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Polymer 47 (2006) 5196–5205

polymer

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Insight into molecular interactions between constituents in polymer clay nanocomposites

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Received 28 February 2006; received in revised form 10 May 2006; accepted 11 May 2006
Available online 2 June 2006

Abstract

The mechanisms responsible for the enhancement of physical properties of polymer clay nanocomposites (PCN) over pristine polymers are not well understood. This knowledge is important for obtaining a better control over the physical properties of PCN and designing PCN with tailored properties. The interactions among the different constituents of PCN may be a key factor for controlling physical properties of PCN. The interaction energy is an important measure of the interactions among different constituents of composites. Molecular dynamics (MD) is a useful tool for studying the nature and quantitative analysis of interaction energies of a molecular system. In this work, the interaction energies among different components of intercalated organically modified montmorillonite (OMMT) and PCN have been investigated. Here, the interaction of polymer or organic modifier with clay and polymer and modifier is studied. Also, the nature and quantitative contributions arising from functional groups or backbone chain have been assessed. This investigation provides important insight into the mechanism of intercalation, and specific information about the interactions of different constituents in the nanocomposites system. In this current work using MD, for the first time, we have provided a detailed quantitative picture of interactions among the different components of OMMT and PCN.

Keywords: Molecular interactions; Polymer clay nanocomposites; Polyamide 6

1. Introduction

Polymer clay nanocomposites (PCN) are novel composite material systems. These composites show significant improvement in mechanical properties [1–12] thermal properties [13–20], liquid barrier properties [11,17,21] over pure polymer and conventional microcomposites of polymer and clay. In PCN, the layered crystals of expansive clay minerals are dispersed in the polymer matrix at a length scale of nanometer. Expansive clay minerals with periodic layered structure like sodium montmorillonite (Na-MMT) are generally the clay used in the synthesis of PCN. The basal spacing of montmorillonite depends on adsorbed water content and the spacing can vary from 9.6 to 19.6 Å [22]. Hydrophobic polymers such as polyamide 6 (PA 6), polycaprolactone, etc. are mixed with clay for synthesis of PCN. The interlayer adsorbed water in clay inhibits the miscibility of hydrophobic polymer with clay. Hence, for synthesis of PCN containing hydrophobic polymer, generally, organic modifiers are used for modifying the clay, which replaces the adsorbed water from the interlayer of Na-MMT [23]. Thus, the three constituents of PCN are polymer, clay and organic modifier. Also by dispersing clay in the polymer, two types of nanocomposites can be formed. These are shown schematically in Fig. 1: (i) intercalated PCN where the periodic layered structure of clay is maintained in nanocomposites; and, (ii) exfoliated PCN in which the clay nano particles become delaminated in the polymer matrix breaking the periodic 1 structure of clay. This morphology of PCN strongly depends upon the preparation method as well as the selection of organic modifier [24].

However, the fundamental reasons for the enhanced properties are not clearly established. Unless the mechanisms responsible for property enhancement are known, PCN with desired properties cannot be designed with adequate control and accuracy. Recently, the structure, dynamics, and interactions of PCN have been investigated extensively using MD [25–29], Monte-Carlo simulation [30–33], Density functional theory [34–38], and Fourier transformation infrared spectroscopy [39–42]. Our recent work [43,44] has showed that only non-bonded interactions exist among different constituents in PCN. The interaction energies between clay–organic modifiers–polymer at interfaces are unknown. The properties

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doi:10.1016/j.polymer.2006.05.026

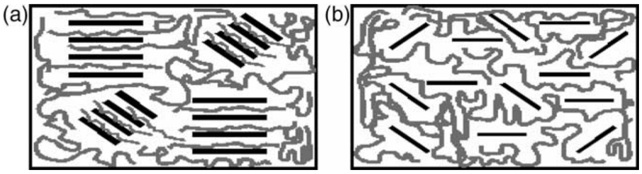

Fig. 1. Schematic representation of (a) intercalated nanocomposites, (b) exfoliated nanocomposites.

of composites largely depend on interaction of the interfaces of the constituent materials [45,46]. These results suggest that the non-bonded interactions among the different constituents in PCN may have an important role in property enhancement. MD simulation is an excellent tool for evaluating characteristics and quantitatively analysing the interactions of different components in a molecular system. In this work, we have evaluated the non-bonded interactions of different constituents of OMMT and PCN using MD.

Ma et al. [9] in their experimental investigation showed that organic modifiers have some role in the property enhancement of PCN. To assess the influence of interlayer density of polymer on the molecular organizations of PCN of poly(ε-caprolactone), Gardebien et al. [24,47] studied the intercalated and exfoliated PCN with varying density of interlayer polymer chains. Balazs et al. [34–38] have studied the free energy properties of polymer intercalated in OMMT to find the driving force of insertion of polymer in the interlayer spacing of OMMT. Using mean field model, Vaia et al. [48] examined the effect of silicate functionalization, annealing temperature, molecular weight of polymer on interactions of PCN. In nylon 6,6 exfoliated PCN, Tanaka et al. [49] showed that binding energy between clay and polymer is highest and it decreases almost linearly as the volume of adsorbed organic modifier in clay increases.

