To the nanoscale, and beyond!
Multiscale molecular modeling of polymer-clay nanocomposites

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Abstract
In this work, we present an innovative, multiscale computational approach to probe the behavior of polymer-clay nanocomposites (PCNs). In details, our modeling recipe is based on (i) quantum/force-field-based atomistic simulation to derive interaction energy values among all system components; (ii) mapping of these values onto mesoscale simulation (MS) parameters; (iii) mesoscopic simulations to determine system density distributions and morphologies (i.e., intercalated vs. exfoliated); (iv) simulations at finite-element levels to calculate the relative macroscopic properties. Through these calculations, we could in principle modify the characteristic of the organic modifiers, polymers, and even substrate, and thus isolate the factors that drive the polymers to permeate the clay galleries. This, with the ultimate goal of limiting the efforts of synthetic chemists in following the inefficient Edisonian prescription of creating all possible mixtures in order to isolate the desired materials.

Keywords: Polymer-clay nanocomposites; Multiscale molecular modeling; Dissipative particle dynamics; Finite-elements calculations; Materials design

1. Introduction

Polymer-clay nanocomposites (PCNs) are one of the most exciting and promising classes of materials discovered in the last years [1–3]. A number of physical properties are successfully enhanced when a polymer matrix is modified with a small amount of layered silicate, on condition that the filler is dispersed to nanoscopic levels. Optical clarity, stiffness, flame retardancy, barrier properties, and thermal stability are mainly influenced, and in some cases also the mechanical strength increases [4].

These composites are obtained by dispersion in a polymeric matrix of small amounts (typically 1–5%) of a clay filler having one of the three dimensions of nanometric scale. Fabricating these materials in an efficient and cost-effective manner, however, poses significant synthetic challenges. PCNs can be obtained following three main different routes: intercalation from solution, in situ polymerization, and melt intercalation. Amongst these, the latter is the most appealing and, hence, the route most frequently adopted for both laboratory and industrial preparation of PCNs, as it can be realized by standard polymer production equipment.

The layered silicates most commonly used in PCN production (montmorillonite being a prime example) belong to the structural family known as 2:1 phyllosilicates. Their crystal lattice consists of 2-D layers where a central octahedral sheet of alumina or magnesium is fused into two external silica tetrahedron by the tip, so that the oxygen ions of the octahedral sheet do also belong to the tetrahedral sheet. These layers organize themselves to form stacks with a regular van der Waals gap in between them, called interlayer or gallery. Isomorphous substitution of some elements within the layers — e.g., Al³⁺ with Mg²⁺ as in montmorillonite (MMT), or Mg²⁺ with K⁺ — generates negative charges that are
counterbalanced by alkali or alkaline earth cations situated in the interlayers. The lateral dimensions of these layers may vary from approximately 200 Å to several microns or more, depending on the peculiar composition of the silicate, while the spacing between the closely packed sheets is also of the order of 1 nm, which is smaller than the radius of gyration of typical polymers. Consequently, there is a large entropic barrier that inhibits the polymer from penetrating this gap and becoming intermixed with the clay.

Thus, there are several issues that need to be addressed in order to optimize the production of these PCNs. Of foremost importance is isolating conditions that promote the penetration of the polymer into the narrow gallery. If, however, the sheets ultimately phase-separate from the polymeric matrix, the mixture will not exhibit the improved strength, heat resistance, or barrier properties. Therefore, it is also essential to determine the factors that control the macroscopic phase behavior of the mixture. To enhance polymer-clay interaction, the clay interlayer surfaces of the silicate are chemically treated to make the silicate less hydrophilic and therefore more wettable by the polymer. A cation exchange process accomplishes this, where hydrophilic cations such as Na+, K+ or Ca2+ are exchanged by a surface modifier, usually selected from a group of organic substances having one or more alkyl radicals containing at least six carbon atoms (usually quaternary ammonium salts, or quats). The role of this organic component in organosilicates is to lower the surface energy of the inorganic host and improve the wetting characteristic with the polymer. Intuitively, the nature and the structure of these “surfactants” determines the hydrophobicity of silicate layers and, hence, the extent of their exfoliation.

Indeed, the driving force for nanodispersion – that is the negative change in free energy – depends on the delicate balance between the enthalpic term, due to the intermolecular interactions, and the entropic term, associated with the configurational changes in the constituents. Using a recently developed mean-field model [5], it has been shown that the entropy loss associated with the polymer confinement is approximately compensated by an entropy gain associated with the increased conformational freedom of the surfactant molecules as the gallery distance increases due to the polymer intercalation. Therefore, enthalpy determines whether or not polymer intercalation will take place.

