Multiscale molecular modeling in nanostructured material design and process system engineering

Maurizio Fermeglia*, Sabrina Pricl

University of Trieste, Department of Chemical, Environmental and Raw Materials Engineering, Piazzale Europa 1, 34127 Trieste, Italy

ARTICLE INFO

Article history:
Received 6 September 2008
Received in revised form 13 February 2009
Accepted 28 April 2009
Available online 5 May 2009

Keywords:
Multiscale modeling
Mesoscale simulation
Product design

ABSTRACT

Atomistic-based simulations such as molecular mechanics, molecular dynamics, and Monte Carlo-based methods have come into wide use for material design. Using these atomistic simulation tools, we 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 simulations, it is less realistic to predict the mesoscopic structure defined on the scale of 100–1000 nm, for example the morphology of polymer blends and composites, which often dominates actual material properties. For the morphology on these scales, mesoscopic simulations such as the dynamic mean field density functional theory and dissipative particle dynamics are available as alternatives to atomistic simulations. It is therefore inevitable to adopt a mesoscopic simulation technique and bridge the gap between atomistic and mesoscopic simulations for an effective material design. Furthermore, it is possible to transfer the simulated mesoscopic structure to finite elements modeling tools for calculating macroscopic properties for the systems of interest.

In this contribution, a hierarchical procedure for bridging the gap between atomistic and macroscopic modeling passing through mesoscopic simulations will be presented and discussed. The concept of multiscale (or many scale) modeling will be outlined, and examples of applications of single scale and multiscale procedures for nanostructured systems of industrial interest will be presented. In particular the following industrial applications will be considered: (i) polymer-organoclay nanocomposites of a montmorillonite–polymer–surface modifier system; (ii) mesoscale simulation for diblock copolymers with dispersion of nanoparticles; (iii) polymer–carbon nanotubes system and (iv) applications of multiscale modeling for process systems engineering.

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. This is of particular importance in the field of polymer nanocomposites, where the properties of the material depend on the nanostructure.

In fact, 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 nanometres. Polymeric structures in melts, blends and solutions can range from nanometre scales to microns, millimetres 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. This situation is further complicated by the presence of nanoparticles (from few to tens nanometres in size). No single model or simulation algorithm currently available can encompass this range of length and time scales. In order to simulate such systems one must consider models that range from those including quantum effects and electronic degrees of freedom to chemically realistic, classical models. One promising approach towards the solution of these problems is the tight integration of different methods and theories in the so-called multiscale molecular modeling which became in recent years one of the most important issues in computational materials research. With this approach the bridging of length and time scales, and the consequent linking of computational methods are used to predict macroscopic properties and behaviour from fundamental molecular processes (Charpentier, 2002; Glotzer & Paul, 2002).

In this paper, we will show hierarchical procedures for bridging the gap between atomistic and macroscopic model-
ing passing through mesoscopic simulations. In particular, we will present and apply to some cases of industrial interest the concept of “message passing multiscale modeling”. Examples considered will be (i) polymer-organoclay nanocomposites of a montmorillonite–polymer–surface modifier system; (ii) mesoscopic simulation for diblock copolymers with dispersion of nanoparticles; (iii) polymer–carbon nanotubes system and (iv) evaluation of the environmental impact of a process based on toxicological data.

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 sections.

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 atomic 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 behaviour of molecules or materials. It is based on a series of approximations 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 (Allen & Tildesley, 1987; Gubbins & Quirke, 1996; Haile, 1992). Mesoscale modeling uses a basic unit (an agglomeration of atoms, called bead, obtained through a coarse-graining procedure) just above the molecular scale, and is particularly useful for studying the behaviour of polymers and soft materials. It can model even larger molecular systems, but with the commensurate trade-off in accuracy. Examples of mesoscale theories are dynamic mean field density functional theory (Mesodyn) and dissipative particle dynamics (DPD) (Altevogt, Evers, Fraaije, & van Vlimmeren, 1999; Fraaije et al., 1997; Groot & Warren, 1997). Furthermore, it is possible to transfer the simulated mesoscopic structure to finite elements modeling tools for calculating macroscopic properties for the systems of interest (Gusev, 2001).

