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Multiscale modeling for polymer systems of industrial interest

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Abstract

Atomistic-based simulations such as molecular mechanics (MM), molecular dynamics (MD), and Monte Carlo-based methods (MC) have come into wide use for materials design. Using these atomistic simulation tools, one can analyze molecular structure on the scale of 0.1–10 nm. Although molecular structures can be studied easily and extensively by these atom-based simulations, it is less realistic to predict structures defined on the scale of 100–1000 nm with these methods. For the morphology on these scales, mesoscopic modeling techniques such as the dynamic mean field density functional theory (Mesodyn) and dissipative particle dynamics (DPD) are now available as effective simulation tools. Furthermore, it is possible to transfer the simulated mesoscopic structure to finite element modeling tools (FEM) for calculating macroscopic properties for a given system of interest. In this paper, we present a hierarchical procedure for bridging the gap between atomistic and macroscopic modeling passing through mesoscopic simulations. In particular, we will discuss the concept of multiscale modeling, and present examples of applications of multiscale procedures to polymer–organoclay nanocomposites. Examples of application of multiscale modeling to immiscible polymer blends and polymer–carbon nanotubes systems will also be presented.

Keywords: Multiscale modeling; Nanocomposite; Mesoscopic simulation

1. Introduction

The main goal of computational materials science is the rapid and accurate prediction of properties of new materials before their development and production. In order to develop new materials and compositions with designed new properties, it is essential that these properties can be predicted before preparation, processing, and characterization.

Polymers are complex macromolecules whose structure varies from the atomistic level of the individual backbone bond of a single chain to the scale of the radius of gyration, which can reach tens of nanometers. Polymeric structures in melts, blends and solutions can range from nanometer scales to microns, millimeters and larger. The corresponding time scales of the dynamic processes relevant for different materials properties span an even wider range, from femtoseconds to milliseconds, seconds or even hours in glassy materials, or for large scale ordering processes such as phase separation in blends. No single model or simulation algorithm currently available can encompass this range of length and time scales. In order to simulate a polymeric system one must consider models that range from those including quantum effects and electronic degrees of freedom to chemically realistic, classical models.

One of the most important issue in computational materials research is the multiscale simulation, namely the bridging of length and time scales, and the linking of computational methods to predict macroscopic properties and behavior from fundamental molecular processes [1,2]. Despite the advances made in the modeling of the structural, thermal, mechanical, and transport properties of materials at the macroscopic level (finite element analysis of complicated structures), there remains tremendous uncertainty about how to predict many properties of industrial interest.

In this paper, we present a hierarchical procedure for bridging the gap between atomistic and macroscopic (FEM) modeling passing through mesoscopic simulations. In particular, we will present and discuss the concept of “message passing multiscale modeling”, and present examples of applications of multiscale procedures for the estimation of the binding energy and basal spacing in polymer–organoclay nanocomposites. Examples of application of message passing multiscale modeling to...
immiscible polymer blends and polymer–carbon nanotubes systems will also be presented and illustrated.

The strategy described in this paper is based on an overlapping array of successively coarser modeling techniques. At each plateau (a range of length and time scales), the parameters of the coarse description are based on representative results of the immediately finer description, as it will be explained in the following paragraphs.

2. Multiscale molecular modeling

Molecular modeling and simulation combines methods that cover a range of size scales in order to study material systems. These range from the sub-atomic scales of quantum mechanics (QM), to the atomistic level of molecular mechanics (MM), molecular dynamics (MD) and Monte Carlo (MC) methods, to the micrometer focus of mesoscale modeling.

Quantum mechanical methods have undergone enormous advances in the past 10 years, enabling simulation of systems containing several hundred atoms. Molecular mechanics is a faster and more approximate method for computing the structure and behavior of molecules or materials. It is based on a series of assumptions that greatly simplify chemistry, e.g., atoms and the bonds that connect them behave like balls and springs. The approximations make the study of larger molecular systems feasible, or the study of smaller systems, still not possible with QM methods, very fast. Using MM force fields to describe molecular-level interactions, MD and MC methods afford the prediction of thermodynamic and dynamic properties based on the principles of equilibrium and non-equilibrium statistical mechanics [3–7]. Mesoscale modeling uses a basic unit just above the molecular scale, and is particularly useful for studying the behavior of polymers and soft materials. It is based on an oversimplification, van der Waals interactions and other quantities that accurately reproduce the QM calculations. With the FF, the idea of multiscale modeling is straightforward: one computes information at a smaller (finer) scale and passes it to a model at a larger (coarser) scale by leaving out, i.e., coarse-graining, degrees of freedom [12–15].

The ultimate goal of multiscale modeling is then to predict the macroscopic behavior of an engineering process from first principles, i.e., starting from the quantum scale and passing information into molecular scales and eventually to process scales.