Finally, the properties of the hybrid commonly depend on the structure of the material; thus, it is of particular interest to establish the morphology of the final composite. This can be defined exfoliated (only single platelets can be found in the final bulk structure) or intercalated (where polymer penetrates the galleries, but stacks remain clearly recognizable). However, in the vast majority of cases, the final morphology results in a mixture of the two different situations described above.

Many papers have been published in recent years addressing all possible issues of nanocomposites design, production, and characterization. After the pioneering work carried out at the R&D center of Toyota [6–9], experimental investigations have focused especially on processing conditions and chemical formulation of components, and their relative influence on morphology and final properties. Every possible aspect has been analyzed, from matrix molecular weight to surfactant chemistry [4]. Nonetheless, mechanisms that lead to clay intercalation or exfoliation within polymer matrix have not yet been fully understood, due to the amount of parameters involved and the difficulty of developing tools capable of monitoring intercalation processes in the melt. This is mainly due to the fact that fundamental variables defining final morphology and properties of polymer nanocomposites need to be quantified at length scales that are difficult to probe experimentally. Accordingly, many efforts have been made also in the field of nanocomposites modeling and simulation [10]. In particular, multiscale simulation techniques seem to be ideally suited to investigate main microscale and mesoscale characteristics of such materials, as long as the smaller parts of the systems must be solved with great accuracy, but at the same time higher scales features needs to be modeled with lower level of detail in order to avoid excessively high computational times.

Our recent efforts in polymer-clay nanocomposites simulation were initially concerned with binding energy evaluations for well-characterized systems [10(c–e)], using atomistic molecular dynamics (MD) methods. At the same time, part of our activities was focused on the development and application of mesoscale simulation (MS) tools to polymer blends morphology investigations, and on the integration of these tools with atomistic approaches [11–14]. In this work, we propose a global, innovative, multiscale molecular modeling (M³) approach which allows us to calculate the macroscopic properties of a given PCN material starting only from the chemical information on the nature of matrix and fillers. The further element of novelty of the M³ approach presented here is that the concept of partial exfoliation and platelet orientation can be implemented in the corresponding model morphology, and intercalated stack properties can be calculated from mesoscale (MS) simulations. Polyamide-based nanocomposite such as MMT/Nylon6 was selected as the ideal reference system, by virtue of the numerous experimental studies available for this PCN in the scientific literature. Precisely, the following two systems were selected to test our M³ approach: MMT/Nylon6/trimethyl-dehydrogenated tallown quaternary ammonium chloride and MMT/Nylon6/dimethyl-dehydrogenated tallown quaternary ammonium chloride, respectively.

As far as simulation methods are concerned, we established a hierarchical procedure [11] for bridging the gap between atomistic and mesoscopic simulation for PCN design. The Dissipative Particle Dynamics (DPD) [15,16] is adopted as the mesoscopic simulation technique, and the interaction parameters of the mesoscopic model are estimated by mapping the corresponding binding energy values obtained from atomistic MD simulations. Finally, we employ a finite-element (FE) software Palmyra [17] in order to estimate some of the macroscopic properties for both the intercalated stack and the exfoliated nanocomposite. As some of the low-middle length scale computational recipes of M³ are reported in our previous work [10(c–e),11], here we will focus on the detailed description of the last part of our multiscale procedure, i.e., from MS to FE calculations.
2. Theory and calculations

Briefly, our modeling recipe is based on (i) quantum/molecular mechanics-based atomistic simulation to derive interaction energy values among all system components; (ii) mapping of these values onto mesoscale parameters and subsequent simulations to determine system density distributions; (iii) simulations at finite-element levels to calculate the relative macroscopic properties.