Fig. 1 shows the class of models that are available at each single scale. QM, MM and mesoscale techniques cover many decades of both length and time scale, and can be applied to arbitrary materials: solids, liquids, interfaces, self-assembling fluids, gas phase molecules and liquid crystals, to name but a few. There are a number of factors, however, which need to be taken care of to ensure that these methods can be applied routinely and successfully.

First and foremost of course are the validity and usability of each method on its own, followed by their interoperability in a common and efficient user environment. Of equal importance is the integration of the simulation methods with experiment.

Multiscale simulation can be defined as the enabling technology of science and engineering that links phenomena, models, and information between various scales of complex systems. 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 (Doi, 2002; Goddard et al., 2001; McGrother, Golbeck Wood, & Lam, 2004).

The ultimate goal of multiscale modeling is then to predict the macroscopic behaviour 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 field still require time and length scales far too large for practical MD. Hence, the need to model the system at the mesoscale (a scale between the atomic and the macroscopic) and to pass messages from the atomic scale to the mesoscale and to the macroscopic. This linking through the mesoscale in which the microstructure can be described is probably the greatest challenge to develop reliable first principles method for practical materials’ design applications. Only by establishing this connection from microscale to mesoscale it is possible to build first principles method for describing the properties of new materials and (nano)composites.

The problem here is that the methods of coarsening the description from atomistic to mesoscale or mesoscale to continuum is not as obvious as it is going from electrons to atoms (Glotzer & Paul, 2002). For example, the strategy for polymers seems quite different than for metals, which seem different from ceramics or semiconductors. In other words, the coarsening from QM to MD relies on basic principles and can be easily generalized in a method and in a procedure, while the coarsening at higher scales is system specific.

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 (Abraham, Broughton, Bernstein, & Kaxiras, 1998). 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 (2002) has developed a suite of state-of-the-art simulation tools that model polymers at the molecular and mesoscopic 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, and macroscopic continuum finite element techniques have been carried out. Significant advances in uniquely mapping atomistic models of polymers onto coarse-grained models (Fermeglia & Pricl, 2002; Müller-Plathe, 2002; Scocchi, Posocco, Fermeglia, & Pricl, 2007) 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 modeling can be done in different ways. Any ‘recipe’ for passing information from one scale to another (upper) scale is based on the definition of multiscale modeling which consider ‘objects’ that are relevant at that particular scale (Fig. 2), disregard all degrees of freedom of smaller scales and summarize those degrees of freedom by some representative parameters.

All approaches are initially based on the application of a force field that transfers information from quantum chemistry to atomistic simulation.

From atomistic simulation to mesoscale, one can use a traditional approach based on the estimation of the characteristic ratio, the Kuhn length, and the Flory–Huggins interaction parameter (Fermeglia & Pricl, 2007). This approach for determining the input parameters for mesoscale simulation is based on the following information: (i) the bead size and Gaussian chain architecture, (ii) the bead mobility $M$, and (iii) the effective Flory–Huggins $\chi$ interaction parameters. With this approach, the 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. 2: the particle in mesoscopic simulation is related to a group of several atoms in the atomistic simulation. Mesodyn and DPD mesoscale theory and simulation protocols are fully described in the literature (Altevogt et al., 1999; Fraaije et al., 1997; Groot & Warren, 1997).

The traditional approach can be enhanced and improved by considering the detailed structure at the interface polymer–nanofiller (Scocchi et al., 2007). If one resorts to a particle based method for describing the system at mesoscale, atomistic MD simulation gives the necessary details of the interface with a particular attention to the binding energies among components. Mapping of the binding energies on mesoscale beads by means of a combinatorial approach to repulsive parameter for particles is then carried out and the system is simulated at mesoscale. If both particle based and field based methods are to be used at mesoscale, then an hybrid method can be adopted (Fraaije, 2009) in which particles are treated as described above and field interaction is calculated from pair–pair distribution functions.