Thus, based on accurate QM calculations, a force field (FF) is determined, which includes charges, force constants, polarization, van der Waals interactions and other quantities that accurately reproduce the QM calculations. With the FF, the dynamics is described with Newton’s equations (MD), instead of the Schrödinger equation. The MD level allows predicting the structures and properties for systems much larger in terms of number of atoms than for QM, allowing direct simulations for the properties of many interesting systems. This leads to many relevant and useful results in materials design; however, many critical problems in this filed still require time and length scales far too large for practical MD. Hence, the need to model

![Fig. 1. Multiscale molecular modeling: characteristic times and distances.](image-url)
the system at the mesoscale (a scale between the atomistic and the macroscopic) and to pass messages from the atomistic scale to the mesoscale and to the macroscale. This linking through the mesoscale in which the microstructure can be described is probably the greatest challenge to developing reliable first principles methods for practical materials’ design applications. Only by establishing this connection from microscale to mesoscale it is possible to build first principles methods for describing the properties of new materials and (nano) composites.

The problem here is that the methods of coarseening the description from atomistic to mesoscale or mesoscale to continuum is not as obvious as it is in going from electrons to atoms [2]. For example, the strategy for polymers seems quite different than for metals, which seem different from ceramics or semiconductors. In other words, the coarseening form QM to MD relies on basic principles and can be easily generalized in a method and in a procedure, while the coarseening at higher scales is system specific.

This paper focuses the attention to the prediction of macroscopic properties of polymer systems and polymer nanocomposites with particular attention to interface phenomena. Finite element analysis software is used to this aim, but the physical properties input to such programs are consequence of the microstructure at few nanometers scale. Fig. 2 gives an indication of the kind of properties that may be computed at different scales from atomistic to continuum finite elements methods.

One of the first breakthrough examples of multiscale modeling of materials is the linking of quantum and classical molecular methods with continuum methods to study crack propagation in silicon [16]. Here tight-binding MD was carried out near the crack tip, classical MD was employed farther away, and finite element calculations were performed far enough from the crack that a continuum approximation was valid. By developing clever schemes to link the three methods together both spatially and temporally, the entire hybrid simulation could be carried out with all three techniques operating simultaneously in the appropriate areas.

Multiscale simulation poses, in some sense; greater challenges for polymer materials than for metallic and ceramic systems due to the larger range of length and time scales that characterize macromolecules. In this respect, for example, Doi [15,17] has developed a suite of state-of-the-art simulation tools that model polymers at the molecular and mesoscale level. Although each tool performs calculations using only one technique, the output from one level can be used directly as input for another, allowing an off-line bridging of length and time scales. To achieve what he and others refer to as “seamless zooming”, namely the ability to spawn higher resolution simulations using more detailed methods where needed, will require additional theoretical and computational advances.

Along similar lines, off-line multiscale simulations of nanofilled polymers using coarse-grained molecular dynamics, mesoscopic time dependent Ginsburg-Landau theory (TDGL), and macroscopic continuum finite element techniques have been carried out. Significant advances in uniquely mapping atomistic models of polymers onto coarse-grained models [18] have been made in recent years, in some cases providing nearly exact quantitative agreement between the two models for certain quantities, but these mappings, too, are performed off-line, and the various methods are not linked within a single simulation.

Scale integration in specific contexts in the field of polymer blends modeling will be the core of the following paragraphs. Integration of MC and quantitative structure property relationship (QSPR) procedures, coupled with MD simulation will be described as a way to introduce input data for mesoscale modeling. Further, integration between mesoscale modeling and FEM will be given.

2.1. Integration of atomistic with mesoscale simulation

Atom-based simulations such as MD and MM methods have come into wide use for materials design. As mentioned above, using these atomistic simulation tools, one can analyze molecular structure on the scale of 0.1–10 nm. However, difficulty arises concerning limitations of the time- and length-scale involved in the simulation. Although a possible molecular structure can be simulated by the atom-based techniques, it is less realistic to predict a mesoscopic structure, defined on the scale of 0.1–10 nm (e.g., the morphology of polymer blend and composite), which often dominates actual material properties, with these tools. For the morphology on these scales, mesoscopic simulations are available as an alternative to atomistic modeling.

There are various simulation methods by which to study a mesoscopic structure, e.g., the TDGL theory, the dynamic density functional theory, lattice-gas automata, and the lattice Boltzmann equation [2]. Some of these simulation methods, such as the dynamic mean field theory (Mesodyn) [8] and dissipative particle dynamics (DPD) [9] utilize coarse-grained molecular models to study the morphology of inhomogeneous materials using Flory–Huggins $\chi$ parameters between components.

In the procedure described later in this paper, Flory–Huggins $\chi$ parameters between two components of the coarse-grained molecular models in the mesoscopic simulation are estimated through the atomistic simulation, and a mesoscopic structure is predicted using these parameters.

Mesoscopic simulations are performed using a coarse-grained molecular model as shown in Fig. 3, characterized by the
Flory–Huggins $\chi$ parameter. The particle in mesoscopic simulation is related to a group of several atoms in the atomistic simulation.

Mesodyn and DPD theory and simulation protocols are fully described in the literature [8–10]. Suffice to mention here that in both cases two parameters are of paramount importance in the definition of the system at mesoscale level: (i) the Flory–Huggins $\chi$ parameter and (ii) the bead structure and length. On top of these two parameters, which are common to the two mesoscale methods, a third parameter is need for Mesodyn, namely (iii) the bead self-diffusion coefficient. In the next paragraphs, the procedure for calculating these three parameters from atomistic simulations will be described.