2.1. Quantum/molecular mechanics-based atomistic simulation

Atomistic simulations of the quat and polymer conformations on MMT layers and binding energy calculations have been performed following a well-established route [10]. Accordingly, the procedure will only be briefly reviewed here. As far as the MMT model is concerned, starting from relevant crystallographic coordinates [18] we built the unit cell of a pyrophyllite crystal using the Crystal Builder module of the Materials Studio molecular modeling package (v. 4.1, Accelrys, San Diego, CA, USA). The MMT model is characterized by a cation exchange capacity (CEC) of approximately 92 meq/100 g (roughly corresponding to the CEC of the most commonly employed commercial products), and the corresponding unit formula is \((\text{Al}_{3.33}\text{Mg}_{0.67})\text{Si}_{8}\text{O}_{20}(\text{OH})_4-\text{Na}_{0.67}\). The charges on the individual atoms were placed following the charge scheme proposed by Li and Goddard [23] using the charge scheme proposed by Li and Goddard [23] and M3C18, respectively. The quat conformational search was carried out using the Compass force field (FF) [20, 21] (as implemented in the Discover module of Materials Studio), and applying our well-validated combined molecular mechanics/molecular dynamics simulated annealing (MDSA) protocol [10(c–e), 22].

The procedure for polymer modeling consisted in building and optimizing the polymer constitutive repeating unit (CRU) using the Compass FF, which was then polymerized to a conventional degree of polymerization (DP) equal to 10. Then, 3 chains were used to build 10 different model conformations, using the Amorphous Builder module of Materials Studio. Explicit hydrogens were used in all model systems. Each polymeric structure was then relaxed and subjected to the same MDSA protocol applied to model thequat molecule. Each chain structure was assigned atomic charges [23] using the charge scheme proposed by Li and Goddard [24].

Subsequently, we employed MD simulations in the constant volume–constant temperature (NVT) ensemble in order to retrieve information on the interaction and binding energy values between the different components of our PCN systems. This procedure has been extensively described in previous papers [10(c), 11] and will not be reported here.

2.2. Mesoscale parameters mapping and simulation

In order to simulate the morphology of the organic species between the montmorillonite layers at a mesoscopic level, we used the DPD simulation tool as implemented in the Materials Studio modeling package. In the framework of a multiscale approach to PCN simulation, the interactions parameters needed as input for the mesoscale level DPD calculations have been obtained by a mapping procedure of the binding energy values between different species obtained from simulations at the atomistic scale, as described in Section 2.1.

In the DPD method a set of particles moves according to Newton’s equation of motion, and interacts dissipatively through simplified force laws; the force acting on the particles, which is pairwise additive, can be decomposed into three elements: a conservative \(F^{C}_{ij}\), a dissipative \(F^{D}_{ij}\), and a random \(F^{R}_{ij}\) force. Accordingly, the effective force \(f\) acting on a particle \(i\) is given by:

\[
f_i = \sum_{i\neq j} \left(F_{ij}^C + F_{ij}^D + F_{ij}^R\right)
\]

where the sum extends over all particles within a given distance \(r_c\) from the \(i\)th particle. This distance practically constitutes the only length scale in the entire system. Therefore, it is convenient to set the cutoff radius \(r_c\) as a unit of length (i.e., \(r_c = 1\)), so that all lengths are measured relative to the particles radius. The conservative force is a soft repulsion, given by:

\[
F_{ij}^C = \begin{cases} 
  a_{ij}(1 - r_{ij}) \mathbf{r}_{ij}, & (r_{ij} < 1) \\
  0, & (r_{ij} \geq 1)
\end{cases}
\]

where \(a_{ij}\) is the maximum repulsion between particles \(i\) and \(j\), \(r_{ij}\) the magnitude of the particle–particle vector \(\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j\) (i.e., \(r_{ij} = |\mathbf{r}_{ij}|\)), and \(\mathbf{f}_{ij} = \mathbf{r}_{ij}/r_{ij}\) is the unit vector joining particles \(i\) and \(j\). The other two forces, \(F_{ij}^D\) and \(F_{ij}^R\), are both responsible for the conservation of the total momentum in the system, and incorporate the Brownian motion into the larger length scale. In the DPD model, individual atoms or molecules are not represented directly by the particle, but they are coarse-grained into beads. These beads represent local “fluid packages” able to move independently. Incorporation of chain molecules simply requires the addition of a harmonic spring force between the beads. More detailed information about the DPD method can be found elsewhere [15, 16, 25].

Defining \(a_{ij}\) parameters and bead dimensions are probably the most questionable tasks in setting a DPD simulation. According to our procedure, repulsive DPD parameters are coupled to the energy values resulting from the atomistic MD simulations through a simple combinatorial approach. The technique used to define the beads and the method to calculate \(a_{ij}\) parameters have already been reported in Ref. [11]; accordingly, it will be only briefly summarized below.