Minisini et al. [50] studied the influence of surfactant on the electrostatic potential bonding between two clay layers in OMMT using MD. In a separate work [51], they found that for functionalized polypropylene (PP) based PCN, interaction of PP increases in the presence of specific functional group in polymer. Also using MD, Shah et al. [52] estimated the force, which breaks surfactant micelle at the silica interfaces. Farmeglia [53,54] found that with the increase in concentration of organic modifier, the binding energy decreases between polymer and clay; and increases between modifier and clay, and, modifier and polymer. Luo et al. [55] developed a 3-phase model of exfoliated and intercalated PCN by MD for predicting the modulus of the nanocomposites. Beyer et al. [56] studied the effect of surfactant-length on the morphology of polymer layered silicate nanocomposites. Sinsawat et al. [57] by MD simulation investigated the influence of parameters such as temperature, polymer architecture, etc. on the morphology of PCN. A mean field lattice based model of polymer melts intercalated in organically modified silicate (OLS) composite was proposed by Vaia and Giannelis [58]. Using MD simulation, Gaudel-Siri [59] studied the mechanism of intercalation process of ε-caprolactone based PCN.

Thus, a broad overview about interaction among the different constituents of OMMT and PCN is available in literature. However, the specific details about quantitative contribution of different constituents and different parts of a particular constituent towards the interactions with other constituents in OMMT and PCN were not assessed in the past investigations. Unless these quantities and nature of interactions are clear, a good control over the physical properties of PCN cannot be obtained. Hence, in this current work, for the first time, we have provided a quantitative picture of interactions among the different components of OMMT and PCN using MD. The qualitative (van der Waals, and electrostatic) and quantitative nature of interactions arising from different parts of each constituent (backbone chain, functional groups, etc.) and their specific influence over the total interactions with other constituents in OMMT and PCN have been analyzed. Such a study can help in the selection of suitable polymer or organic modifiers and designing PCN of required properties.

2. Computational methodology

In this study, we have used molecular dynamics simulation to investigate the interactions between polymer, clay, and organic modifier in organically modified clay and polymer clay nanocomposites. NAMD2.5 [60] was used as molecular dynamics software. VMD1.8 [61] was used for all interactive studies and visualization. In the present study, PA, sodium montmorillonte (Na-MMT) and 12-aminolauric acid were used as polymer, clay and organic modifier, respectively. In the synthesis of OMMT, the organic modifier was protonated by hydrochloric acid in aqueous solution and then mixed with Na-MMT to prepare OMMT. The protonated 12-aminolauric acid used as organic modifier has 11 carbon atoms and 22 hydrogen atoms in the backbone chain; and protonated amine group (N^+H_3) at one end and carboxylic group (–COOH) at the other end. The structure of 12-aminolauric acid, PA 6, and Na-MMT all were made using the module Builder™ of InsightII™ 2005 of Accelrys, Inc., San Diego, CA, USA. The force field used for 12-aminolauric acid and PA 6 was CHARMm 27 [62]. After building the models of polymer and organic modifiers, the structures were minimized for sufficiently long time using Accelrys group software, Insight-II™ 2005. These energy minimized structures were then used in making the initial models for OMMT and PCN. The partial charges of organic modifier, 12-aminolauric acid and polymer, PA 6 containing three typical monomers are shown in the Fig. 2. Each strand of 12-aminolauris acid has the net charge of +1, and polymer, PA 6 is charge neutral.

In our study, isomorphically ion substituted Na-MMT of unit cell-composition $[NaSi_{16}(A_{16}FeMg)O_{40}(OH)_8]$ was used. The positions of the atom were derived directly from the empirical model proposed by Skipper et al. [63,64]. The charge of each atom in Na-MMT was obtained from the work of Teppen et al. [65]. The Na-MMT unit cell has the typical T–O–T structure where the aluminum octahedral layers are sandwiched in between two layers of silica tetrahedra.

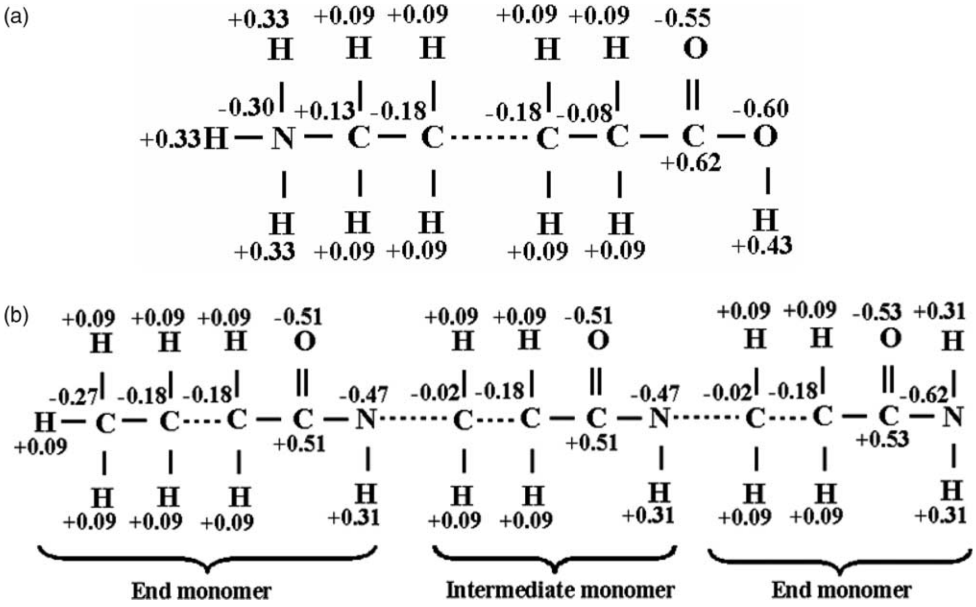

Fig. 2. Chemical structure and partial charges of different atoms in (a) 12-aminolauric acid, and, (b) polyamide 6 Ref. [44].