Mesoscale simulation typical result is the morphology and the structure of the matter at nanoscale level at the desired conditions of temperature, composition and shear.

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 behaviour 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 property of a complex material such as a polymer blend with phase segregation and/or a polymer with microinclusion of nanosized platelets (Groot & Warren, 1997; Gusev, 1997, 2004; Gusev & Lusti, 2001). Mesoprop 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 mesoscopic 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 macroscopic properties. Palmyra is a different method that allows the simulation at FEM level with a variable grid methodology that allows to extend the size of the system studied.

Fig. 2. Coarse-grained modeling from atomistic model.
Fig. 3 shows how the mapping from mesoscale to macroscale is done. At FEM level each finite element corresponds to one phase, with property tensor $P_i$, at mesoscale (Mesodyn or DPD) each element contains mixture of phases, with concentration $C_i$. It is necessary to perform a geometry mapping by converting mesoscale cubic elements to Palmyra tetrahedrons. Once this is done, the Laplace equation is solved directly to obtain direct properties such as electric conductance, diffusion, permeability, etc. Local deformation allows the calculation of mechanical properties.

Integration between these methods (from mesoscale to macroscale) is of paramount importance for the estimation of the properties of the materials, as it will be described in the following sections with some illustrative examples of application.

3. Multiscale modeling for nanostructured material design

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

3.1. Polymer-organoclay nanocomposites (PCN)

Polymer-organoclays are important materials since the addition of a small amount of nanoclay to a polymer matrix enhances the macroscopic properties of the nanostructured material (Alexandre and Dubois, 2000). To do this the nanofiller must be completely exfoliated in the polymer and this is normally achieved by modifying the surface of the nanofiller with a particular components that is responsible of the exfoliation (Alexandre and Dubois, 2000). For designing the best surface modifier it is necessary to estimate binding energy and basal spacing of a montmorillonite–polymer–surface modifier system. This will also allow the calculation of the necessary parameters to be passed at the upper scale for the estimation of the morphology at mesoscale and the mechanical properties at macroscale.

The system considered as an example is the acrylonitrile–butadiene–styrene (ABS) with montmorillonite (MMT) (Cosoli, Scocchi, Pricl, & Fermeglia, 2008). Atomistic simulations allowed us to rank different surface modifiers (quaternary ammonium salts – quats) for the selected clay/polymer system. Fig. 4 shows a 3D periodic cell for ternary simulations of the ABS-based PCN, while Table 1 lists the binding energies for the best quat resulting from the screening, which is the quaternary, double-tailed ammonium salt Cloisite 20A® and the relevant spacing between the clay platelets.

ABS is a complex system, being constituted by an acrylonitrile (AN)–styrene (S) block copolymer (SAN) and a branched copolymer (polyB-SAN) with a main butadiene (B) chain and lateral chains of SAN. Accordingly, in Table 1 the SAN copolymer is oriented with the S block next to MMT surface and the ANS polymer is the same macromolecule but oriented with AN block next to MMT surface. Similarly, polyB-SAN presents the main chain of B ori-
Table 1
Binary binding energy (kcal/mol) and basal spacing (Å) with cloisite 20A® and MMT for homopolymers AN, S, B and block copolymer SAN and polyB-SAN/a.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{\text{MMT-pol}}$ [kcal/mol]</th>
<th>$E_{\text{MMT-quat}}$ [kcal/mol]</th>
<th>$E_{\text{pol-quat}}$ [kcal/mol]</th>
<th>Basal spacing [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>$-24$</td>
<td>$-1216$</td>
<td>$-32$</td>
<td>3.108</td>
</tr>
<tr>
<td>PB</td>
<td>$-7$</td>
<td>$-1266$</td>
<td>$-16$</td>
<td></td>
</tr>
<tr>
<td>PAN</td>
<td>$-41$</td>
<td>$-1248$</td>
<td>$-100$</td>
<td></td>
</tr>
<tr>
<td>SAN</td>
<td>$-9$</td>
<td>$-1165$</td>
<td>$-36$</td>
<td></td>
</tr>
<tr>
<td>ANS</td>
<td>$-15$</td>
<td>$-1102$</td>
<td>$-146$</td>
<td></td>
</tr>
<tr>
<td>PolyB-SAN</td>
<td>$-5$</td>
<td>$-1386$</td>
<td>$-116$</td>
<td></td>
</tr>
<tr>
<td>PolyB-SANa</td>
<td>$-19$</td>
<td>$-1230$</td>
<td>$-71$</td>
<td></td>
</tr>
</tbody>
</table>