MD simulations, MC atomistic simulations and group additive methods are the atomistic simulation options for estimating input parameters for a mesoscale simulation. The procedures reported are perfectly suitable for single-phase polymers, for polymer blends, for block co-polymers and for polymer–solvent interactions. In the case of nanofiller inclusions, a different procedure must be applied.

### 2.1.1. Flory–Huggins parameter estimation

Several computational methods are available for the estimation of $\chi$ parameters between polymer–polymer, polymer–solvent, or solvent–solvent systems. In what follows, we estimate $\chi$ parameters from bulk atomistic simulations of blends and single component systems via the relevant cohesive energies. Indeed, the cohesive energies are calculated for pure components and their mixture using a MM technique. The cohesive energies are calculated for pure blends and single component systems via the relevant cohesive energy densities for pure components and the binary mixture, respectively. In general, the cohesive energy density is defined as the ratio of the cohesive energy $E_{\text{coh}}$ and the molar volume $V$ at a given temperature; $E_{\text{coh}}$, in turn, is defined as the increase in internal energy per mole of substance if all intermolecular forces are eliminated. In our approach, each chain is surrounded by other chains that are simply displaced images of the chain itself. The cohesive energy is the energy of interactions between these images. Accordingly, the values of $E_{\text{coh}}$ at different temperatures can be obtained, both for mixtures and pure components, from simulation by calculating the difference between the non-bonded energy of the periodic structure and the corresponding value of an isolated parent chain in vacuum:

$$E_{\text{coh}} = E_{\text{isolated}} - E_{\text{Periodic}}$$

The quality of this atomistic study depends on the adopted force field. In order to ensure reliable calculations, the use of a high quality force field and the validation of the cohesive energy by comparison with known experimental values are indispensable.

All simulations such as those described above can be performed using Materials Studio (v. 4.0, Accelrys, San Diego, CA, USA) and the details of the calculations are reported elsewhere [4,19,20].

In some cases, the method outlined above can be time consuming and not suitable to the task. An alternative method, based on a less precise procedure is to obtain an estimation of $\chi$ using advanced Quantitative Structure-Property Relationships (QSPRs) such as Synthia (Materials Studio v. 4.0, Accelrys, San Diego, CA, USA). The value of $\chi$ can also be determined by MC simulation of polymer blend using the following expression:

$$\chi = \frac{Z \Delta E_{12}}{RT}$$

where $Z$ is the coordination number and $\Delta E_{12}$ is the interaction energy between the two systems A and B.

The following approximation is then used for calculating $\chi$:

$$\chi = \frac{V_{\text{ref}}(\delta_1 - \delta_2)^2}{RT}$$

where $V_{\text{ref}}$ is a reference volume, taken to be the mean molar volume of the two monomers.

### 2.1.2. Bead structure and length estimation

In Mesodyn and DPD the polymer chain is the fundamental building block of the model. In this description, the intra-chain correlations can, in principle, be treated by any suitable model. In practice, a Gaussian chain model is used because it allows a factorization of the interactions; hence it is computationally very efficient. It can be proved that a Gaussian chain may be used as a statistical model for a real chain; therefore, for each real, atomistic force field model, a Gaussian chain representation with the same response function can be found. In the hypothesis of Gaussian chain, the systems needs parameters to determine the number $n$ and the length $a$ of the beads (Kuhn segment).

To reduce computational time to reasonable limit, the molecular weight of each chain can be scaled by a given factor (e.g.,
The resulting polymer chains are mapped onto Gaussian chains by imposing that the mean square end-to-end distance and the length of a fully extended (all-trans) chain be equal for the real and the Gaussian chain. Thus, the number \( n \) and the length \( a \) of the Gaussian chain segments are estimated by the following relationships:

\[
a = C_\infty l
\]

\[
n = \frac{N}{C_\infty}
\]

where \( N \) is the degree of polymerization, \( l \) the monomer unit length, and \( C_\infty \) is the characteristic ratio of an infinite length chain. The characteristic ratio represents the stiffness of the chain:

\[
C_\infty = \frac{\langle r^2 \rangle_0}{Nl^2}
\]

with

\[
l^2 = \sum_{i=1}^{N} l_i^2
\]

where \( N \) is the number of monomers, \( l \) the monomer length and \( \langle r^2 \rangle_0 \) is the mean end-to-end distance.

If the chain has \( N \) monomers with a length \( l \), this can be approximated to a freely jointed equivalent chain with a number of segments \( n \) and a bond length \( a \). The choice is subjected to conditions:

\[
\langle r^2 \rangle_0 = C_\infty Nl^2 = n\bar{a}^2
\]

\[
n\bar{a} = l_{\text{max}}
\]

and we obtain the equations defining \( a \) and \( n \) reported above. This operation can be represented graphically in Fig. 4, in which the mapping of a polymer chain into beads is depicted. The value of \( N \) can be obtained from the molecular weight of the polymer; \( C_\infty \) is an intrinsic property of the chain and can be estimated by MD or with QSPRs.