The first step necessary to obtain the DPD input parameters generally consists in defining the DPD bead dimensions, thus implicitly determining the characteristic length of the system \(r_c\). As illustrated above, the interaction range \(r_c\) sets the basic length-scale of the system; in other terms, \(r_c\) can be defined as...
the side of a cube containing an average number of $\bar{\rho}$ beads. Therefore:

$$r_c = (\bar{\rho} V_b)^{1/3}$$

(3)

where $V_b$ is the volume of a DPD bead. Thus, even in a heterogeneous system consisting of several different species, such as PCNs, a basic DPD assumption is that all bead-types (each representing a single species) are of the same volume $V_b$. Since the quat molecules basically consist of a strongly polar head and two almost apolar tails, we assumed that they could be described by two different kinds of beads. Further, in the light of the above mentioned assumption, we decided divide each single alkylammonium molecule in five or three beads, one for the head and two for each tail, as illustrated in Fig. 1 for M$_3$C$_{18}$.

In order to compute the $a_{ij}$ parameters, we applied the following combinatorial approach. Considering a system made up of single particles $i$ and $j$, the total energy of the system is given, in the hypothesis of neglecting the ternary contributions to interaction, by Eq. (4):

$$E_{\text{system}}^{\text{tot}} = n_{ii} E_{ii} + n_{jj} E_{jj} + n_{ij} E_{ij} + n_{ji} E_{ji}$$

(4)

where:

$$n_{ij} = \frac{n_i(n_i - 1)}{2}$$

(5)

is the number of contacts between $n_i$ particle of type $i$, and

$$n_{ij} = \frac{n_i n_j}{2}$$

(6)

is the number of contacts between $n_i$ particles of type $i$ and $n_j$ particles of type $j$. Since the mixed energy terms $E_{ij}$ and $E_{ji}$, and the number of contacts $n_{ij}$ and $n_{ji}$ are the same, the expression for the system total energy, i.e., Eq. (4), becomes:

$$E_{\text{sys}}^{\text{tot}} = n_{ii} E_{ii} + n_{jj} E_{jj} + 2 n_{ij} E_{ij}$$

(7)

The values of self-interaction energies $E_{ii}$ and $E_{jj}$ are easily obtainable dividing the corresponding values calculated through classical MD simulations by the appropriated number of contacts, whilst the value of the system total energy $E_{\text{sys}}^{\text{tot}}$ is derived straightforward from the MD simulation. Accordingly, the remaining mixed energy term, $E_{ij}$, is calculated by applying Eq. (7). Table 1 reports all the values of the self- and mixed rescaled energies calculated in this work.

The bead–bead interaction parameter for polymer–polymer interaction was set equal to $a_{PP} = 25$ for both systems, in agreement with the correct value for a density value $\rho = 3$ [25]. For the nanocomposite characterized by M$_3$C$_{18}$ as quat, the value of the head–head interaction ($a_{HH} = 500$) was set with respect to polymer–polymer repulsion to describe both qualitatively and quantitatively the effect of repulsion between two nearly charged heads. This second value was set based on our previous experience [11], according to which such parameter proved to be effective to mimic a strong electrostatic repulsive interaction. Having fixed these two parameters, all the remaining DPD interaction parameters $a_{ij}$ could be easily derived from the corresponding scaling law. This means that, once, we have defined these two values, we can calculate the energy difference matching a single unit difference in the $a_{ij}$ parameters. In this way, we can determine a linear correspondence between the rescaled energies and the corresponding DPD parameters. In the case of MMT/MMT interaction, since no energy values could be extracted from the MD simulations, we set $a_{MM} = 15$ in order to mimic a rigid covalent structure. Finally, for the pair $M/H$ the corresponding parameter $a_{ij}$ was not calculated using the scaling law, but we set it to the value of 5, because of its strong negative value of the rescaled energy. Had we used the scaling law described above, the parameter would have been negative, and as such not usable as an input parameter in Materials Studio DPD simulation tool. For the nanocomposites based on M$_2$(C$_{18}$)$_2$, we used the same parameters reported in our previous paper [11]. The final set of DPD parameters for both systems, obtained from the scaling procedure starting from atomistic MD simulation energies are listed in Table 2. Finally, we made use of the option available in the DPD commercial software of including a smooth wall in the simulation box perpendicular to the

![Image](image_url)
Table 3
Palmyra solver values for stack properties for the two PCN systems considered