By looking at the values of the $E_{\text{pol-quat}}$ term in Table 1, it is evident that the most polar AN homopolymer is more affine to quat than all other ABS homopolymer chain components. In an analogous way, B homopolymer binding energies are smaller. Finally, if one considers the mean binding energy of SAN and ANS (91.0 kcal/mol) and the binding energy for AN, the corresponding values are, respectively, very similar. The same can be noticed if one compares the mean values of the binding energy for polyB-SAN (93.5 kcal/mol), and SAN or AN. This can be sensibly explained with a minor contribution afforded to the total binding energy by the S and B blocks. This last consideration ultimately allow us to consider the smaller, rigid and less ramified SAN block copolymer into MMT layers, as the most probable mode of insertion.

This conjecture was later confirmed by ABS mesoscale modeling and by literature data (Stretz, Paul, & Cassidy, 2005): rubbery phase (polyB-SAN) seems to segregate, forming round islands. This can also be seen in Fig. 5, a 3D mesoscale volumetric visualization.

Once again, binding energies and literature data (Stretz et al., 2005) confirm that these nanocomposites have the same structure, where only SAN partially exfoliates MMT layers, and polyB-SAN creates islands outside the stacks, surrounded by a SAN bulk phase.

In Fig. 6, a scheme of our two-phases FEM Palmyra simulations is presented: the MMT stack with SAN intercalation (where overall Young’s modulus has been calculated with the first Palmyra simulation), and the whole system with MMT stacks and rubbery phases.

The pure polymer bulk properties have been taken from Cosoli et al. (2008).

Table 2 shows overall results for ABS and nanocomposite Young’s modulus predicted by Palmyra. The small discrepancy between the experimental and the calculated data is due to the slightly different formulation of ABS used in the calculation, as ABS has a wide

Table 2
Young’s modulus for ABS–MMT nanocomposite and comparison with Stretz et al. (2005).

<table>
<thead>
<tr>
<th>Overall properties</th>
<th>% MMT</th>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_0$ [GPa]</td>
<td>0</td>
<td>2.42</td>
<td>2.20</td>
</tr>
<tr>
<td>$G$ [GPa]</td>
<td>2</td>
<td>3.15</td>
<td>2.75</td>
</tr>
<tr>
<td>$G/G_0$</td>
<td>2</td>
<td>1.30</td>
<td>1.25</td>
</tr>
</tbody>
</table>
range of compositions. For this reason, a comparison of $G_\text{MMT}/G_\text{Nylon6}$ ratio (ratio of nanocomposite and pure ABS Young's modulus) between simulations and experiments were also done.

Another example in the area of polymer clays is the polyamide based system. In this case, atomistic simulation allowed us to calculate binding energies between the different beads that we defined in order to fit the particular structure (polymer intercalated clay) we wanted to simulate. We used mesoscale simulation to model the space between two intercalated clay layers and subsequently imported the resulting density fields in Palmyra (see Fig. 7), in order to calculate mechanical and barrier properties for small stacks of intercalated particles. This clearly constitutes a different method with respect to the one discussed for ABS PCN. Finally, models of the whole PCN (a box containing 36 single layer and stack clay particles, see Fig. 8) have been modeled with Palmyra using different degrees of exfoliation and different stack dimensions and properties, according to literature data (Duncan & Izzo, 2005; Esfand & Tomalia, 2001) and DPD box analysis, respectively.

In this study, the interaction 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, using a simple combinatorial procedure described in details in our previous paper (Scocchi et al., 2007).