Fig. 5 reports the calculation schema if the \( C_\infty \) is estimated with MD via the rotational isomeric state (RIS) method [21]. The RIS generates a given number of configurations; each configuration is simulated independently with MM minimization and annealing before running a constant volume/constant temperature (NVT) MD run. After the simulation is done, the polymer end-to-end distance is estimated and the \( C_\infty \) is calculated. The procedure is repeated, for each configuration at different chain length until a constant value of \( C_\infty \) is obtained (see Fig. 6).

The true value of \( C_\infty \) is estimated by averaging over all the configurations considered.

As an example, Fig. 7 reports the end-to-end distance distribution for polycarbonate at 563 K for different number of monomers (10, 25 and 50). Fig. 8 shows, again for polycarbonate, that the Gaussian behavior is satisfied (i.e., points are nicely correlated by a straight line).
Finally, Fig. 9 reports the characteristic ratio of polycarbonate as a function of the number of polymer constitutive repeating units (CRU), in which the tendency to a constant value is verified at high CRUs. It is also interesting to compare the calculated units (CRU), in which the tendency to a constant value is verified as a function of the number of polymer constitutive repeating units making up each set are calculated as averages over different trajectories such a set by means of the Einstein equation. The MSDs for generated from different initial configurations, such as those used previously for the cohesive energy density calculations.

Finally, the self-diffusion coefficients of the beads are estimated from the linear portion of the corresponding MSD versus time curves. The details of the molecular dynamics simulation are the same as those reported previously for the determination of the Flory–Huggins parameter [4,19,20].

The bead self-diffusion coefficient can also be obtained by QSPRs in a much less expensive way by means of a data regression method directly from the fraction of each polymer in the blend. The great saving in CPU time obtained by this method compensates the loss in accuracy for the data; this is acceptable also because this parameter is not crucial in the mesoscale simulation.

As stated in the introduction, in Mesodyn the bead self-diffusion coefficient is an explicit input parameter, while in DPD it is not introduced, as diffusion is an output, which shows the average diffusivities of each bead in the simulation.

\[ \tau = \beta^{-1} M h^{-2} \Delta t \]  
\[ (12) \]

where \( \tau \) is the non-dimensional time step used in the Mesodyn calculation algorithm, \( \Delta t \) the effective time step, \( h \) the cell dimension and \( (\beta^{-1} M) \) is the bead self-diffusion coefficient. For each mixture under study, a proper set of atoms, equivalent to the number of the constitutive repeating units making up a bead of the corresponding chain, is selected in the trajectory file of the relevant mixture 3D periodic isochoric–isothermal ensemble \( \text{(NPT)} \) MD simulations [5]. Diffusion coefficients are calculated from the mean square displacement (MSD) of such a set by means of the Einstein equation. The MSDs for each set are calculated as averages over different trajectories generated from different initial configurations, such as those used previously for the cohesive energy density calculations.

![Fig. 8. Verification of the Gaussian behavior for polycarbonate at 563 K.](image)

![Fig. 9. Characteristic ratio as a function of CRU for polycarbonate: (●) is the simulated value and (▲) is the experimental value.](image)
It is evident by this description that a fundamental role here is played by the surface modifier. An MD run at atomistic level is able to yield the binding energies of the ternary (MMT, polymer, surface modifier) system. The most important information obtained by the atomistic simulation is the part of the platelet that is in contact with the polymer (S) and the amount of the energy of this interaction with respect to the interaction energy of the polymer–surface modifier interaction (E). These two values are used later on in the model.

At mesoscale level we can use DPD or Mesodyn for the simulation of the system in terms of beads. The properties of the polymer beads (Flory–Huggins parameter and bead dimension) are calculated as described in the previous chapter, while the properties of the solid are calculated as follows.

The Flory–Huggins parameter of the solid is calculated assuming that the surface is averaged among the value of the Flory–Huggins parameter of the surface modifier (that is calculated according to classical MD) and the values of E and S, being E the ratio of the interaction energy of the polymer with the pure solid and the pure surface modifier. In summary two possible conditions there exists:

- platelet completely surrounded by surface modifiers: the interaction surface modifier–polymer (binary system) can be evaluated by performing an atomistic simulation;
- platelet non-saturated by surface modifier (a situation that most likely will occur): evaluation of the ‘holes’ is obtained by atomistic simulation (parameter S), by which the surface of platelet exposed can be determined. Solubility parameter of platelet is calculated by using the parameter E determined via atomistic simulation and the average solubility parameter can then be estimated.

An alternative method to calculate the interaction energy of a platelet–platelet interaction is the application of the definition of cohesive energy density directly to the MMT structure. One can run a simulation under periodic boundary conditions of several platelets of MMT, and compare the energy of this system with the energy of a single platelet of MMT, thus obtaining by definition the solubility parameter. This solubility parameter can be later used in the mesoscale simulation for describing the platelet–platelet interaction.

The bead dimension of the solid phase is determined by the crystallographic data and the shape factor (ratio of two non-nanoscale dimensions).

