COMPUTATIONAL MODELS FOR CLAY MINERALS

Nikita SIMINEL

Technical University of Moldova, Chişinău, Moldova,
Institute of Applied Physics, Chișinău, Moldova

*Corresponding author: Nikita Siminel, siminel.n@gmail.com

Abstract. *In the past decades, the production and the use of plastics in the world have been enormously increased, worsening the problem of the waste disposal. The search for renewable biodegradable materials to replace conventional oil-based plastics is a fast growing research area. In particular, within the packaging industry, the research are driven towards eco-friendly coating materials for paper or paperboard to provide barrier properties to it by reducing or eliminating the permeability of gases, water vapour and odours through the material. Novel biodegradable starch-plasticiser/clay nanocomposites is a real option for sustainable packaging. There is lack of fundamental understanding of such multicomponent nanocomposite, however. The aim of this work is to provide an insight into the interaction between polymers and clay by means of computer simulation techniques.*

Keywords: *food packaging, biodegradable materials, clay minerals, computer simulation, force field*

Introduction

Over past decades, the production and the use of petroleum-derived plastics in the world have increased enormously, which raises concerns not only from environmental point of view, but also from an economic perspective. Packaging is a substantial part of everyday life and impacts multiple industries. Terms such as "biodegradable", "biocompatible", "environmentally-friendly" are becoming more frequent in packaging-related industry and literature. Strict regulations on waste and recyclability of the materials has driven a shift towards a more eco-efficient packaging materials [1].

The search for renewable biodegradable materials to replace conventional oil-based plastics is a fast growing research area as it provides an important factor for sustainable growth of the packaging industry. Amongst these, clay is promising material. Clay minerals are a family of layered materials and have a wide range of potential and actual uses due to their ability to intercalate a variety of inorganic and organic species. Compared with traditional fillers in composite materials, this offers substantial advantages in terms of improved adhesion and lower required filler volume to achieve equivalent properties. As such, clay containing composite materials have numerous current and potential commercial applications in the automotive, packaging, health care, coatings and pigments sectors, as well as in other industries [2].

Unfortunately, current experimental techniques are lacking in performance for the investigation of intercalated layered materials. Only rarely are sufficiently large crystals for full structural determination by conventional X-ray diffraction obtained. Likewise, it is not possible to ascertain what organic materials occupying clay interlayer region.

Because of these limitations, interest in the use of computational methods for studying these layered solids and their intercalates has increased. The aim of this project is to use computer simulation techniques to extend the understanding of the roles played by the clay, water and organic materials in these systems. Selecting an appropriate set of potential terms for the corresponding components of this nanocomposite is essential to obtaining credible results. In the current work, we will present some historical development, functional form and description of potentials used for simulation clays.

Potential Models for Clay Minerals

While molecular simulations of organic materials are a well developed research area, only comparatively recently has simulation of clay minerals techniques developed to a state where it is able to reproduce the mechanical and chemical properties of all clay minerals. Importantly, it has also proved able to produce robust results when the clay is interacting with other phases (e.g. water, organic molecules and exchangeable cations). The very first computational model of montmorillonite was developed by Skipper, Refson and McConnel in 1991 [3]. It was used to simulate the structure of interlayer water in the presence of two exchangeable cations – Na^+ and Mg^{2+}. The computational approach used considered only intermolecular potential interactions, and to model a clay-water-cation system. The clay-water interactions were based on the discrete MCY water model [4]. Skipper et al. positioned a water molecule on each site where basal oxygen was found at the clay surface, and directed the hydrogen atoms towards the silicon sites. The potentials used were, therefore, based on the assumption that the electronic structure of an oxygen atom bonded to two silicon atoms is similar to that bonded to two hydrogen atoms in water. Due to the intermolecular potentials used, all atoms in the clay layer had to be immobile, the unit cell of montmorillonite being represented by an ideal crystallographic cell of pyrophyllite with some level of isomorphous substitution in the octahedral sheet to induce the layer charge. This approach showed reasonable accuracy in calculation of the water absorption isotherm. This model went on to be widely used for Monte Carlo and Molecular Dynamics calculations of the hydration dynamics [5-8], structure of interlayer water in Mt [3, 5, 8-11] and diffusion of water and various interlayer cations [12]. The model was also used to approximate the free energy, entropy of hydration and swelling isotherms of Mt with different exchangeable cations in the interlayer [13-15].

A major advantage of Skipper's model is its computational efficiency, which was largely achieved from the movement restrictions imposed on the atoms comprising the clay layer. However, it should be noted that, this approach may change the mobility of interlayer molecules, especially if their oscillation frequencies match those of the clay surface. Another limitation of the model is the fact that hydrogen bonds are not taken into account. This can introduce a significant change in the behaviour of absorbed material closest to the clay surface. Lastly, this Mt model cannot be used for thermomechanical analyses as it cannot reproduce thermal expansion of the clay layer. As a result, validation of the computational model can be difficult because comparing it to the experimental techniques such as IR-spectroscopy would not be possible.