The aluminum ions (Al^{+3}) were isomorphically substituted by iron (Fe^{+2}) and magnesium (Mg^{+2}) in the every alternate unit cells. This isomorphic substitution produces the net negative charge of -1 in each unit cell of Na-MMT. In our previous work, the force field parameters of Na-MMT were derived for the CHARMm force field from the force field parameters of montmorillonite in CFF force field [66,67]. In the present study, the parameters corresponding to CHARMm force field for Na-MMT have been used. The MD simulation was run at the high performance computing center (CHPC) in the North Dakota State University, USA. The system consists of 64 DakTech nodes and 128 processors (3 Gigahertz Intel/Xeon processors).

2.1. Model of organically modified montmorillonite (OMMT)

The intercalated model of OMMT contains two layers of montmorillonite (MMT) sheets. Each layer of MMT sheet contains periodically replicated 18 unit cells out of which six unit cells are in the *X* are in the *Y* direction. The dimensions of the starting intercalated OMMT model are $a=31.68$ Å, $b=27.44$ Å, and $c=24.16$ Å. The final structure of OMMT model is shown in the Fig. 3. The initial *d*-spacing of the OMMT model was 17.60 Å. The net charge of each layer of MMT was -9. To bring about the charge neutrality in the OMMT model, nine strands of 12-aminolauric acid were inserted in the interlayer clay spacing. From our previous study [44], we have seen that the orientation of organic modifiers in the intercalated OMMT is flat and parallel to the interlayer clay surface. Hence in the initial OMMT model, the organic modifiers were placed parallel to the interlayer clay surface and at the center of the interlayer clay spacing. To impart periodicity in the *Z*-direction of the model, the organic modifiers were placed in two layers with an initial spacing of 17.60 Å (i.e. equal to the initial *d*-spacing) from the preceding layer of organic modifier. The natural sodium montmorillonite contains both the sodium ions and adsorbed water at interlayer clay spacing depending on its degree of saturation [67,68]. From our previous PA-FTIR study [43], we found that the interlayer water is absent in the OMMT. The interlayer sodium cations of clay are replaced by organic modifiers through cationic substitution during the synthesis of OMMT [23]. Hence in the OMMT model, interlayer sodium cations and water molecules were not introduced.

2.2. Model of polymer clay nanocomposites (PCN)

From our previous study [44], we have found that for PA 6 based PCN, eight monomer polymer chain for the intercalated model of PCN containing 18 MMT unit cells in the each layer is representative of polymer in clay gallery in PCN. In the synthesis of PA 6 based PCN, the OMMT is mixed with the PA 6. Accordingly, the initial model of PCN was obtained by inserting the annealed and minimized structure of polymer chain in the interlayer clay gallery of final OMMT model.

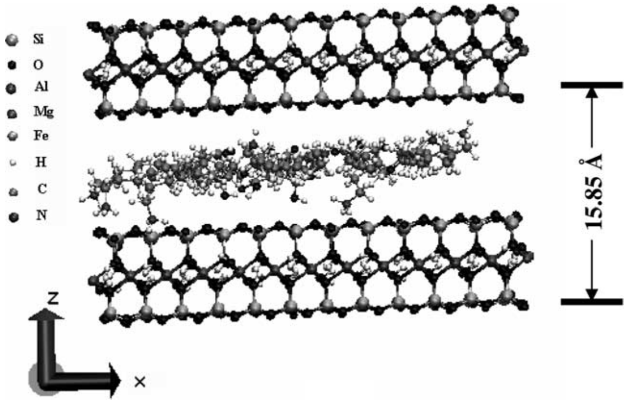

Fig. 3. Molecular model of OMMT after MD simulation.

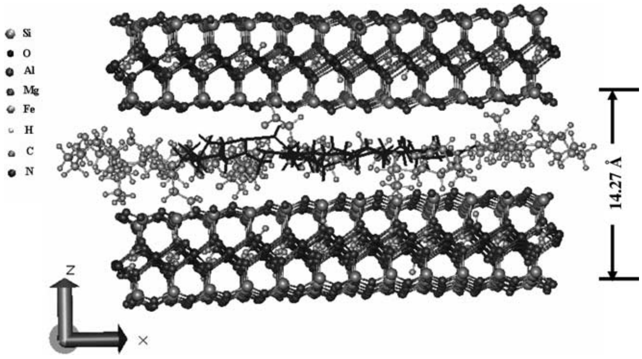

Fig. 4. Molecular model of PCN after MD simulation. Polymer is represented by Licosice rendering form and organic modifiers in ball and stick model in the interlayer clay gallery of PCN.

The final model of intercalated PCN is shown in the Fig. 4. The initial size of the PCN model was $a=33.55$ Å, $b=28.902$ Å, and $c=22.41$ Å. The simulation cell for the PCN model was replicated in all three directions through cellBasisVectors, which were maintained 40, 34, and 31.70 Å in the x, y, and z-directions, respectively. For Van der Waals interaction, the switch and cut off distance for this model was maintained 14 and 16 Å, respectively.