2.3. Integration of mesoscale simulation with macroscopic simulation

For the description of flow of polymeric materials on a processing scale, one must employ a hydrodynamic description and incorporate phenomena occurring on mesoscopic to macroscopic length and time scales. For example, to capture the non-Newtonian properties of polymer flow behavior one can either use special models for the materials stress tensor, or obtain it from a molecular simulation using the instantaneous flow properties of the hydrodynamic fields as input. In the area of high-performance materials and devices, polymer composites are finding a widespread application, and the modeling of these materials was until recently done primarily through finite element methods (FEM), and are beyond the realm of application of molecular modeling approaches. Nonetheless, a real problem in using FEM is the definition of the physical properties of a complex material such as a polymer blend with phase segregation and/or a polymer with micro inclusion of nanosized platelets [9, 22–24]. Mesoprop technique is a method based on finite elements for estimating properties of a complex material starting from the density distribution at mesoscale. The method uses the results of a mesoscale simulation under the form of three dimensional density maps, and transforms such information into a fixed grid that is used for the integration of the equations to determine macrosopic properties.

Integration between these methods (from mesoscale to macroscale) is of paramount importance for the estimation of the properties of the materials.

3. Applications of multiscale modeling

In the following paragraphs, some applications of the message passing multiscale modeling described in the previous sections will be presented and discussed.

3.1. Simulation of polymer systems nanocomposites

Organic–inorganic nanoscale composites have attracted great interest since they frequently exhibit unexpected hybrid properties synergistically deriving from two components. One of the most promising composite systems is a hybrid based on an organic polymer and an inorganic clay mineral (e.g., a layered silicate). To model the entire system it is necessary to start from the atomistic 3D model of the nanoparticle, which is built starting from structural information about its crystal. As most of minerals, montmorillonite is present in nature with a variety of chemical compositions and structural features; nonetheless, properties can be considered as derived from those of pyrophyllite by random substitution of Al by Mg ions [19].

The organic modifiers and the polymers are then modeled separately using an appropriate force field by MM and MD techniques. Finally, the ternary system is investigated in isothermal–isochoric (NVT) MD experiments, and the calculation of the binding energy is performed.

The total potential energy of a ternary system composed, for example, by poly(propylene), montmorillonite and a quaternary alkylammonium salts (quat), may be written as the summation of the energies of all the pure components and all the binary systems involved. By definition, the binding energy is the negative of the interaction energy.

Results of binding energies for different quats used as surface modifiers in the montmorillonate nanofillers have been studied [19, 20, 25, 26] for a large selection of quats and a given number of polymers: nylon 6, nylon 6-6, polypropylene, polypropylene maleated, polymethyleneacylate, polystyrene, polycarbonate, polyethylene terephalate and ABS. The binding energies allow identifying the best system from a thermodynamic point of view.
Very important information on the nanostructure of the filler is the spacing between the platelets after the surface modification has occurred. This is important because the enlargement of the galleries is directly related to the capacity of the polymer to penetrate into the interlayer spaces, thus providing a totally exfoliated nanocomposite. In previous work we developed a procedure for estimating the basal spacing of a nanofiller–quat system [20,25,26]. Fig. 10 shows the simulation of a MMT platelet with the quat and the polymer (left) and the calculation of the basal spacing (right) in which two platelets are evidenced.

Some examples of the use of atomistic simulations for estimating basal spacing and binding energies among the components are reported below. These information can be used for studying the macroscopic systems as described above.

### 3.1.1. Polypropylene, polypropylene maleated/montmorillonite

The procedure outlined above is applied to the prediction of the binding energies and basal spacing of polymer/clay nanocomposites based on polypropylene (PP) and maleated polypropylene (PPMA), montmorillonite, and different quats as surface modifiers. The objective is to identify the quat that gives the MMT–polymer highest binding energy. A comparison of the effect of maleated group in the PP chain is also reported. This is done by evaluating binding energy between the clay and the polymer of both PP and PP maleated. The surface modifiers considered in this investigation is given below: (i) trimethylhexyl quat (H₃C)₃N(C₆H₁₃), (ii) trimethyldecylquat (H₃C)₃N(C₁₂H₂₅), (iii) trimethylstearyl quat (H₃C)₃N(C₁₈H₃₇), (iv) methylstearyldiethylexidquat (H₃C)₃N(C₁₈H₃₇)(C₂H₄OH)₂, (v) trimethylethleniminoenetraquat (H₃C)₃N(CH₂)₆COOH, (vi) trimethylomega-aminolauric quat (H₃C)₃N(CH₂)₁₁COOH and (vii) dimethyldistearyquat (H₃C)₂N(C₁₈H₃₇)₂.

It is interesting to look at the results in terms of binding energies (Fig. 11) as a function of quat volume. The numerical values of the binding energies are reported in Table 2 for the PPMA, and in Table 3 for the PP. The

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>( E_{\text{bind}} ) (PPMA–MMT) (kcal/mol)</th>
<th>( E_{\text{bind}} ) (PPMA–quat) (kcal/mol)</th>
<th>( E_{\text{bind}} ) (MMT–quat) (kcal/mol)</th>
<th>( V(\text{Å}^3) )</th>
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<td>Pristine</td>
<td>124.0</td>
<td>47.0</td>
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<td>(H₃C)₃N(C₆H₁₃)</td>
<td>115.1</td>
<td>74.1</td>
<td>1246.5</td>
<td>280</td>
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<td>(H₃C)₃N(C₁₂H₂₅)</td>
<td>87.6</td>
<td>88.2</td>
<td>1108.6</td>
<td>383</td>
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<tr>
<td>(H₃C)₃N(C₁₈H₃₇)</td>
<td>45.3</td>
<td>103.0</td>
<td>1096</td>
<td>665</td>
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<tr>
<td>(H₃C)₂N(C₁₈H₃₇)₂</td>
<td>13.8</td>
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binding energy between clay and polymer decreases with increasing molecular volume of the surfactant. On the other hand, the binding energy between the polymer and the quat increases with increasing molecular volume of the quat, which is reasonable. The binding energy between clay and quats is mainly affected by presence of the polar group in a quat, which reflects in an increase of $E_{\text{bind}}$ (MMT/quat), and secondarily by quat volume. When only the quat volume parameter is considered, we can observe a decreasing trend of the $E_{\text{bind}}$ (MMT/quat) with increasing volume of the quat.