<table>
<thead>
<tr>
<th></th>
<th>$L_p$ (nm)</th>
<th>$H_p$ (nm)</th>
<th>$V_p$ (nm³)</th>
<th>$H_g$ (nm)</th>
<th>$H_s$ (nm)</th>
<th>$V_s$ (nm³)</th>
<th>$AR_s$</th>
<th>$#s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMT/Nylon6/M2(C18)₂</td>
<td>60</td>
<td>1</td>
<td>11,304</td>
<td>4</td>
<td>6</td>
<td>30</td>
<td>3,39,120</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1</td>
<td>11,304</td>
<td>4</td>
<td>4</td>
<td>20</td>
<td>2,260,80</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1</td>
<td>11,304</td>
<td>4</td>
<td>2</td>
<td>10</td>
<td>1,130,40</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1</td>
<td>11,304</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>1,130,40</td>
<td>120</td>
</tr>
<tr>
<td>MMT/Nylon6/M3C18</td>
<td>60</td>
<td>1</td>
<td>11,304</td>
<td>4</td>
<td>4</td>
<td>20</td>
<td>2,260,80</td>
<td>6</td>
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<tr>
<td></td>
<td>60</td>
<td>1</td>
<td>11,304</td>
<td>4</td>
<td>2</td>
<td>10</td>
<td>113,040</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1</td>
<td>11,304</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>113,040</td>
<td>120</td>
</tr>
</tbody>
</table>

* $L_p$: Platelet length.
* $H_p$: Platelet thickness.
* $V_p$: Platelet volume.
* $H_g$: Gallery height.
* $\#p/s$: Number of platelets per stack.
* $H_s$: Stack thickness.
* $V_s$: Stack volume.
* $AR_s$: Aspect ratio of stack.
* $\#s$: Number of stacks.

The $z$-axis at the origin. Accordingly, the wall interacts with each bead in the system with a potential of the same form as the bead–bead conservative force. This force is soft and short-range, so the beads are not strictly forbidden from passing through the barrier. We set a very soft repulsion between the MMT bead and the wall, in order to fill the space between the two surfaces, and thus represent the MMT platelet. As far as the remaining beads/wall repulsive parameters are concerned, we decided to simply scale up the interaction parameters with the MMT bead by a factor of 10. In this way, we preserved the proportion of interaction energies between clay and organic species and, at the same time, we prevented the beads from crossing the wall, taking an effective flat solid surface. The values for the interaction with the wall used in the simulations are reported the last column of Table 2.

2.3. Finite-elements calculation of macroscopic properties

In order to calculate macroscopic properties of the investigated nanocomposite systems we performed FEM simulations with fixed and variable grid using the software Palmyra software (v. 2.5, MatSim, Zürich, CH). This software has been validated on different composite material morphologies by several authors [12,26,27], yielding reliable results. In this work, we applied the software solver in order to analyze both platelet stack and nanocomposite overall properties, using fixed and variable grid, respectively. In particular, we decided to focus our attention on Young modulus and permeability, since in these properties lies most of the industrial interest towards these new materials.

As far as platelet-stack modeling is concerned, we successfully imported the density fields obtained with DPD MS into Palmyra after an appropriate formatting of Materials Studio DPD output files. Once imported, the density fields are divided into mesh elements. The mesh is represented as a fixed regular cubic lattice, but the solver works on the basis of a space-filling tetrahedral mesh, i.e., without voids. The mapping of cubic grid elements to a tetrahedral mesh results in six isochoric tetrahedrons for each cubic grid element [17]. For arbitrary composite morphologies, Palmyra uses a numerical method to determine the overall properties from the properties of the components based on small homogeneous grid elements. The morphology is defined by a number of phases in a periodically continued base cell of cubic or orthorhombic shape where the phases may consist of any material. For each of the grid elements it is possible to specify the fraction of each phase contained in that particular position.

Two methods can be chosen for calculating the properties of each grid element that is a combination of different phases: serial (arithmetic) averaging or parallel averaging. These names come from the meaning of the method in electronic circuits, where resistors can be connected in series or in parallel. There are no clear rules available yet about which method should be used for multi-component mixtures. After several trials for different morphologies and relative comparison to experimental results, we decided to focus on the parallel averaging method, which was found to yield the most reliable results.
data, we decided to use the serial averaging system in order to calculate mechanical and permeation properties of our stack model. The meshed volume from DPD simulation of M₃C₁₈-based nanocomposite can be seen in Fig. 2.