2.3. Simulation details of OMMT model

For conducting MD of OMMT, isothermal–isobaric ensemble, constant number, pressure, and temperature (NPT) was applied. The configuration of starting simulation cells was replicated in all three directions using the periodic boundary conditions. The periodic boundary condition was maintained throughout the simulation through the cellBasisVectors, which were 36, 34, and 35.20 Å in the x, y, and z-directions, respectively. For van der Waals interaction, the switch and cut off distances used were 14 and 16 Å, respectively, in the OMMT model. Ewald simulation method [69] was used to model electrostatic interaction. Using MD software NAMD, the OMMT model was initially run in vacuum at temperature, 0 K. The temperature was then raised to room temperature, 300 K. Then pressure was raised gradually from 0 to 1 atmospheric pressure (1.013 bars) under the constant temperature of 300 K. The temperature in the simulation was controlled by Langevin dynamics. The pressure was raised in four steps in the sequence of 0.25, 0.50, 0.75, and 1.013 bars. Next, the temperature of the system was further raised to 333 K at 1 atmospheric pressure, which was following by reducing the temperature to 300 K under same pressure replicating the actual synthesis procedure of OMMT [43]. At every stage of pressure and temperature change, the simulation was run for a duration of 25 ps. Finally, the whole system was run for a duration of 200 ps (10^{-12} s) at 300 K temperature and 1 atmospheric pressure for the complete convergence of energy of OMMT model. The energy versus time plot shows that the duration (200 ps) of simulation is sufficient for attaining equilibrium for OMMT model. Some simulations have been run for higher duration of 400 ps to verify that 200 ps run time is sufficient for attaining equilibrium for this molecular system. It is seen that the conformations and energy versus time plot of the model of duration 400 ps does not change appreciably from those obtained for 200 ps. The Nose'-Hoover Langevin piston method was used for controlling pressure in the simulation [70,71]. The Verlet algorithm and the time step of 0.5 femto seconds (fs) was used through out the simulation. A force-constraint of 1 Kcal/mol Å was applied only in the x and y-directions to all the atoms in MMT, keeping z-direction movement of MMT free. Organic modifiers were kept unconstrained in all the directions.

2.4. Simulation details of PCN model

The simulation procedure of PCN model was same as of OMMT except the maximum temperature of simulation was 300 K as used in the synthesis route of PCN [43,44]. The energy versus time plot shows that the 200 ps duration of simulation is sufficient for attaining equilibrium for PCN model. In all stages of simulation, a constraint of 1 Kcal/mol Å was applied to all the atoms of MMT in x and y-direction only.

3. Calculation of interaction energy

The interaction energies in the present study are evaluated using energy evaluation tool of NAMD, MDEnergy™ [60]. The interaction energies for any given sets of atoms and for specified cutoff and switch distance can be calculated by MDEnergy™ from the trajectory files obtained from MD simulation. All MD simulations are run for a duration of 200 ps. The average of results for last 25 ps was considered for calculating the bonded and non-bonded energies.

4. Results and discussion

The total energy in the molecular system is the summation of bonded energy and non-bonded energy. The bonded energy terms are the summation of energies corresponding to bonds, angles, and dihedrals pertaining to the models. The non-bonded energy term is the summation of van der Waals (VDW), electrostatic (Elec), and, hydrogen bond (H-bond) energy. NAMD calculates the hydrogen bond and van der Waals together. Hence in this discussion, the hydrogen bond-energy has been included in the van der Waals energy. As mentioned in Section 3, the interactions among the different constituents of OMMT and PCN are non-bonded in nature. Hence, the non-bonded interaction energies among different constituents of OMMT and PCN have been calculated.

4.1. Non-bonded interactions in OMMT

The non-bonded interactions between clay and organic modifiers in OMMT have been presented in Table 1. As seen, smaller the magnitude of interaction energy, stronger is the attractive interaction. The negative and positive energies indicate the attractive and repulsive interaction between interacting molecular systems, respectively. Hence, from

Table 1
Non-bonded energies between clay and different parts of organic modifiers in OMMT

Components of clay–modifier interaction in OMMT (Col-I)	Van der Waals energy (Kcal/mol) (Col-II)	Electrostatic energy (Kcal/mol) (Col-III)	Total non-bonded energy (Kcal/mol) (Col-IV) = Col (II + III)
Clay–modifier	−288	−378	−666
Clay–modifier backbone hydrogen	−62	−408	−470
Clay–modifier backbone carbon	−172	+296	+123
Clay–modifier backbone chain	−234	−112	−346
Clay–modifier functional hydrogen	−4	−515	−519
Clay–modifier functional nitrogen	−7	+118	+111
Clay–modifier functional oxygen	−28	+287	+259
Clay–modifier functional carbon	−15	−156	−171
Clay–modifier end functional groups	−54	−266	−320

Table 1 it is observed that there is an attractive interaction between clay and organic modifiers in OMMT. The structure of organic modifier has been divided into two parts: (i) backbone chain containing 12 carbon and 22 hydrogen atoms, and (ii) end functional groups having one carboxylic and one protonated amine group in the end functional groups. The end functional groups and backbone chain of organic modifiers, both contribute in the attractive interactions with clay; however, the contribution from backbone chain is higher than the contribution from end functional groups of organic modifiers. As seen from Fig. 2, although the partial charges of individual backbone chain-hydrogen atoms are smaller compared to functional group-hydrogen atoms, their presence in large numbers actually results in significant interactions with clay.