As reported in Table 2 for PPMA, shorter hydrocarbonic chains are more effective in producing favorable binding energies with respect to longer ones, and the substitutions of hydrogen atoms with polar groups on the quaternary ammonium salt generally results in greater interaction between quat and both polymer and clay.

Under the hypothesis that montmorillonite platelets are uniformly dispersed in a polymer matrix, the modified polypropylene yields higher interfacial strength with clay than neat polypropylene.

The molecular simulation techniques are also used for the calculation of the basal spacing of the MMT platelets in presence of the surface modifiers. The final result of the simulation is the distance between two platelets in presence of the quat alone. The numerical results of the spacing calculation for the quats and the polymers investigated are reported in Table 4. The values refer to the situation after 250 ps of NPT molecular dynamics simulations.

The use of neat PP and quats with higher molecular volume result in higher values of the basal spacing and thus, in principle, they should be more effective in the exfoliation process [27].

### Table 3

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>$E_{\text{bind}}$ (PP–MMT) (kcal/mol)</th>
<th>$E_{\text{bind}}$ (PP–quat) (kcal/mol)</th>
<th>$E_{\text{bind}}$ (MMT–quat) (kcal/mol)</th>
<th>$V (\text{Å}^3)$</th>
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<td>1471.1</td>
<td>179</td>
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<td>(H3C)3N(C6H13)</td>
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<td>(H3C)3N(C12H25)</td>
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<td>93.1</td>
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<td>1105.2</td>
<td>665</td>
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<td>(H3C)2N(C14H29)2</td>
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</table>

### Table 4

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<tr>
<th>Quat</th>
<th>Spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPMA</td>
<td>PP</td>
</tr>
<tr>
<td>(H3C)3N(C6H13)</td>
<td>31.19</td>
</tr>
<tr>
<td>(H3C)3N(C18H37)</td>
<td>36.20</td>
</tr>
<tr>
<td>(H3C)2N(C18H37)2</td>
<td>40.02</td>
</tr>
</tbody>
</table>

#### 3.1.2. Polyethylene terephthalate/montmorillonite

Polyethylene terephthalate (PET) is considered an important polymer for the packaging industry. In view of such applications it is important to focus the attention on the exfoliation capability of the system and on the barrier effect for gas penetration. To this aim, the system to be simulated is a three-component system including PET, MMT and a surface modifier. The list of surface modifiers investigated is the following: (i) Cloisite 10A, (ii) Cloisite 20A, (iii) Cocco 12, (iv) Cocco 14, (v) Dellite 43B, (vi) Dellite 65G.

The results of the simulations permit to rank the different systems in order of quality of the surface modifier for an optimal exfoliation.

Fig. 12 right shows the results of the specific binding energy (binding energy per volume of surface modifier) calculations in which it can be seen that the first four chemicals have good characteristics as far as the energy is concerned (energy values close to the pristine material). Fig. 12 left shows the results of the basal spacing for the same systems: the higher the value, the better (larger channels). Therefore, the best chemical for basal spacing is the first one, all others being utterly similar.

Considering both effects with the same weight, the best surface modifiers to obtain exfoliation are (i) Cloisite 20A, (ii)
Cloisite 10A and (iii) Cocco 12. The characteristics of these systems are summarized in Table 5.

### 3.2. Simulation of polymer blends

A relevant issue in polymer technology is the possibility to predict the morphology and the phase behavior for immiscible blends. Multiscale modeling is suitable to this aim, since atomistic models can give information on the interaction that occurs between the component of the system as well as on the chain characteristics (e.g., characteristic ratio and Khun length). The information may be used as input for the mesoscale level of simulation in which the system is treated alternatively as particles (DPD) or as a density field (Mesodyn). In this last case, the simulation at mesoscale gives as output an order parameter (OP) and a distribution of single component densities in space, thus evidencing morphology and phase behavior. The last element in this chain is given by the FEM simulation that calculates, from the morphology provided by the mesoscale simulation, the mechanical properties of interest.

This procedure has been applied by our group to several systems: polyethylene/polypropylene, polyethylene terephthalate–polyethylene naphtalate, polyvinylchloride–polyethylene, polymethylmethacrylate–polycarbonate, ABS–polymethylmethacrylate [28,29].