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). Discrepancies between virtual and experimental data could be due to a different degree of crystallinity or different crystalline forms of Nylon6 in presence of MMT nanofillers, as claimed by some authors (Fraaije, 1993; Malik et al., 2000). All estimated values for the nanocomposite with $M_3\text{C}_{18}$ as quat are higher than the corresponding ones relative to the PCN with $M_2\text{C}_{18}$, in harmony with the different degree of exfoliation that has been modeled. As far as permeability 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). Data are reported in Table 3.

### 3.2. Mesoscale simulation for diblock copolymers with dispersion of nanoparticles

Mixing microphase-separating diblock copolymers and nanoparticles can lead to the self-assembly of organic/inorganic hybrid materials that are spatially organized on the nanometer scale. Controlling particle location and patterns within the polymeric matrix domains remains, however, an unmet need. Computer simulation of such systems constitutes an interesting challenge since an appropriate technique would require the capturing of both the formation of the diblock mesophases and the copolymer–particle and particle–particle–particle interactions, which can affect the ultimate structure of the material. In this example (Maly, Posocco, Pricl, & Fermeglia, 2008) we discuss the application of dissipative particle dynamics (DPD) to the study of the distribution of nanoparticles in lamellar and hexagonal A–B diblock copolymer matrices. The DPD parameters of the systems were calculated according to a multiscale modeling approach, i.e., from lower scale (atomistic) simulations.

In agreement with some experimental evidence, we found that, depending on the nature and type of nanoparticle covering (e.g., only A- or B-type covering), the particles can segregate into the centers of the corresponding compatible domains (these being lamellae or cylinders), forming nanowire-like structures that extend throughout the material. The density distribution of the species in Fig. 9 (left) shows clearly that the nanoparticles (black line) density reaches their maximum in correspondence of the maximum of A (in blue). In effect, the interplay between microphase separation and favorable interactions do result in the self-assembly of spatially ordered nanocomposites.

Should these particles be, for instance, metals or semiconductors, these systems could constitute a sort of nanoelectrode array, which could be utilized to fabricate organized nanodevices. On the other hand, for a different covering type (e.g., A6B6), the particles segregate at the interfaces instead of the centers of the lamellae (or cylinders). Fig. 10 (left) shows clearly how the density distribution

<table>
<thead>
<tr>
<th>$E_{xx}$ [GPa]</th>
<th>$E_{yy}$ [GPa]</th>
<th>$E_{zz}$ [GPa]</th>
<th>$P_{xx}$ [barrier]</th>
<th>$P_{yy}$ [barrier]</th>
<th>$P_{zz}$ [barrier]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.85 $\times$ 10²</td>
<td>3.76 $\times$ 10²</td>
<td>3.20 $\times$ 10⁹</td>
<td>1.52 $\times$ 10⁻²</td>
<td>1.52 $\times$ 10⁻²</td>
<td>1.37 $\times$ 10⁻²</td>
</tr>
<tr>
<td>4.04 $\times$ 10²</td>
<td>4.03 $\times$ 10²</td>
<td>3.23 $\times$ 10⁹</td>
<td>1.52 $\times$ 10⁻²</td>
<td>1.54 $\times$ 10⁻²</td>
<td>1.34 $\times$ 10⁻²</td>
</tr>
</tbody>
</table>

**Fig. 7.** Morphology of the PCN system made up by a MMT platelet, Nylon6, and $M_3\text{C}_{18}$ quat molecules obtained via DPD simulation.

**Fig. 8.** Morphology of the PCN system made up by a MMT platelet, Nylon6, and $M_3\text{C}_{18}$ quat molecules obtained with Palmyra.

**Table 3**

Values of the Young modulus ($E$) and $O_2$ permeability ($P$) in the $x$, $y$, and $z$ directions for the 36 particles boxes of both PCNs considered.
of nanoparticles is radically different from that of Fig. 9 and now indicates that the nanoparticles are located at the interface, as it is shown in Fig. 10 (right).

In these cases, for instance, if the copolymer matrix was to be dissolved from the system, the remaining inorganic phase could give origin to a nonporous material, with a regular arrangement of uniform pores, which could find applications, for instance, in separation or catalytic processes.