4.2. Intercalation process

The total energies of polymer, OMMT and PCN are given in the Table 2. At the beginning of synthesis of PCN, when the OMMT is added to the polymer, and the composite has not formed, that state may represent the immiscible state of polymer and OMMT. The energy of that immiscible state can be expressed as the summation of the individual energies of OMMT and polymer, which is −256,803 Kcal/mol. From Table 2, we find that the total energy of the PCN is −257,061 Kcal/mol Å, which is 282 Kcal/mol Å less than the energy of immiscible blend of polymer and OMMT. Thus, from the energy consideration, it can be inferred that the PCN formed as final product from the polymer and intercalated OMMT, exists as a stable system.

4.3. Non-bonded interactions of different components in PCN

The interaction energies among three different constituents of PCN are calculated and presented in Table 3. Because of the presence of relatively higher partial charges in the atoms of the functional groups of organic modifier and polymer; and their closure presence with in the PCN, the constituents of PCN are prone to undergo non-bonded interactions with each other. The interaction energy between clay and organic modifier being lowest indicates the strongest interaction between clay and organic modifiers followed by interactions between clay and polymer. The interactions between the polymer and organic modifier are the smallest among all the combinations of constituents.

Table 2
Comparison of total non-bonded energies among PCN, OMMT, and polymer

Materials	Total energy (Kcal/mol)
Polymer clay nanocomposites (PCN)	−257,062
OMMT	−256,804
Pure polymer	+24

4.4. Interaction of different segments of organic modifiers and polymer with clay in PCN

The interaction energies between clay and different parts of organic modifiers in PCN are presented in the Table 4. It is seen that in PCN, the end functional groups of organic modifiers have higher interaction with clay in comparison to the backbone chain. As seen in Fig. 2, the partial charges on the hydrogen atoms of the end functional groups of organic modifiers are relatively higher, and consequently their interactions with clay is strongest. Next higher interaction is between backbone chain-hydrogen atoms and clay. Like OMMT, end functional groups and backbone chain of organic modifier, both interact with the clay in PCN.

The interactions from different parts of polymer with clay in PCN are presented in the Table 5. As seen in Table 5, the functional groups of polymer have almost no interactions with clay; however, the backbone chain of polymer has attractive interaction with clay. Among all components of polymer, the backbone chain-hydrogen atoms of polymer have the highest interaction with clay. Backbone hydrogen atoms in polymer have relatively lower partial charges compared to end functional group-hydrogen atoms. However, their presence in

Table 3
Non-bonded energies between different constituents in PCN

Components of interaction in PCN (Col-I)	Van der Waals energy (Kcal/mol) (Col-II)	Electrostatic energy (Kcal/mol) (Col-III)	Total non-bonded energy (Kcal/mol) (Col-IV) = Col (II + III)
Clay–modifier	−109	−1	−110
Clay–modifier	−158	−389	−547
Polymer–modifier	+28	−92	−64

Table 4
Non-bonded energies between clay and different parts of organic modifiers in PCN

Components of clay–modifier interaction in PCN (Col-I)	Van der Waals energy (Kcal/mol) (Col-II)	Electrostatic energy (Kcal/mol) (Col-III)	Total non-bonded energy (Kcal/mol) (Col-IV) = Col (II + III)
Clay–modifier	−158	−389	−547
Clay–modifier backbone hydrogen	+2	−356	−354
Clay–modifier backbone carbon	−115	+252	+137
Clay–modifier backbone chain	−113	−104	−217
Clay–modifier functional hydrogen	−5	−504	−509
Clay–modifier functional nitrogen	0	+117	+117
Clay–modifier functional oxygen	−27	+237	+210
Clay–modifier functional carbon	−14	−134	−148
Clay–modifier end functional groups	−45	−285	−330

large numbers makes their total contribution so high in interacting with clay.

4.5. Comparison of interaction between clay and organic modifier in OMMT and PCN

From Tables 1 and 4, it is seen that the interaction between clay and organic modifier is much stronger in OMMT than that in PCN. It seems that the presence of polymer reduces the interaction between clay and organic modifier in PCN. If we separate the total clay–modifier interaction into the interactions coming from different parts of modifier, the main difference in interactions occur because of difference in interactions between backbone chain-hydrogen atoms of modifier and clay. This portion of interaction energy in PCN has increased by +115 Kcal/mol in comparison to OMMT. It indicates comparatively weaker interactions between backbone-hydrogen atoms of organic modifier and clay in PCN. However, the interactions between clay and other portions of organic modifier have changed marginally in PCN in comparison to those in OMMT.

4.6. Non-bonded interactions of polymer and organic modifiers with different components of clay in intercalated PCN

From Fig. 4 it is evident that in PCN, the intercalated organic modifiers and polymer lie in closest vicinity to the interlayer surface-oxygen atoms amongst all the atoms of the clay sheet. In this paper, the interlayer surface oxygen atoms of clay have been referred to as ‘clayoxy’. The interactions of clayoxy with different parts of organic modifiers and polymer are presented in the Tables 6 and 7, respectively. It is seen that organic modifiers and polymer, both have attractive interactions with clayoxy; however the interactions of organic modifiers (−8533 Kcal/mol) are much stronger than the interactions of polymer (−161 Kcal/mol) with clayoxy.

