

# **Polymer-Clay Nanocomposites Based on PEO-Diacrylate Macromolecules: a Combined Computational/Experimental Study**

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## **ABSTRACT**

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. Materials variables which can be controlled and which can have a profound influence on the nature and properties of the final nanocomposite include the type of clay, the eventual choice of clay pre-treatment, the selection of polymer component and the way in which the polymer is incorporated into the nanocomposite. The synthetic route of choice for making a nanocomposite depends on whether the final material is required in the form of an intercalated or exfoliated hybrid. In the case of an intercalate, the organic component is inserted between the layers of the clay such that the inter-layer spacing is expanded, but the layers still bear a well-defined spatial relationship to each other. In an exfoliated structure, the layers of the clay have been completely separated and the individual layers are distributed throughout the organic matrix. A third alternative is dispersion of complete clay particles (tactoids) within the polymer matrix, but this simply represents use of the clay as conventional filler. In recent years, there has been extensive study of the factors which control whether a particular organo-clay hybrid can be synthesized as an intercalated or exfoliated structure. Since clay nanocomposites can produce dramatic improvements in a variety of properties, it is important to understand the factors that affect delamination of the clay. These factors include, besides the exchange capacity of the clay and the polarity of the reaction medium, the chemico-physical properties of interlayer cations.

In this work we present the results of a jointed computational/experimental effort aimed at the study and comprehension of the interactions which occur, at a molecular level, in

the formation of polymer-clay nanocomposites based on PEO-diacrylate macromolecules.

## **1. 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. Materials variables which can be controlled and which can have a profound influence on the nature and properties of the final nanocomposite include the type of clay, the eventual choice of clay pre-treatment, the selection of polymer component and the way in which the polymer is incorporated into the nanocomposite. The synthetic route of choice for making a nanocomposite depends on whether the final material is required in the form of an intercalated or exfoliated hybrid. In the case of an intercalate, the organic component is inserted between the layers of the clay such that the inter-layer spacing is expanded, but the layers still bear a well-defined spatial relationship to each other. In an exfoliated structure, the layers of the clay have been completely separated and the individual layers are distributed throughout the organic matrix. A third alternative is dispersion of complete clay particles (tactoids) within the polymer matrix, but this simply represents use of the clay as conventional filler. In recent years, there has been extensive study of the factors which control whether a particular organo-clay hybrid can be synthesized as an intercalated or exfoliated structure. Since clay nanocomposites can produce dramatic improvements in a variety of properties, it is important to understand the factors that affect delamination of the clay. These factors include, besides the exchange capacity of the clay and the polarity of the reaction medium, the chemico-physical properties of interlayer cations.

In this work we present the preliminary results of a jointed computational/experimental effort aimed at the study and comprehension of the interactions which occur, at a molecular level, in the formation of polymer-clay nanocomposites based on PEO-diacrylate macromolecules. In particular, we have investigated PEO-diacrylate nanocomposite systems with different number of monomers both in an anhydrous and solvated environment, with the two-fold purpose of (i) understanding the behavior of the polymer chains and water molecules near the clay surface during the polymerization, and (ii) finding out which of the monomers offers the best results in terms of system energetics. Also, we investigated the effect of molecular weight on the

interactions between individual the individual system components.

## 2. Computational details

The crystal structure of MMT was taken from our previous work;<sup>1-3</sup> the resulting lattice is monoclinic, with space group C2/m, and characterized by the following lattice parameters:  $a=5.20 \text{ \AA}$ ,  $b=9.20 \text{ \AA}$ ,  $c=10.13 \text{ \AA}$  and  $\alpha=90^\circ$ ,  $\beta=99^\circ$ ,  $\gamma=90^\circ$ . The generation of accurate model amorphous structures for co-polymers was conducted as follows. First, the constitutive repeating unit (CRU) of different polymers was built and its geometry optimized by energy minimization using Compass.<sup>4,5</sup> Hence, the CRU was polymerized to a given degree of polymerization (DP). The DP of PEO in each co-polymer was fixed to 10, whilst the DP for all diacrylate monomers considered were set to 1, 25 and 50, respectively. Explicit hydrogens were used in all model systems. The Rotational Isomeric State (RIS) algorithm,<sup>6</sup> as modified by Theodorou and Suter,<sup>7</sup> was used to create the initial polymer conformation at  $T = 300 \text{ K}$ . The structure was then relaxed to minimize energy and avoid atoms overlaps using the conjugate-gradient method. The TIP3P model was chosen to represent water molecules.<sup>8</sup> After each system component was modeled (i.e., MMT platelet,  $\text{H}_2\text{O}$  molecules, and polymers), binary systems (MMT/polymer) and ternary systems (MMT/ $\text{H}_2\text{O}$ /polymers) were built. A ternary simulation model consists of a MMT unit cell, one polymer chain, and 240 water molecules, which create approximately a  $30 \text{ \AA}$  thick layer of water. Of course, the size of the model is dictated by reasonable computational times. At the same time, however, such models will allow us to calculate the interactions between the all components near the clay surface.