The properties of the quat molecules where chosen to match those of MMT and Nylon6 for the cation heads and tails, respectively. Mechanical and permeation properties for the silicate and polymer were taken from the available literature [28–30]. Our DPD box resulted in a 100 × 100 × 30 Palmyra volume element, containing 300,000 nodes and 1,800,000 tetrahedrons (see Fig. 2). After properties are assigned to each grid element, stack properties are calculated using the method described below for the variable grid mesh. The corresponding solver results for stack properties are reported in Table 3.

Subsequently, we retrieve overall nanocomposite properties by defining a morphology similar to the corresponding TEM images [28,29], applying a variable grid mesh to our model, and finally run Palmyra solver. The solver method is the same employed in fixed grid calculations. For the mechanical properties, it applies six different infinitesimally small deformations to the composite and minimizes the total strain energy for each of these deformations in order to calculate the elastic composite properties. Since composite materials are usually anisotropic, the symmetry class of the tensor is triclinic; if, however, the material has some symmetry, the corresponding tensor specifications may be simplified. The total elastic energy $E_{\text{el}}$, which is a quadratic function of the displacements of the nodes, is defined as the sum over the element contributions:

$$F = \sum_{i=1}^{n_{\text{Tot}}} f_i = \frac{1}{2} \sum_{i=1}^{n_{\text{Tot}}} V_i C_{ik} e_i e_k$$

where $f_i$ is the elastic energy of tetrahedron $i$, $V_i$ its volume, $C_{ik}$ the elastic constants, and $e_i$ is the local strains. In general, the $e_i$ are made up of mechanical and thermal parts. The units of the energy $F$ are [$L^3 \text{GPa}$], where $L$ is the length unit of the simulation cell.

The local stresses are calculated from the nodal displacements at the end of each minimization run, assuming linear elastic behavior. The local hydrostatic pressures $P$ are calculated for each tetrahedron as the sum of the principal components of the stress tensor of that volume element:

$$P = \frac{1}{3}(\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ})$$

The deviatoric von Mises stress for a mesh element is defined as:

$$\tau = \sqrt{\frac{\left((\sigma_{xx} - \sigma_{yy})^2 + (\sigma_{yy} - \sigma_{zz})^2 + (\sigma_{zz} - \sigma_{xx})^2\right)}{2} + 6(\sigma_{xx}^2 + \sigma_{yy}^2 + \sigma_{zz}^2)}$$

This value is listed in the output file for every applied deformation; the units are the same – [GPa] – as for the elastic constants. On the other hand, to calculate permeability properties, a Laplace solver is used, that applies a field in the three main directions to the finite-element mesh and minimizes the energy of the composite [26].

In order to build our nanocomposite model for FEM simulation, we started defining an appropriate number of platelets to be contained in our simulation boxes. Relying on previous studies on determination of relevant volume element for similar systems [17,26] for both nanocomposites models we decided to build boxes containing 36 MMT platelets, characterized by a thickness of 1 nm and a diameter of 120 nm, respectively. Twelve of these were considered to be exfoliated, while the other 24 were considered to be part of stacks of different sizes, according to the data reported in Table 3. The simulation cubic cell was characterized by a length of 0.3135 μm (and a volume of 0.0308 μm³) for the M₂(C₁₈)₂-based system, and by a length of 0.3052 μm (and a volume of 0.02842 μm³) for the M₃C₁₈-based PCN. These values stem from the choice of trying to reproduce the same nanocomposites described in Refs. [28,29] in order to test the simulation results against experimental data. The volume fractions for the platelets were calculated considering the density values reported in Ref. [29] and, for stacks, an interlamellar gallery height of 4 nm. These considerations yielded a MMT volume fraction of 0.01863.