#### 3.2.1. Polymethylmethacrylate/polycarbonate

The use of PC–PMMA blends is common in automotive applications. In this investigation we evaluated the miscibility of these two components applying a multi-scale model. Input parameters for the mesoscale simulation were all obtained from MM and MD at atomistic level: characteristic ratios \( C_\infty \), Flory–Huggins \( \chi \) parameters and self-diffusion coefficients \( D \) (see details in previous sections).

Mesoscale simulations were performed on PC/PMMA system with composition 70% PC and 30% PMMA in different shear conditions to simulate the behavior during manufacturing of the polymer. The shear rate was set in accordance with typical values for extrusion, injection molding and blow molding, ranging from \( (10^2 \text{ to } 10^6 \text{ s}^{-1}) \).

The results, as given in Figs. 13 and 14, show complete immiscibility for high and low shear rates, indicating the formation of segregate domains with 10–20 nm diameters. Different shear rates show domains of different shape: elongated in the presence of high shear rates, more regular (spheres) under low or no shear. These results show clearly that there is no miscibility in the system PMMA/PC. If miscibility is desired, it is necessary to introduce a compatibilizer.

#### 3.2.2. Polypropylene/polyethylene

Blends of polypropylene and polyethylene are suitable for several applications like food packaging or household electric devices. The aim of this investigation is to study the behavior of blends of PP and PE (linear and branched PE) in terms of phase segregation and morphology at different composition and at different shear rate. Moreover, the mechanical properties are predicted with a many-scale simulation with the use of a finite-element technique.

MM and MD were used to obtain input parameters \( (\chi, C_\infty, D) \), while mesoscale simulations gave indications about morphology and phases segregation. The density profiles obtained by mesoscale simulations were employed in finite element calculations to estimate mechanical properties, such as Young’s modulus. This procedure has been applied to the case of the 47/53% PP/LDPE (grafted PE).

Table 6 reports the characteristics of the structures investigated.

### Table 6

<table>
<thead>
<tr>
<th>System</th>
<th>( \Delta E_a ) (kcal mol(^{-1})Å(^{-3} ))</th>
<th>Spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloisite 10A</td>
<td>−0.065</td>
<td>23.43</td>
</tr>
<tr>
<td>Cloisite 20A</td>
<td>−0.053</td>
<td>31.08</td>
</tr>
<tr>
<td>Cocco 12</td>
<td>−0.231</td>
<td>20.93</td>
</tr>
</tbody>
</table>

Fig. 13. 3D structure for the system PMMA/PC (applied shear of \( 2 \times 10^5 \text{ s}^{-1} \)).

Fig. 14. 3D structure for the system PMMA/PC (no shear).
The mesoscale simulations show complete miscibility for all systems, with moderate or without shear applied. Only under very high shear values, higher than values commonly applied in processing, segregation occurs. This indicates that LDPE can be used in blends with PP, as it does not influence the quality of the final product, thus giving the advantage of reduced cost and the possibility of recycling. To quantify the prediction capability of the method, Young’s modulus and other properties have been calculated starting from the predicted morphology obtained from the mesoscale simulation. Predictions of Young’s modulus for PP/PE (47/53%) blends obtained were compared with literature and showed good agreement with experimental data [30]. $G_{\text{CDT}} = 0.668 \text{ GPa}$, $G_{\text{M}} = 0.720 \text{ GPa}$ with an error of 7%.

### 3.2.3. Polycarbonate/acrylonitrile-butadiene-styrene (ABS)

PC transparency and ABS reflecting characteristics are commonly combined in PC–ABS blends. Multiscale molecular modeling can evaluate the possibilities to improve characteristics of PC–ABS blends for recycling and obtain information in order to (i) improve PC viscosity, (ii) compensate surface resistance losses for recycled PC, and (iii) improve resistance at low temperatures.

To simulate the system with these objectives, a multi-scale molecular simulation approach is necessary, since morphology and mechanical properties are equally important. For these reasons, calculations at room and process temperature and at injection conditions (with application of a shear rate) were done.

The PC polymer was modeled by splitting a PC monomer and considering two fragments (PC01 and PC02) to limit the dimension of the real PC monomer, which was too big for a mesoscale simulation with one single bead, in comparison with other monomers. In Table 7, the characteristics of the systems investigated are reported, while in Table 8 the input data for mesoscale (Mesodyn) simulations are presented.

Mesoscale simulations results show phase segregation for all systems, revealing the presence of small, circular or oval domains with dimension of 10–20 nm. In general, styrene (S) is better distributed, while acrylonitrile (AN) shows a higher degree of segregation, probably due to higher $\chi$ values. In fact, S bridges between AN and PC-B (non-polar components). Systems with higher fractions of PC have generally larger, circular domains of PC. Temperature does not exert an appreciable influence. Shear application also does not influence the tendency to segregation: it only modifies the form of the domains, which are more elongated along the shear direction.

At nanoscale level structures definitely show a segregation tendency. 3D structure images are also confirmed by comparison with TEM images [31].

Fig. 15 shows some of the results of mesoscale simulations. Order parameter and field distribution are reported in the upper part of Fig. 15, showing stability in the structure and the segregation of phases at mesoscale level. In the lower part of Fig. 15, a tri-dimensional image of the segregation domains is compared with a TEM image for the same system PC/ABS [31]. The good agreement between the simulated and the experimental structure clearly speaks in favor of simulation reliability.