From Table 8, it is seen that the interaction of organic modifiers and polymer with clayoxy is higher than the interactions when whole clay structure is considered. Especially, in case of organic modifiers the interaction with clayoxy is much higher (1560%) than the interactions with whole clay sheet. This indicates that the interior atoms of clay sheet actually reduce the attractive interactions with the organic modifiers and polymers, and the attractive interactions of organic modifiers and polymer mainly result from clayoxy. The interactions of organic modifiers with clay are dominantly electrostatic. From Table 8 it is calculated that the interactions of organic modifiers with clayoxy are mainly electrostatic (97.86% of their total interactions). This large interaction between clay and organic modifier is attributed to the high negative partial charge (−0.70) of surface clay oxygen atoms and the high positive charges of the hydrogen and carbon atoms in the functional group of the modifier. Although the partial charges of backbone hydrogen atoms of organic modifiers are relatively smaller, however, their presence in large amounts makes the total attractive interactions with the clayoxy very significant. Hence, high attractive electrostatic interactions are

Table 5
Non-bonded energies between clay and different parts of polymer in PCN

Components of clay–polymer interaction in PCN (Col-I)	Van der Waals energy (Kcal/mol) (Col-II)	Electrostatic energy (Kcal/mol) (Col-III)	Total non-bonded energy (Kcal/mol) (Col-IV) = Col (II + III)
Clay–polymer	−109	0	−109
Clay–polymer backbone hydrogen	+3	−140	−137
Clay–polymer backbone carbon	−79	+108	+29
Clay–polymer backbone chain	−76	−32	−108
Clay–polymer functional hydrogen	−1	−59	−60
Clay–polymer functional nitrogen	−11	+82	+71
Clay–polymer functional oxygen	−7	+81	+74
Clay–polymer functional carbon	−14	−72	−87
Clay–polymer end functional groups	−33	+32	−1

Table 6
Non-bonded energies between interlayer surface oxygen atoms of clay and different parts of organic modifiers in PCN

Components of clayoxy–modifier interaction in PCN (Col-I)	Van der Waals energy (Kcal/mol) (Col-II)	Electrostatic energy (Kcal/mol) (Col-III)	Total non-bonded energy (Kcal/mol) (Col-IV) = Col (II + III)
Clayoxy–modifier	−182	−8351	−8533
Clayoxy–modifier backbone hydrogen	−46	−15,419	−15,464
Clayoxy–modifier backbone carbon	−101	+12,175	+12,074
Clayoxy–modifier backbone chain	−147	−3243	−3390
Clayoxy–modifier functional hydrogen	−3	−12,424	−12,427
Clayoxy–modifier functional nitrogen	0	+2459	+2459
Clayoxy–modifier functional oxygen	−22	+10,473	+10,451
Clayoxy–modifier functional carbon	−11	−5617	−5627
Clayoxy–modifier end functional groups	−35	−5108	−5143

Table 7
Non-bonded energies between interlayer surface oxygen atoms of clay and different parts of polymer in PCN

Components of clayoxy–polymer interaction in PCN (Col-I)	Van der Waals energy (Kcal/mol) (Col-II)	Electrostatic energy (Kcal/mol) (Col-III)	Total non-bonded energy (Kcal/mol) (Col-IV) = Col (II + III)
Clayoxy–polymer	−154	−8	−162
Clayoxy–polymer backbone hydrogen	−34.10	−10,033	−10,067
Clayoxy–polymer backbone carbon	−73	+8015	+7942
Clayoxy–polymer backbone chain	−107	−2018	−2125
Clayoxy–polymer functional hydrogen	0	−3945	−3945
Clayoxy–polymer functional nitrogen	−18	+5515	5497
Clayoxy–polymer functional oxygen	−12	+5714	+5702
Clayoxy–polymer functional carbon	−17	−5274	−5290
Clayoxy–polymer functional groups	−47	+2010	+1963

seen between clayoxy and organic modifiers. The polymer–clayoxy interactions are also van der Waals in nature and they are contributed mainly by the backbone chain of polymer. The polymer–clayoxy interaction is more attractive than clay–polymer interaction; however, the change is not so large like clayoxy–modifier.

4.7. Comparison of interactions between clay, organic modifier, and polymer in PCN

4.7.1. Interaction between clay and organic modifiers

From Table 4 it is calculated that interaction energy coming from functional end groups of organic modifiers with clay is about 60% and that from backbone chain is about 40%. Again if we breakdown the total non-bonded interaction energy between clay and organic modifier in PCN into electrostatic and van der Waals, it is seen that electrostatic interaction (71% of total interaction between clay and modifier) is greater than the van der Waals interaction (29%). The end functional groups of organic modifier have higher interaction with clay compared to its backbone chain and atoms of the functional groups of organic modifiers mainly have electrostatic interaction with the interlayer surface-oxygen atoms of clay because of its high partial charges. These two factors are basically responsible for stronger electrostatic interaction between clay and organic modifier. For interaction between backbone chain of or modifiers and clay in PCN, van der Waals and electrostatic interactions, both have considerable contribution, although electrostatic interaction is more. Partial charges of atoms present in the end functional groups of organic modifiers are high. This mainly results in electrostatic interaction with clay. As calculated from Table 4, the interaction of end functional groups of organic modifiers with clay is found to be dominantly electrostatic (86% of total interaction).