The results also indicate that the morphologies of the organic/inorganic hybrid materials can be tailored by adding particles of specific size and chemistry. The findings highlight the fact that, in such complex mixtures, it is not simply the ordering of the copolymers that templates the spatial organization of the particles: the particles do not play a passive role and can affect the self-assembly of the polymeric chains. In fact, we detected a phase transition from the hexagonal to lamellar morphology induced by a nonselective (i.e., A6B6(h)) block–particle interaction, indication that the particles actively contribute to the determination of the system structure.

In conclusion, the proposed multiscale computational approach, which combines atomistic and mesoscale simulations, can yield important information for the design of nanostructured materials with desired morphology for novel applications.

3.3. Polymer–carbon nanotubes system

Carbon nanotubes (CNT) are interesting for several applications in different fields: structural, electromagnetic, chemical and mechanical. They have already been used as composite fibres in polymers and concrete to improve the mechanical, thermal and electrical properties of the bulk product. In this example we show 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 an atomistic model of single wall CNT 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 a bundle and another one with a single isolated CNT. The difference between the two values of energy the energy that is necessary to extract one CNT out of the bundle, namely the ‘bundling–de-bundling energy’. For the polymer the traditional approach to calculate the Flory–Huggins interaction parameter in MD and MC is followed (Toth et al., 2004).

A comparison of the interaction parameters obtained shows that only CNT of a given diameter are soluble in a given polymer. The

---

Fig. 9. Distribution of A covered nanoparticles in diblock copolymers: nanoparticles are located in the center of each domain; left: density distribution of the species; right: position of the center of mass of the nanoparticles in the simulation box.

Fig. 10. Distribution of A and B equal coverage nanoparticles in diblock copolymers: nanoparticles are located at the interface of the domains; left: density distribution of the species; right: 3D representation of the nanoparticles at the interface.
calculations enable to predict the CNT diameter to be used for obtaining a good dispersion of CNT in a polymer matrix.

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 have been used (Maiti, Wescott, & Goldbeck-Wood, 2005) for estimating the morphology of a polymer CNT system and simulate, with FEM code, the electric conductance as a function of copolymer morphology.

4. Multiscale modeling for process systems engineering

In the previous examples, multiscale molecular modeling has been applied to the material design rather than to process design. Process system engineering is an interesting area in which the concept of multiscale molecular modeling can be successfully applied, particularly for the estimation of physical properties to be used at process engineering level into process simulation software (Gani, 2004; Vlachos, 2005).

The example reported here refers to the integration of molecular modeling within the Cape Open standard for providing toxicological data to be used in conjunction with results from process simulation software, for the estimation of the environmental impact of a given process. In fact, chemical process sustainability, a complex issue which has been investigated for more than 20 years, can be estimated using different sustainability indicators. The quantitative estimation of those indicators is necessary for two main reasons: (i) for evaluating the environmental impact of a chemical process and (ii) for choosing the best design among different available alternatives. In order to accomplish these goals, the computerized calculation of sustainability indicators requires the use of three advanced computer design tools: process simulation, molecular modeling and a sustainability indicators software code. A specific and complete software tool, process sustainability prediction (PSP) framework, integrated with process simulator programs, which support the Cape Open standard interfaces, has been recently developed (Toma, 2008).

The idea is to use molecular modeling techniques to estimate different toxicological data, which are furthermore considered in the calculation of some sustainability indicators. With the objective of providing an easy-to-implement method for applying indicators for the purpose of analyzing industrial systems for sustainability, Sikdar (2003) proposed a typology of indicators, considering the three dimensions of sustainability in three distinct hierarchical groups: (1) one-dimensional (1D) indicators, which provide information about only one dimension of sustainability: economical, ecological, or social; (2) two-dimensional (2D) indicators, which provide information simultaneously about two dimensions of sustainability: socio-ecological, socio-economical, or economic-ecological; (3) three-dimensional (3D) indicators, which provide information about all three dimensions of sustainability (Martins, Mata, Costa, & Sikdar, 2007).