To generate a mineral surface apt for the simulation, the lattice constant  $c$  of the MMT cell with the polymer and water molecules on one side was extended to  $150 \text{ \AA}$ . Coulombic and van der Waals interactions were treated with a direct cut off radius of  $8.5 \text{ \AA}$ . Then, to equilibrate the system, we performed one cycle of combined molecular mechanics/molecular dynamics simulated annealing (MDSA) protocol<sup>9-11</sup> in order to achieve temperature and velocity of atoms. Then, 500 ps of isothermal–isochoric (NVT) molecular dynamics experiments were run at  $300 \text{ K}$ . During the productive MD simulations, the positions of the MMT and  $\text{Na}^+$  atoms were fixed, but all remaining system components (polymers, and water molecules) were allowed to move accordingly. The estimation of the molecular surface areas ( $SA$ ) and volumes ( $V$ ) was performed via the Connolly dot algorithm,<sup>12</sup> corrected to account for quantum effects

using the method proposed by Rellick and Becketl.<sup>13</sup> In this way, no assumption was made about the value of the radii of individual atoms.<sup>14</sup>

### 3. Results and discussion

In order to find out the effect of water molecules on the interactions between polymer and clay platelets, we have performed all simulations both in an anhydrous and in a solvated environment. Table 1 reports the binding energies between individual components of the system with two monomers (marked as 1) in both situations (water and non-water systems).

Model abbreviation	Binary systems	Ternary systems			V(Å <sup>3</sup> )	SA(Å <sup>2</sup> )
	E <sup>bind</sup> (MMT/Pol) (kcal/mol)	E <sup>bind</sup> (MMT/Pol) (kcal/mol)	E <sup>bind</sup> (MMT/H <sub>2</sub> O) (kcal/mol)	E <sup>bind</sup> (Pol/H <sub>2</sub> O) (kcal/mol)		
PGDA-AA1	1645	1187	20729	-43	637	763
PGDA-VAc1	1770	649	19296	47	717	891
PGDA-MMA1	1808	900	19318	145	744	961
PGDA-HEMA1	2661	599	20096	259	755	899
PGDA-IBM1	3284	2336	19347	149	843	995

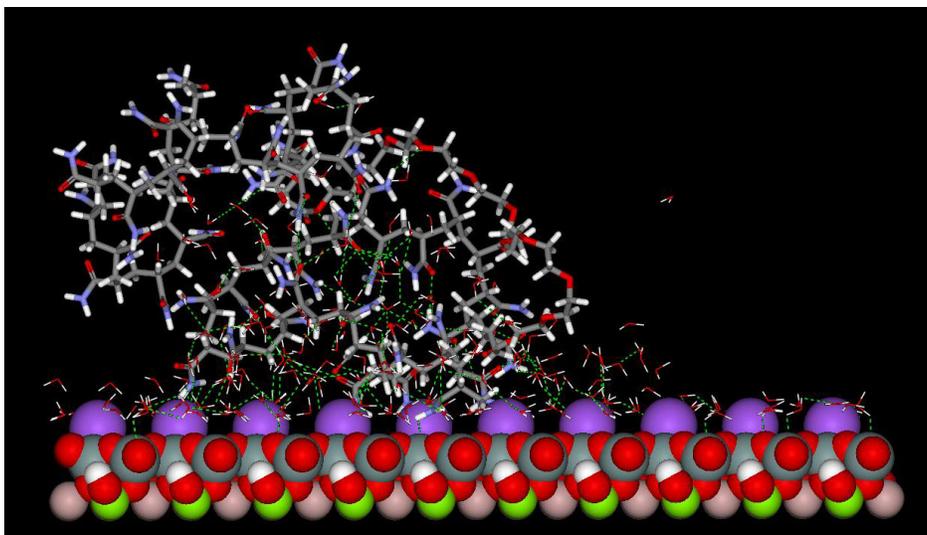
**Table 1.** Binding energy in binary (anhydrous) and ternary (water) systems with PEO-diacrylate polymers featuring only one diacrylate monomer on each side of the PEO chain.

In the non-water system, the binding energy between MMT and polymer clearly increases with increasing polymer chain volume. Moreover, from this trend we obtain that IBM monomer should offer the most favorable interactions with MMT platelet. A similar behavior is observed for higher DP systems, (see Table 2 as an example), although further parameters also play a role, as discussed later.