4.7.2. Interaction between clay and polymer

From Table 5, it is calculated that about 99% of total non-bonded interactions of polymer with clay are through its backbone chain. We further see that about 99% of total non-bonded interaction between polymer and clay is van der Waals

Table 8
Comparison of non-bonded energies between clay and oxygen atoms of interlayer clay surface (clayoxy) with polymer and organic modifier in PCN

Components of interaction in PCN (Col-I)	Van der Waals energy (Kcal/mol) (Col-II)	Electrostatic energy (Kcal/mol) (Col-III)	Total non-bonded energy (Kcal/mol) (Col-IV) = Col (II + III)
Interlayer surface oxygens of clay–polymer	−154	−8	−162
Clay–polymer	−109	−1	−110
Interlayer surface oxygens of clay–organic modifier	−182	−8351	−8533
Clay–organic modifier	−158	−389	−547

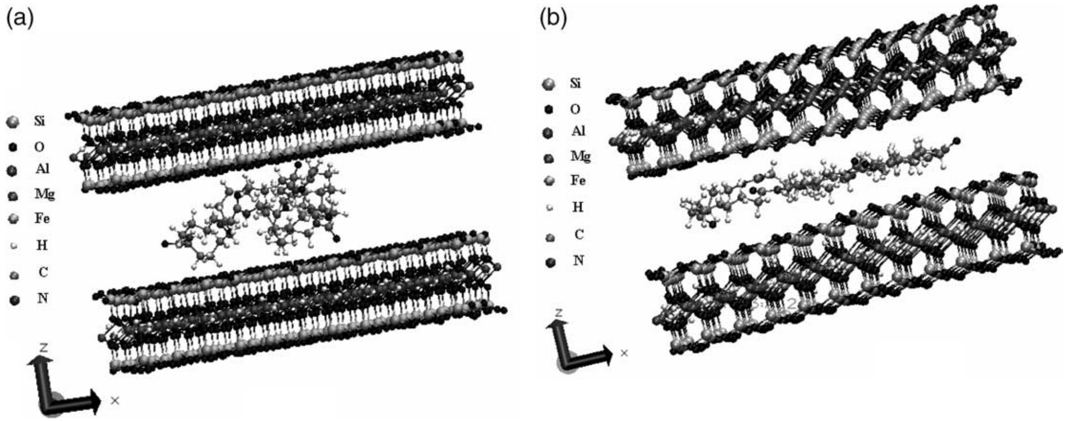

Fig. 5. (a) Initial shape of polymer in intercalated PCN model before MD simulation, (b) final shape of polymer in intercalated PCN after MD simulation. (Organic modifiers are present in the interlayer clay spacing in both the figures; however, they are not shown in this two figures).

in nature. Thus, it can be inferred that the interaction of clay with polymer is mainly through the backbone chain of polymer, which is van der Waals in nature.

From earlier study [44], we found that the final conformation of polymer in PCN changes from an initial three-dimensional cuboidal conformation to a lamellar conformation after simulation as shown in Fig. 5. For better visibility of intercalated polymer in PCN, the intercalated organic modifiers have been eliminated from the Fig. 5. In PCN, as the interaction of clay with polymer is mainly through its backbone chain, hence after intercalation, polymer tries to increase its interaction with clay via backbone chain. This results in the unfolding of polymer chain in order to maximize its interactions with clay. This consequently transforms the shape of polymer into an almost two-dimensional lamella.

4.7.3. Interaction between polymer and organic modifiers

The interaction energies between polymer and different parts of organic modifier in PCN are shown in Table 9. It is seen that the attractive interaction between polymer and organic modifiers are mainly contributed by the end functional groups of organic modifiers, which is −78 Kcal/mol. However, the interaction between backbone chain of organic modifiers and polymer is repulsive, which lowers the resultant interaction between polymer and organic modifiers.

Table 9
Non-bonded energies between polymer and different parts of organic modifiers in PCN

Components of polymer–modifier interaction in PCN (Col-I)	Van der Waals energy (Kcal/mol) (Col-II)	Electrostatic energy (Kcal/mol) (Col-III)	Total non-bonded energy (Kcal/mol) (Col-IV) = Col (II + III)
Polymer–modifier	+28	−92	−64
Polymer–modifier backbone hydrogen	+9	−43	−34
Polymer–modifier backbone carbon	+17	+32	+49
Polymer–modifier backbone chain	+26	−11	+15
Polymer–modifier functional hydrogen	−1	−106	−107
Polymer–modifier functional nitrogen	+6	+22	+28
Polymer–modifier functional oxygen	−1	+12	+11
Polymer–modifier functional carbon	−2	−8	−10
Polymer–modifier end functional groups	+2	−81	−79

Table 10
Non-bonded energies between organic modifiers and different parts of polymer in PCN

Components of modifier–polymer interaction in PCN (Col-I)	Van der Waals energy (Kcal/mol) (Col-II)	Electrostatic energy (Kcal/mol) (Col-III)	Total non-bonded energy (Kcal/mol) (Col-IV) = Col (II + III)
Modifier–polymer	+28	−92	−64
Modifier–polymer backbone hydrogen	−1	+551	+550
Modifier–polymer backbone carbon	−2	−446	−448
Modifier–polymer backbone chain	−3	+104	+102
Modifier–polymer functional hydrogen	0	+195	+195
Modifier–polymer functional nitrogen	+9	−302	−293
Modifier–polymer functional oxygen	+17	−413	−396
Modifier–polymer functional carbon	+5	+323	+329
Modifier–polymer end functional groups	+31	−197	−165

Table 11
Non-bonded energies between different parts of polymer with different parts of organic modifiers in PCN