Exfoliated platelets were taken to exhibit the mechanical properties reported in Ref. [29], while stacks were assigned values according the procedure described above, i.e., starting from the corresponding DPD density profiles. Moreover, we decided to define an orientation for stack and single particles. Each orientation can be described by the three Cartesian components $(p_1, p_2, p_3)$ of a unit vector $p$ pointing along the particle axis. The components of the orientation vector $p$ can be expressed by the angles $\varphi$ and $\theta$ in the following way:

$$p_1 = \sin \theta \cos \varphi$$
$$p_2 = \sin \theta \sin \varphi$$
$$p_3 = \cos \theta$$

Only two vector components are independent since the length of $p$ is normalized to 1. Orientation tensors can be defined by forming dyadic products for each vector $p$ that characterizes the orientation of an object and subsequently integrating the product of the resulting tensors with the distribution function over all possible directions of $p$. The second order orientation $a_{ij}$ tensor can be calculated as following:

$$a_{ij} = \int \rho(p) \psi(\rho) d\rho$$

For any orientation state we can define a coordinate system where all off-diagonal components of the orientation tensor become zero. In this case, the diagonal components correspond to the eigenvalues and their sum equals 1 because we deal with normalized orientation vectors $p$. In Palmyra, the adjustment of the orientation tensor is done by predefining the targeted second order orientation tensor, entering two eigenvalues of the tensor. The third eigenvalue is determined by the fact that the sum of the eigenvalues must be 1. In our study, we set eigenvalues 1 and 2 (corresponding to the $x$ and $y$ direction, respectively) equal to 0.06. Accordingly, eigenvalue 3 (relative to $z$ direction) was 0.88.
Fig. 3. Frame extracted from the equilibrated MD trajectory of the PCN system made up by a MMT platelet (polyhedron style), Nylon6 (stick style), and M\textsubscript{3}C\textsubscript{18} quat molecules (CPK style).

Fig. 4. Morphology of the PCN system made up by a MMT platelet, Nylon6, and M\textsubscript{3}C\textsubscript{18} quat molecules obtained via DPD simulation. (Top) Ternary system; (bottom) detail of MMT and quat species. Color code: orange, MMT; blue, surfactant heads; light green, surfactant tails; dark green, polymer. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
In this way, we created a morphology in which the platelets are oriented parallel to the \( x \)-\( y \) plane, as if the nanocomposite were extruded perpendicular to the \( z \) direction. Finally, after having created the appropriate volume mesh, we run the Palmyra solver.

### 3. Results and discussion

The \( M^3 \) strategy to obtain some macroscopic, industrially relevant properties of polymer-clay nanocomposites rely on the obtainment of interaction energy values among the system components (i.e., polymer, clay and organic surface modifier or quat) from atomistic MD simulation. As an example, Fig. 3 shows a frame of the equilibrated MD trajectory of the PCN made up of montmorillonite, Nylon6 and \( M_3 \)C18. As the simulation proceeds in time, the surfactant chains flatten onto the clay surface. However, contrarily to what happens in the case of the “double-tailed” surfactant\[11\], in the case of the organic bearing a singly hydrocarbonic chain some parts of the MMT surface remain available to the polymer. This constitutes the best balance between attractive and repulsive forces in the overall system, leading to a complete exfoliation of this PCN, as verified experimentally by Fornes and Paul\[28\].

The interaction energy values calculated for these systems, and aptly scaled via the procedure described in the previous sections (see Table 1), lead to the definition of the Dissipative Particle Dynamics input parameters listed in Table 2. According to the \( M^3 \) recipe, then, the corresponding DPD simulations are performed, and the relevant MS morphologies of the systems are obtained. Fig. 4 shows the DPD simulation results for the system with \( M_3 \)C18 as quat.

As can be seen comparing Figs. 3 and 4, a good agreement between the atomistic and the mesoscale predictions is found. A fixed wall of nanoclay is obtained, by which the polar heads of the surfactant molecules are attracted to, and onto which the long, apolar hydrocarboxylic surfactant tail is flattened. As can be appreciated from Fig. 4, the charged parts of the surfactant remain close to the MMT layers, leaving the tails of the organic molecules to interact with the Nylon6 chains. However, areas are available on the clay surface for entering in contact with the polymer, thus rendering the effective binding between the components of the nanosystem almost ideal.

The final step in the \( M^3 \) ansatz consists in setting up and performing the FE simulations based on the system morphologies obtained at the previous, MS step. The results of FE calculations of the mechanical and permeability properties for the DPD two platelet-stack structure, and the 36 particles box for both PCN systems considered in this work are reported in Table 4.

The calculations of the Young modulus yielded results which are comparable to experimental data if we consider the values along the \( x \) and \( y \) directions (i.e., parallel to the simulated extrusion direction). Eventual discrepancies between virtual and experimental data could be due, for instance, to a different degree of crystallinity or different crystalline forms of Nylon6 in presence of MMT nanofillers, as claimed by some authors\[31,32\]. All estimated values for the nanocomposite with \( M_3 \)C18 as quat are higher than the corresponding ones relative to the PCN with \( M_2(C_{18})_2 \), in harmony with the different degree of exfoliation that has been modeled.