Model abbreviation	Binary systems	Ternary systems			V(Å <sup>3</sup> )	SA(Å <sup>2</sup> )
	E <sup>bind</sup> (MMT-Pol) (kcal/mol)	E <sup>bind</sup> (MMT-Pol) (kcal/mol)	E <sup>bind</sup> (MMT-H <sub>2</sub> O) (kcal/mol)	E <sup>bind</sup> (Pol-H <sub>2</sub> O) (kcal/mol)		
PGDA-AA25	5450	2234	18483	315	3099	2980
PGDA-VAc25	7720	2080	18220	606	3675	3517
PGDA-MMA25	4098	3650	17781	702	4458	4213
PGDA-HEMA25	4677	4322	19344	778	5270	4734
PGDA-IBM25	1743	1071	19396	791	7013	6175

**Table 2.** Binding energy in binary (anhydrous) and ternary (water) systems with PEO-diacrylate polymers featuring 25 diacrylate monomer on each side of the PEO chain.

Water molecules preferably reside on the surface of the clay, by virtue of strong Coulombic interactions and hydrogen bond formation with the free OH group of the MMT layer (see Figure 1). Also the simulation numerical results confirm this arrangement of molecules near the clay surface, as the binding energies in all cases decrease in the order  $E_{\text{bind}}(\text{MMT}/\text{H}_2\text{O}) > E_{\text{bind}}(\text{MMT}/\text{Pol}) > E_{\text{bind}}(\text{Pol}/\text{H}_2\text{O})$ . As we can observe from Tables 1 and 2, the presence of water molecules in the system always results in a decrease of the binding energy between the clay and the polymer, in harmony to what already observed for other, similar systems.<sup>15</sup>



**Figure 1.** Equilibrated frame of MD trajectory for a ternary system with DP of 25 for the diacrylate polymer. Hydrogen bonds are depicted in green broken lines.

In considering the behavior of  $E_{\text{bind}}(\text{Pol}/\text{H}_2\text{O})$  we found out that, aside for the volume effect, also the presence of polar functional groups in the monomers play a role in these interactions. In fact, non only the binding energy increases with the polymer volume, but also the greater contribution to  $E_{\text{bind}}(\text{Pol}/\text{H}_2\text{O})$  is found for the HEMA monomer. This CRU features both a CO group and an OH moiety, and both concur to favorably the interactions between the polymer and water by creating a hydrogen bond network.<sup>15</sup>

The effect of polar functional group is also quite evident in the case of AA and VAc monomers. In the corresponding water systems, the  $E_{\text{bind}}(\text{MMT}/\text{Pol})$  term for these two monomers is just opposite to its counterpart in an anhydrous environment (see Table 1). Sensibly, in the absence of water, the major effect exerted on the system is that of the molecular dimensions (i.e.,  $SA$  and  $V$ ), while in a solvated environment, the  $\text{H}_2\text{O}$  molecules contribute the formation of a hydrogen bond network with the oxygens in VAc monomer, thus increasing the corresponding  $E_{\text{bind}}(\text{Pol}/\text{H}_2\text{O})$  term [ $E_{\text{bind}}(\text{PGDA-VAc-H}_2\text{O}) > E_{\text{bind}}(\text{PGDA-AA-H}_2\text{O})$ ], and simultaneously decreasing the interactions between PGDA-VAc and the clay platelets.<sup>15</sup>

As mentioned above, the molecular weight has a significant effect on the interactions and arrangements of the molecules near the clay surface. With growing of the polymer chain during polymerization, the binding energy between the clay and polymer increases till the moment when the polymer is so long that intrachain polymer interactions prevail; accordingly,  $E_{\text{bind}}(\text{MMT}/\text{Pol})$  starts to decrease. In particular, the IBM containing monomers show a decreasing trend in the  $E_{\text{bind}}(\text{MMT}/\text{Pol})$  term already at  $\text{DP} = 25$ , thus highlighting the effect of polymer growth on the energetics of polymer/clay nanocomposite systems.

Monomer abbreviation	$E^{\text{bind}}$ (MMT-Pol1) (kcal/mol)	$E^{\text{bind}}$ (MMT-Pol25) (kcal/mol)	$E^{\text{bind}}$ (MMT-Pol50) (kcal/mol)
AA	1645	5450	4327
VAc	1770	7720	6670
MMA	1808	4098	3290
HEMA	2661	4677	2896
IBM	3284	1743	1220

**Table 3.** Binding energy in binary systems as a function of the copolymer molecular weight.

At the time of writing this summary, the SAXS, crio-TEM and other experimental measurements on all the systems considered in this study are currently being performed at the Synchrotron radiation facility “Elettra”, located at the Area Science Park in Trieste, Italy, and at the Technical University of Eindhoven, The Netherlands. Accordingly, the results and the relevant comments will be presented in the poster at the FOMMS conference.

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