Components of interaction of different parts of polymer with different parts of modifier in PCN (Col-I)	Van der Waals energy (Kcal/mol) (Col-II)	Electrostatic energy (Kcal/mol) (Col-III)	Total non-bonded energy (Kcal/mol) (Col-IV) = Col (II + III)
Polymer backbone–modifier backbone	+2	+35	+37
Polymer backbone–modifier functional	−5	+69	+64
Polymer functional–modifier backbone	+24	−47	−23
Polymer functional–modifier functional	+7	−150	−143

In Table 10, we find that in terms of interaction between organic modifiers and different parts of polymer in PCN, the interaction is strongest between organic modifiers and functional groups of polymer, which has the interaction energy of −165 Kcal/mol. The resultant interaction between modifier and polymer becomes weaker because of the repulsive interaction between organic modifiers and backbone chain of polymer. The amide functional groups of polymer only interact with the end functional groups of organic modifiers.

The interactions between polymer and organic modifiers in PCN have been summarized in Table 11. It is seen that the functional groups of polymer also have relatively attractive interaction with backbone chain of organic modifiers. Functional groups of polymer undergo strong attractive interactions with the functional groups of organic modifiers. Hence, for increasing the attractive interactions between polymer and organic modifier, the compatibility between the functional groups of polymer and organic modifiers is crucial.

4.7.4. Summary of interaction between clay, polymer, and organic modifiers in PCN

From the interaction of organic modifiers and clay, it is found that the backbone chain and end functional groups of organic modifiers both interact with clay. From the interaction between clay and polymer it is seen that the backbone chain of polymer only interacts with clay, functional groups of polymer remain almost inert. The functional groups of polymer only have significant attractive interactions with the functional groups of organic modifiers in PCN. However, the interaction between the functional groups of polymer and backbone chain of organic modifiers is relatively weaker. Based on these results, the attractive interactions among different constituents in PCN have been represented schematically in Fig. 6. In Fig. 6, the weaker attractive interaction has been represented in dashed line. The relatively stronger interactions have been presented in solid line. The figure shows that the organic modifiers act as important constituent for enhancing the interactions between clay and polymer in the PCN.

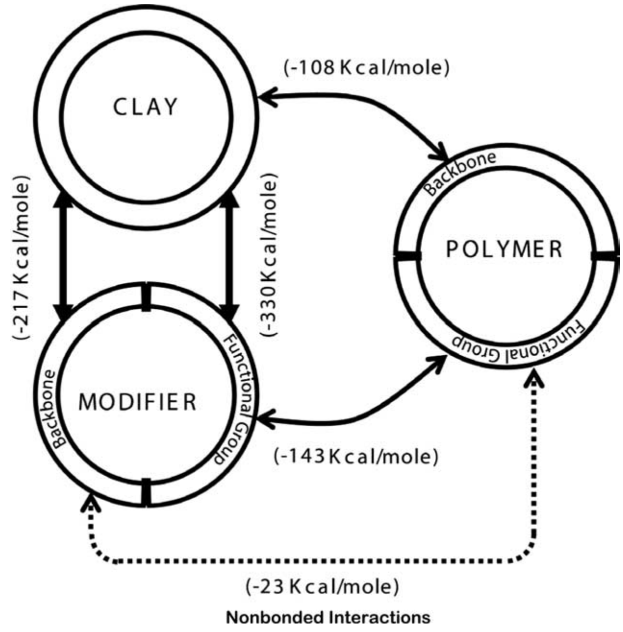

Fig. 6. Schematic representation of significant attractive non-bonded interactions in PCN.

5. Conclusions

(1) All physical systems try to attain the least energy conformation, which is the most stable conformation. The total energy in PCN is smaller than that of sum of the individual energy of polymer and OMMT, which indicates that PCN is more stable system than the mixture of polymer and OMMT in immiscible state.
(2) In PCN, the interaction between clay and organic modifier is highest followed by interaction between clay and polymer.
(3) Between organic modifier and clay in PCN, although the highest interaction is between the end functional group-hydrogen atoms and clay, the backbone chain-hydrogen atoms also have significant interaction with clay.
(4) In PCN, the organic modifier end functional groups and backbone chain both interact with clay, although more interaction results from the end functional groups and is dominantly electrostatic in nature.
(5) In the case of interaction between polymer and clay in PCN, the backbone chain-hydrogen atoms collectively have higher interaction with clay as compared to the interactions with the functional group-hydrogen atoms. The large numbers of backbone chain-hydrogen atoms contribute significantly to interaction of polymer with clay.
(6) The polymer end functional groups have the negligible interaction with clay; almost all the interactions with clay are with backbone chain of polymer.
(7) Only the functional groups of polymer undergo attractive interaction with the organic modifiers in PCN.
(8) In OMMT, in addition to end functional groups, the backbone chain of organic modifier has significant role in interaction with clay.

(9) The attractive interactions of organic modifiers and polymer with clay are through the interlayer surface-oxygen atoms of clay.
(10) Organic modifier acts as a connecting medium for interaction of the functional groups of polymer with clay in PCN resulting in higher interactions between clay, polymer and organic modifier in PCN.
(11) In this study, a detailed picture of interactions between various constituents of PCN is presented.

Acknowledgements

The authors would like to acknowledge the use of computational resources at the Center for High Performance Computing (CHPC), NDSU and Biomedical Research Infrastructure Network (BRIN). We would like to thank Dr Gregory H. Wettstein for his hardware and software support.

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