internaționale.

Cuvinte cheie: Montmorillonit, biopolimeri, polyetilenglycol (PEG), amiloză, nanocompozite, ambalaje biodegradabile.

Scopul lucrării: Dezvoltarea de noi biopolimeri pe bază de argile Na^+- și Ca^{2+}-montmorillonit, polietilenglicol și amiloză; elucidarea funcțiilor argilei, plastifiantului, amidonului și apei în formarea straturilor nanocompozite cu ajutorul tehnicilor experimentale și de simulare pe calculator (dinamica moleculară); cercetarea afinității reciproce a componentelor și structurilor formate asupra proprietăților de barieră și vitezei de transfer a vaporilor de apă în vederea stabilirii domeniului de aplicare a biopolimerilor în domeniul ambalajelor ecologice.

Obiectivele cercetării: Influența mărimii încărcăturii stratului de argilă și a distribuției acesteia asupra dinamicii de hidratare a mineralelor de argilă smectită în vederea dezvoltării și optimizării modelor potențiale de biopolimeri pe bază de polietilenglicol, amiloză și argile Na^+- și Ca^{2+}-montmorillonit. Investigații experimentale și computaționale ale structurii moleculare a nanocompozitelor în vederea îmbunătățirii proprietăților de barieră și mecanice ale straturilor depuse pe baza acestor materiale biodegradabile. Absorbția simultană a trei adsorbanți - apă, plastifiant și amidon, determinarea afinității relative a componentelor și a modului în care aceasta este influențată de mărimea, localizarea și densitatea încărcăturii stratului și de tipul de cationi schimbabili din stratul intermediar al argilei. Reducerea vitezei de transfer a vaporilor de apă prin spațiul interstrat în vederea creării barierei pentru diminuarea penetrării vaporilor de apă prin materialele de ambalaj destinate produselor alimentare uscate.

Noutatea și originalitatea științifică: Au fost elaborate structure clay-polimerice care oferă o înțelegere cuprinzătoare a comportamentului nanocompozitelor polimer-argilă și a potențialelor lor aplicații ca acoperiri de barieră, ceea ce se așteaptă să aibă implicații semnificative pentru industria ambalajelor alimentare și pentru domeniile mai largi de știința materialelor și fizica polimerilor.

Rezultatele principale: S-a investigat efectul substituției izomorfe din Na^+- și Ca^{2+}-montmorillonita asupra dinamicii de absorbție și a stabilit că argile cu o cantitate mai mare de substituții tetraedrice ar putea avea o capacitate puternică de a reține moleculele de biopolimerice. S-a observat o structură ordonată a lanțurilor de polimeri PEG, paralelă cu suprafața argilei, în modelul de calcul al sistemului PEG/Mt. S-a demonstrat că filosilicații cu o sarcină de strat de < 0,4 electroni pe unitate de formulă pot găzdui amidonul și oferi cea mai mare barieră la vaporii de apă în stratul de acoperire formulat. Pe baza datelor obținute, a fost creat un strat de barieră de 80 de ori mai eficient.

Problema stiintifica principala solutionata: dezvoltarea și optimizarea modelelor potențiale ale biopolimerilor (polietilenglicol și amiloză) și ale argilelor montmorilonite Na^+ și Ca^{2+} pentru a înțelege structura moleculară a compozitelor bazate pe aceste materiale și pentru a îmbunătăți proprietățile de barieră ale acoperirilor formulate folosind aceste bio-compozite.

Semnificatia teoretica si valoarea aplicativa a lucrarii: Pentru prima dată a fost dezvoltat și optimizat modele de biopolimeri pe bază de polietilenglicol, amiloză și argile Na^+- și $Ca2^+$-montmorillonit; studiile experimentale și computaționale au descris comportamentul de gonflare al mineralelor argiloase în prezența plastifiantului și afinitatea relativă a apei și polimerului pentru diferiți cationi; o combinație specifică de biopolimer și argilă a fost propusă, care a redus permeabilitatea stratului obținut cu un factor de 80. A fost obținut 1 brevet de invenție.

