Computer simulation of polymer-organoclay nanocomposites for packaging applications: from binding energy to interlayer spacing predictions

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Introduction

The subject of hybrids based on layered inorganic compounds such as clays has been studied for a considerable time, but the area is enjoying a resurgence of interest and activity as a result of the exceptional properties which can be realized from such nanocomposites. Common clays are naturally occurring minerals, and are thus subject to natural variability in their constitution. Many clays are aluminosilicates, the most common of which is montmorillonite (MMT). Depending on the precise chemical composition of the clay, the sheets bear a charge on the surface and edges, this charge being balanced by counter-ions, which reside in part in the inter-layer spacing of the clay. One important consequence of the charged nature of the clays is that they are generally highly hydrophilic species, and hence naturally incompatible with a wide range of polymer types. A necessary prerequisite for successful formation of polymer-clay nanocomposites is therefore alteration of the clay polarity to make the clay "organophilic". Organophilic clay can be produced from normally hydrophilic clay by ion exchange with an organic cation such as an alkylammonium ion (quat). The way in which this is done has a major effect on the formation of particular nanocomposite product.

Nylon-6 (Ny-6) nanocomposites are the leader polymer-clay nanocomposites (PCNs) since the pioneering work performed at Toyota Central Research Laboratories in the early 1980s. An alternative to traditional Nylon-6 is a polyamide commercialized by the Caffaro Industries (Monterotondo, Rome, Italy) as ADS-40T. Basically, it is a copolymer of ε-caprolactone and 1,1',3-trimethylcyclohexyl-3-methylamine-5-isophtalamide (approximately 5% w/w) (see Figure 1). A notable feature of ADS-40T is a better processability with respect to Nylon-6. Indeed, the addition of the small quantity of the aromatic comonomer results in a lower T_g, without leading to a sensible modification of the characteristics of the polyamides, barrier properties included.

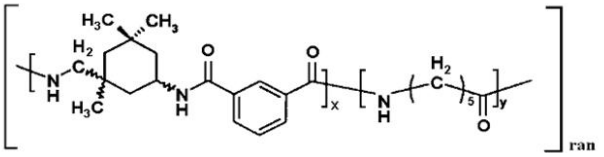

Figure 1. Chemical structure of the comonomer present in ADS-40T. Ran = random substitution.

In this work we present the results obtained by the application of molecular simulation procedures developed ad hoc for these systems [1-3], aimed at determining which of the two polymers (Nylon-6 and ADS-40T) is the most suitable to be used in the design and synthesis of a PCN.

Computational details

The starting crystal structure of MMT was taken from our previous work [1-3]. Several ammonium salts were considered as possible surfactants in this study (Table 1). The model structures of all quats were generated using a well-validated, combined molecular mechanics/molecular dynamics simulated annealing (MDSA) protocol [4]. The electrostatic charges for the geometrically optimized quat molecules were obtained by quantum mechanical calculations. The procedure applied for the generation of accurate model amorphous structures for both Nylon-6 and ADS-40T is also described in our papers [1-3]. After each component was modeled (MMT platelet, quat and polyamide), the overall system was built, the bond between the quaternary nitrogen and the methylene group of each quat being oriented perpendicularly to the xy plane of the mineral, and the same N atom positioned just above the corresponding Mg ion but in such a way that the dispersive terms of the van der Waals forces were favored over the repulsive ones. To generate a proper surface, the lattice constant c of the MMT cell with six quat molecules on one side was extended to 125–150 Å, depending on the length of the quats and the nylon molecules. In this way, even if the model is 3D periodic, there are no interactions between the periodic images in the z-direction, creating a pseudo 2D periodic system.

Acronym	Chemical Formula
M3C6	$(CH_3)_3N(C_6H_{13})$
M3C6COOH	$(CH_3)_3N(C_6H_{12})COOH$
H3C11COOH	$(H_3)N(C_{11}H_{22})COOH$
M3C12	$(CH_3)_3N(C_{12}H_{25})$
M3C12COOH	$(CH_3)_3N(C_{12}H_{24})COOH$
M2C18C2OH	$(CH_3)_2N(C_{18}H_{37})(C_2H_4OH)$
MC18(C2OH)2	$(CH_3)NC_{18}H_{37}(C_2H_4OH)_2$
M2(C18)2	$(CH_3)_2N(C_{18}H_{37})_2$

Table 1. Acronyms and chemical formulas of the quaternary ammonium salts considered in this work.