In 1992 Kawamura introduced atom-atom potentials for computer simulation of multi-component oxides and, in particular, phyllosilicates [16]. The proposed force field was based on three pair-wise interaction potentials including electrostatic interactions, short range VDW interactions and bond stretch interactions described using the Morse potential. A three body interaction or angle bend potential was introduced only for the H-O-H valence angle. Although the model was not extensively used, it was successfully applied for the investigation into the effects of various salts on the hydration process of montmorillonite clays [17].

Five years later, Teppen et al. [18] demonstrated an alternative approach to the development of a clay force field. Unlike previous semi-empirical methods, it was based on an extensive analysis of experimental X-ray diffraction data and charge assignment from quantum mechanical calculations. In their approach, Teppen et al. chose to develop covalent-type potentials for all of the clay mineral atoms and also addressed the issue of octahedral coordination. In the smectite clay minerals, aluminium atoms are octahedrally coordinated by oxygen which results in O-Al-O angles near both 90° and 180°. This is generally not easily modelled by computational techniques as it is difficult to find a function that can characterise these two states simultaneously [18]. The inclusion of cubic and quartic terms to the angle-bending potential was required to create the necessary anharmonicity of the potential function (Figure 1). Most unique in this study, however, was the use of an O-Al-O angle bend potential to simultaneously treat both tetrahedrally and octahedrally coordinated aluminium. Prior to the Teppen et al. [18] study there was no published force field that could be used to properly evaluate this structural peculiarity of clay minerals. The developed set of bonded terms was successfully used to simulate several clay minerals and adsorption of organic materials in their interlayers [19-21].

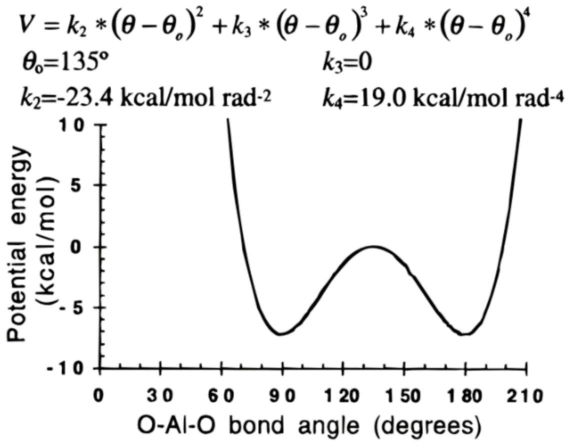

Figure 1. Octahedral O-Al-O angle-bending potential that allows multiple equivalent minima [18]

Despite the fact that the resultant force field showed good performance in simulating several clay structures including gibbsite, kaolinite, pyrophyllite and smectite, transferability proved a major problem in the practical implementation of this force field. Modelling of real polymer/water/clay composites involves the description of complex and poorly characterised crystal structures with low symmetries, large unit cells, variable interlayers and interfaces [22]. For such systems, utilisation of bonded force fields can lead to over-parametrisation due to a lack of relevant experimental data needed to meaningfully constrain the large number of force field parameters necessary to describe all bonded interactions.

Just over a decade ago Cygan, Liang and Kalinichev succeeded in overcoming these problems by designing an organic compatible force field called CLAYFF [22]. Unlike Teppen's covalent approach, CLAYFF is based on an ionic (nonbonded) description of the metal-oxygen interactions. Also, it does not rely on quantum-mechanical calculations alone, but also incorporates a set of experimental crystal structure refinements in the parametrisation of the empirical force field. The CLAYFF force field uses bonded potential parameters from the SPC water model, by Berendsen et al. [23], to describe the hydroxyl and oxygen-oxygen interactions. Metal-oxygen interactions associated with hydrated phases are described by the conventional Lennard-Jones (L-J) function. Parameters for the L-J function are optimised on the basis of known structures of simple oxides and hydroxides [22]. An additional distinct feature of CLAYFF is the incorporation of three-body terms to describe metal adsorption on hydrated surfaces and to improve the vibrational behaviour of hydroxyl groups. This is described by a harmonic function, the optimal parameters for which were determined through an iterative process in which the results of MD simulations were compared with infrared spectra of gibbsite and portlandite.

Conclusions

The relative simplicity, computational efficiency and performance of the CLAYFF force field makes it a very popular choice when simulating phyllosilicates of various types. It has shown good performance in predicting the structure of kaolinite, pyrophyllite, montmorillonite and many other minerals [22] as well as in reproducing vibrational spectra of pyrophyllite and hydrotalcite under normal conditions and under strain. This force field has also been successfully used for mechanical characterisation of clay layers, simulation of clay/organic interfaces and even in the study of electrical conductivity in montmorillonite layers. Validation of the choice of potential models and clay-organic-water is the topic of a separate investigation.

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