Implementarea rezultatelor științifice: Rezultatele cercetărilor au fost implementate în producția de acoperiri barieră © Cailar, produse la Barrcoat AB, Karlstad, Suedia

ANNOTATION

Siminel Nikita: Nanocomposite clay-polymer structures for food packaging, PhD thesis in engineering sciences, Chisinau, 2023.

Thesis structure: The thesis submitted for defense was prepared at the Technical University of Moldova, Chisinau 2023, is written in English and consists of an introduction, five chapters, general conclusions and recommendations, bibliography of 166 titles, 110 pages of basic text, 71 figures and 7 tables. The results were published in 12 scientific papers, including 3 articles in international journals, 2 articles in national journals and 7 articles in national and international conference proceedings.

Keywords: Montmorillonite, biopolymers, polyethylene glycol (PEG), amylose, nanocomposites, biodegradable packaging.

Aims: Development of new biopolymers based on Na^+- and Ca^{2+}-montmorillonite clays, polyethylene glycol and amylose; elucidation of the functions of clay, plasticizer, starch and water in the formation of nanocomposite layers using experimental and computer simulation techniques (molecular dynamics); investigation of the mutual affinity of the formed components and structures on the barrier properties and water vapour transfer rate in order to determine the scope of application of the biopolymers in the field of eco-friendly packaging.

Research objectives: Influence of clay layer loading size and its distribution on hydration dynamics of smectite clay minerals in order to develop and optimize potential biopolymer modes based on polyethylene glycol, amylose and Na^+- and Ca^{2+}-montmorillonite clays. Experimental and computational investigations of the molecular structure of nanocomposites in order to improve the barrier and mechanical properties of layers deposited on the basis of these biodegradable materials. Simultaneous adsorption of three adsorbents - water, plasticiser and starch, determination of the relative affinity of the components and how this is influenced by the size, location and charge density of the layer and the type of exchangeable cations in the clay interlayer. Reducing the rate of water vapour transfer through the interlayer space to create a barrier to reduce water vapour penetration through dry food packaging materials.

Scientific novelty and originality: Clay-polymer structures have been developed that provide a comprehensive understanding of the behaviour of polymer-clay nanocomposites and their potential applications as barrier coatings, which is expected to have significant implications for the food packaging industry and the wider fields of materials science and polymer physics.

Main results: The effect of isomorphic substitution of Na^+- and Ca^{2+}-montmorillonite on adsorption dynamics was investigated and it was determined that clays with a higher amount of tetrahedral substitutions could have a strong ability to retain biopolymer molecules. An ordered structure of PEG polymer chains parallel to the clay surface was observed in the computational model of the PEG/Mt system. It was shown that phyllosilicates with a layer charge of < 0.4 electrons per formula unit can accommodate starch and provide the highest barrier to water vapor in the formulated coating layer. Based on the data obtained, an 80-fold barrier layer was created.

The main scientific problem solved: Developed and optimized potential models of biopolymers (polyethylene glycol and amylose) and montmorillonite Na^+ and Ca^{2+} clays to understand the molecular structure of composites based on these materials and to improve the barrier properties of coatings formulated using these bio-composites.

Theoretical significance and applicative value of the work: For the first time biopolymer models based on polyethylene glycol, amylose and Na^+- and Ca^{2+}-montmorillonite clays were developed and optimized; experimental and computational studies described the swelling behavior of clay minerals in the presence of plasticizer and the relative affinity of water and polymer for different cations; a specific combination of biopolymer and clay was proposed, which reduced the permeability of the obtained coating by a factor of 80. 1 patent was obtained.

Implementation of scientific results: The research results have been implemented in the production of barrier coatings © Cailar, produced at Barrcoat AB, Karlstad, Sweden

SIMINEL NIKITA

CLAY-POLYMER NANOCOMPOSITE STRUCTURES FOR FOOD PACKAGING

253.06 Tehnologii biologice și chimice în industria alimentară

Abstract of the PhD dissertation in Physics

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