DPD models analyzed with Palmyra present very similar results in both cases. It is interesting to note that, within the stack, \( O_2 \) permeability appears to be enhanced instead of reduced along the \( x \) and \( y \) directions. A possible cause for this behavior can be traced to the polymer matrix structure in the proximity of the MMT platelet. Indeed, previous studies\[10,11\] have already pointed out the presence of alternating high and low polymer density planes next to platelet surfaces. Accordingly, in the lower density planes, the oxygen molecules can find a preferential diffusion path. Finally, as far as permeability in the 36 particle boxes is concerned, it is possible to note that, as expected, \( O_2 \) diffusion is hindered only in the \( z \) direction, i.e., perpendicular to platelet \( x \)-\( y \) plane. Permeability is anyway reduced only to a small extent (approximately 10–15%), because of the low nanofillers content (less than 2% in volume).

### 4. Conclusions

There are many levels at which molecular modeling and simulation can be useful, ranging from the highly detailed \textit{ab initio} quantum mechanics, through classical, atomistic molecular modeling, to process engineering modeling. These computations can significantly contribute to reduce wasted experiments, allow products and processed to be optimized, and permit large numbers of candidate materials to be screened prior to production. These techniques are currently used to obtain thermodynamic information about a pure or mixed system. Properties obtained using these microscopic properties assume the system to be

<table>
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<th>( E_{xx} ) (GPa)</th>
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<tr>
<td>1.30 ( \times ) 10^2</td>
<td>1.30 ( \times ) 10^2</td>
<td>2.18 ( \times ) 10^4</td>
<td>3.59 ( \times ) 10^{-2}</td>
<td>3.59 ( \times ) 10^{-2}</td>
<td>0.00</td>
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<tr>
<td>1.26 ( \times ) 10^2</td>
<td>1.26 ( \times ) 10^2</td>
<td>2.00 ( \times ) 10^3</td>
<td>3.47 ( \times ) 10^{-2}</td>
<td>3.47 ( \times ) 10^{-2}</td>
<td>0.00</td>
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<tr>
<td>3.85 ( \times ) 10^2</td>
<td>3.76 ( \times ) 10^2</td>
<td>3.20 ( \times ) 10^0</td>
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<td>1.52 ( \times ) 10^{-2}</td>
<td>1.37 ( \times ) 10^{-2}</td>
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<td>4.04 ( \times ) 10^2</td>
<td>4.03 ( \times ) 10^2</td>
<td>3.23 ( \times ) 10^0</td>
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homogeneous in composition, structure and density, which is clearly a limitation. When a system is complex, comprising several components, eventually sparingly miscible, PCNs being prime examples, peculiar phases with remarkable properties can be observed. These so-called mesophases comprise far too many atoms for atomistic modeling description. Hence, coarse-grained methods are better suited to simulate such structures. One of the primary techniques for MS modeling is Dissipative Particle Dynamics, a particle-based method that uses soft-spheres to represent groups of atoms, and incorporates hydrodynamic behavior via a random noise, which is coupled to a pairwise dissipation. However, retrieving information on mesophase structures is not enough for predicting macroscopic features of such materials. This is possible if mesophase modeling is coupled with appropriate FE tools like Palmrya that – provided properties of pure components are given or can be in turn obtained by simulation – allows obtaining a realistic estimation of many nanocomposites features, if integrated with experimental morphological data.

In this work we presented a hierarchical procedure for obtaining the input parameter necessary to perform polymer-clay nanocomposite DPD simulations from molecular dynamics simulations, thus bridging the gap between mesoscopic (i.e., higher length scale) and atomistic (lower length scale) modeling. Subsequently, we use a FE approach to calculate mechanical and permeability properties of both mesoscopic structures (stacks) and overall nanocomposite. Certainly, the presented approach can be improved in many ways: first of all, in order to realize a true multiscale modeling approach, platelet spatial distribution should be calculated and not defined starting from experimental data. Moreover, different morphologies should be analyzed more precisely, and size distribution for platelets should be taken into account, as reported by other authors [29]. Finally, matrix morphology next to the single exfoliated platelet surface should be considered, and exfoliation rate should be investigated more deeply. All of these issues will be addressed in future works by our group.

References


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