Isothermal-isochoric (NVT) molecular dynamics (MD) experiments were run at 600 K. The solid surface atoms were constrained to their equilibrium positions via harmonic springs, which allowed for thermal vibrations. The Newton atomic equations of motion were integrated numerically using an integration step of 1 fs. It consisted in an equilibration phase of 50 ps, and in a successive data collection phase, which was extended up to 250 ps. For the calculation of the binding energy [3-5] we considered the potential energy of the global system E_{tot} as given by the following summation:

$$E_{(pol//MMT/quat)} = E_{pol} + E_{MMT} + E_{quat} + E_{pol/MMT} + E_{pol/quat} + E_{MMT/quat} \quad (1)$$

in which the first three terms represent the energy of the polymer, MMT, and quat (consisting of both valence and nonbonded terms), and the last three terms are the interactions energies between each of two component pairs (made up of nonbonded terms only). By definition the binding energy is the negative of the interaction energy. To calculate the binding energy E_{bind}(pol/MMT), for example, we first created a polymer–montmorillonite system deleting the quat molecules from an energy minimized conformation and calculated the potential energy of the system $E_{pol/MMT}$ without further minimization. Next, we deleted the MMT platelet and K^+ ions leaving a polyamide molecule alone, and thus calculated the energy of the polymer molecule, E_{pol}. Similarly, we deleted a polypropylene molecule from the polyamide-montmorillonite system and calculated E_{MMT}. Then, the binding energy E_{bind}(pol/MMT) can be calculated from the following equation:

$$E_{bind}(pol/MMT) = E_{pol} + E_{MMT} – E_{pol/MMT} \quad (2)$$

The remaining binding energies between the MMT and the quat, and between the polyamide and the quat, can be calculated in quite an analogous fashion from the corresponding equations. The estimation of the molecular surface areas and volumes of the quats was performed via the Connolly dot algorithm, corrected to account for quantum effects [5]. For the determination of the basal spacing of all systems, we built a three component model consisting of two layers of MMT, several quat molecules and a polymer chain. The c values in the initial model of MMT crystal supercells were prolonged according to a bilayer arrangement of the quats. Isothermal – isobaric (NPT) MD experiments were run at 600 K for a total time of 250 ps. The Ewald summation method was used to handle long range nonbonded interaction. During each MD, both montmorillonite layers were treated as rigid bodies by fixing all cell dimensions except for c, and all atoms in the interlayer space including K^+ cations were allow to move without any constraint.

RESULTS AND DISCUSSION

As the simulation progresses, both in the case of Nylon-6 and ADS-40T the surfactant chains flatten onto the clay surface and cover almost the entire surface, so that the polymer can dock on top of the quats and reach only a small portion of the MMT, if any. In other words, the polymer molecules collapse onto the quats themselves rather than directly on the clay surface, as the quats shield the interactions between the clay and the polymer, the larger the quat the larger the shielding effect. The adsorption of the hydrocarbon chains on the MMT layer of the clay surface finds its origin in the resulting, favorable electrostatic interactions. From the energetical standpoint, the binding energy between the polymer and the quat decreases in an almost linear fashion with increasing quat molecular volume V. Therefore, in principle, smaller quats should provide more efficient interfaces that bigger ones. On the other hand, $E_{bind}(pol/quat)$ and $E_{bind}(MMT/quat)$ both increase with V, although with a different dependency. Since the quat shields the interactions between the polymer and the clay, the system composed by pristine MMT and polyamide is characterized by the highest binding energy, as expected. According to this finding, nanocomposites obtained from untreated clays by, for instance, in situ polymerization, should, in principle, present the best mechanical properties. All these simulation results have been recently verified experimentally by Fornes et al. for Nylon-6 PCN [6]. To limit computational time to reasonable limits, we considered only three systems for further modeling, devoted to the determination of the corresponding basal spacing. Figure 2 illustrates the MMT/C18(C2OH)2/ADS system prior and at the end of the MD simulation. Table 2 shows the values of basal spacing of models with relevant compositions after 250 ps of NPT molecular dynamics simulation. It is evident that, at a given time, all systems based on the ADS-40T polyamide are characterized by a larger basal spacing, index of a greater tendency towards exfoliation. A comparison of the simulated d-spacing for the test system MMT/MC18(C2OH)2 with the corresponding experimental data [7] shows an excellent agreement: 18.2 Å (predicted) vs. 18.5 Å (experimental).