The density field distributions have been used to perform finite-element simulations to obtain the following mechanical properties: (i) density, (ii) elastic constants, and (iii) thermal expansion coefficient. The results of the simulation shows that, even though at nanoscale level the systems are not homogeneous,
the properties obtained at macroscopic level are homogeneous for all sections considered. As an example (see Fig. 16), the Von Mises stress distribution has a Gaussian behavior with one maximum only, while the density distribution in the mesoscale simulations shows more than one peak; they are also distributed along the entire range of densities, showing phase segregation.

Numerical results of the simulation are shown in Table 9. Simulation results have been compared with experimental data for a commercial ABS (Bayblend T85, Bayer), which corresponds to the PC-85/ABS-15. The calculated Young’s modulus is 2.34 GPa (exp. 2.30) and the calculated thermal expansion coefficient is $6.6 \times 10^{-5}$ 1/K (exp. $7.5 \times 10^{-5}$); the agreement between experimental and predicted value is excellent. Consequently, the model allows the determination of the composition of the blend for a given mechanical property value.

### Table 9

Finite elements simulation results for mechanical properties

<table>
<thead>
<tr>
<th>Blend</th>
<th>Young modulus (GPa)</th>
<th>Poisson modulus</th>
<th>Thermal expansion coefficient (1/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PC15-ABS85)</td>
<td>2.67</td>
<td>$5.0 \times 10^{-1}$</td>
<td>$6.92 \times 10^{-5}$</td>
</tr>
<tr>
<td>(PC35-ABS65)</td>
<td>2.77</td>
<td>$5.0 \times 10^{-1}$</td>
<td>$6.80 \times 10^{-5}$</td>
</tr>
<tr>
<td>(PC55-ABS45)</td>
<td>2.87</td>
<td>$5.0 \times 10^{-1}$</td>
<td>$6.72 \times 10^{-5}$</td>
</tr>
<tr>
<td>(PC85-ABS15)</td>
<td>3.02</td>
<td>$4.9 \times 10^{-1}$</td>
<td>$6.56 \times 10^{-5}$</td>
</tr>
<tr>
<td>(PC15-ABS85)s</td>
<td>2.67</td>
<td>$5.0 \times 10^{-1}$</td>
<td>$6.92 \times 10^{-5}$</td>
</tr>
<tr>
<td>(PC35-ABS65)s</td>
<td>2.77</td>
<td>$5.0 \times 10^{-1}$</td>
<td>$6.82 \times 10^{-5}$</td>
</tr>
<tr>
<td>(PC55-ABS45)s</td>
<td>2.87</td>
<td>$4.9 \times 10^{-1}$</td>
<td>$6.71 \times 10^{-5}$</td>
</tr>
<tr>
<td>(PC85-ABS15)s</td>
<td>3.02</td>
<td>$4.9 \times 10^{-1}$</td>
<td>$6.55 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
3.3. Simulation of carbon nanotube systems

Carbon nanotubes (CNT) are interesting for several applications in different fields: structural, electromagnetic, chemical and mechanical. They have already been used as composite fibers in polymers and concrete to improve the mechanical, thermal and electrical properties of the bulk product. In this paper we present one application of computer simulations involving CNT, namely the simulation at mesoscale level of the structure of a polymer CNT system. For simulating the mesoscale morphology of the system, information at atomistic level is necessary. This information is obtained in a ‘multiscale’ fashion. Firstly the same model of CNT developed for the atomistic simulation of the gas adsorption [32] is used to determine the Flory–Huggins interaction parameters of the CNT for different diameters. This is obtained directly from the definition of cohesive energy by running two different simulation, one of the CNT in the bundle and another one with a single CNT isolated. The difference in the energy is the so-called ‘bundling-de-bundling energy’. For the polymer the traditional approach to calculate the Flory–Huggins interaction parameter in MD and MC is followed [27].

A comparison of the interaction parameters obtained shows that only CNT of a given diameter are soluble in a given polymer. The calculations enable to predict the CNT diameter to be used for obtaining a homogeneous mixture.

The Flory–Huggins interaction calculated by molecular modeling are then used at mesoscale level with a particle-based method (DPD) for determining the mesoscopic structure of a CNT–polymer system. Recently these approaches has been used [33] for simulating the morphology of a polymer CNT system and simulate with FEM code the electric conductance as a function of copolymer morphology.

4. Conclusions

In this paper we have introduced the concept of multiscale molecular modeling and discussed the general guidelines for its implementation. The multiscale molecular modeling is applied in many fields of the material science, but it is particularly important in the polymer science and in the coating science, due to the wide range of phenomena accruing at different scales (from quantum chemistry to the mesoscale) influencing the final property of the materials.

In this context, multiscale molecular modeling can play a crucial role in the design of new materials whose properties are influenced by the structure at nanoscale.

Several examples have been reported in this paper showing the methodology and describing the simulation protocols. A general good agreement in the comparison with experimental literature data of mechanical properties and morphologies is obtained, thus showing that the multiscale molecular modeling is a mature tool that may be used in the design and development of new coatings. Advances in computational materials science in general will continue to facilitate the understanding of materials and materials processing, the prediction of properties and behavior, and the design of new materials and new materials phases.