CONCLUSIONS

By applying MD simulation techniques, we verified that the energy of binding between the polymeric matrices and the montmorillonite platelets shows a decreasing trend with increasing molecular volume V of the quaternary ammonium salt used as surfactant. On the other hand, both the binding energy between the polyamides and the quat, and between the quat and the montmorillonite increase with increasing V, although with a different slope. Shorter hydrocarbonic chains are more effective in producing favorable binding energies with respect to longer ones, and the substitution of hydrogen atoms with polar groups, such as –OH or –COOH on the quaternary ammonium salt generally results in a greater interaction of the quat with the polymers. Under the hypothesis that the clay platelets are uniformly dispersed within the polymer matrix, the pristine clay still yields a high interfacial strength between MMT and the polyamines. When comparing the two polymer matrices, the PCN based on the use of the ADS-40T polyamide is characterized by a greater tendency to exfoliation with respect to the corresponding Nylon-6-based system.

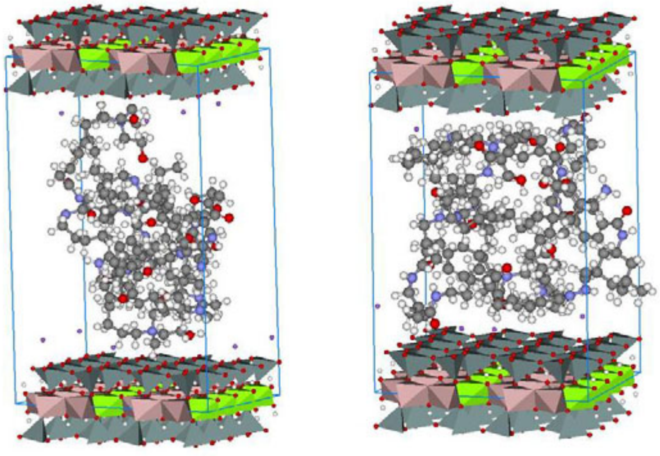

Figure 2. Snapshots of the MMT/ MC18(C2OH)2 system prior (left) and at the end (right) of the MD simulation.

System	d-spacing (Å)
MC18(C2OH)2	18.2
ADS/M3C6COOH	25.9
Nylon-6/M3C6COOH	22.4
ADS/MC18(C2OH)2	26.5
Nylon-6/MC18(C2OH)2	24.2
ADS/M3C12COOH	25.8
Nylon-6/M3C12COOH	23.2

Table 2. d-spacing calculated by MD simulations.

REFERENCES

1. Fermeglia M, Ferrone M, Pricl S. Fluid Phase Eq. 2003; 212: 315-329.
2. Fermeglia M, Ferrone M, Pricl S. Molecular Simulation 2004; 30: 289-300.
3. Fermeglia M, Ferrone M, Coslanich A, Chiellini, E, Toth R, Miertus S, Pricl S. Polymer 2004 in press.
4. M. Fermeglia, S. Pricl, AIChE J. 1999; 45: 2619–2627.
5. Fermeglia M, Pricl S. Fluid Phase Equilib. 1999; 166: 21-37.
6. Fornes TD, Hunter DL, Paul DR. Macromolecules 2004; 37:1793-1798.
7. Incarnato L, Scarfato P, Russo GM, Di Maio L, Iannelli P, Acierno D. Polymer 2003; 44: 4625-4634.