Fig. 11 reports the general scheme in which the different elements for calculating the indicators are presented and integrated in the process sustainability prediction framework (PSP) (Fermeglia et al., in press). The two fundamental sources of information for the PSP are (i) the material and energy balances of the process calculated by a process simulator and (ii) the database of toxicological properties of each component involved in the process. These data are combined and the potential environmental indexes (PEI) are calculated. All the software developed and summarized in Fig. 11 has been included into Cape Open Unit Operation modules and tested versus the most used process simulators available in the market, as well as the public domain software COCO-COFE (Van Baten, 2007).

The PSP needs toxicological data for all the components involved in the process, and in many cases such data are not available in the database. In those cases it is impractical and expensive to perform toxicity tests for all the chemical compounds in use (Ren, Frymier, & Schultz, 2003) and molecular simulation methods became an important tool for toxicological data prediction. The calculation of the environmental impact categories can be reduced to some thermo-physical properties, some of which can be estimated using different molecular modeling techniques (see Fig. 12).

Atmospheric Oxidation Program (AOP), based on structure activity relationship (SAR) calculation, was developed by U.S.EPA. The program has been used in the present work for the estimation of lifetime a compound in the atmosphere, for the reaction rate with ozone and reaction rate with hydroxyl.

For the calculation of the octanol–water partition coefficient, Kow, different molecular modeling methods can be used. For example KOWWIN, the log Octanol–Water Partition Coefficient Program, is a software developed by U.S.EPA which is based on SAR. ClogP is a program, based on group-contribution methods, which can be also used for the octanol–water partition coefficient. ALOGPS is a software based on neural networks developed by the Virtual Computational Chemistry Laboratory. COSMOTherm (conductor like screening model thermodynamics) is an advanced software tool based on quantum mechanics, which calculates different thermo-physical properties such as: vapour pressures, boiling points, activity coefficients, excess enthalpy and entropy. Henry’s law constants, solubility, octanol–water partition coefficient, vapour–liqquid equilibrium, liquid–liquid equilibrium, solid–liquid equilibrium, density and viscosity for pure compounds (COSMOTherm, 2006). COSMOTherm is one of the software used, in the present work, for the estimation of octanol–water partition coefficient.

ECOSAR, developed by the Risk Assessment Division of the U.S.EPA, is a computer program based on SAR, used to predict the aquatic toxicity of chemicals based on their similarity of structure to chemicals for which the aquatic toxicity has been previously measured.

TOPKAT, a computer program developed by Accelrys, employs robust and cross-validated Quantitative Structure Toxicity Relationship (QSTR) models for estimating 16 toxicity endpoints (i.e., Mutagenicity, Rat Oral LD50, Carcinogenicity, Developmental Toxicity, etc.) (Accelrys, 2009).

It is evident, from Fig. 12, that some properties are of fundamental importance for the calculation of the eight environmental impact categories. As it can be noticed, human toxicity potential by inhalation and dermal exposure (HTPE), human toxicity potential by ingestion (HTPI), aquatic toxicity potential (ATP) and terrestrial toxicity potential (TTP) impact categories are related to an equilibrium property, the octanol–water partition coefficient. The other four impact categories: global warming potential (GWP), ozone deple-
Fig. 11. Process sustainability prediction (Toma, 2008).

Fig. 12. Thermo-physical properties and software programs used in the calculation of the environmental impact categories (Toma, 2008).
imensional data end form the data estimated by molecular modeling is within 1%.

The PSP framework has been applied to the analysis of the environmental impact of several processes and it proved to be a generally applicable tool for evaluating the environmental impact of a given process at design time (Fermeglia, Longo, & Toma, 2009).

5. Conclusions

In this paper we have reviewed 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, 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.

Multiscale molecular modeling can also be successfully used in process system engineering applications for the estimation of properties for pure components and mixtures in all cases in which the component data banks properties and interaction parameters of constitutive equations are missing.

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 behaviour, and the design of new materials and new materials phases, thus facilitating the application of process system engineering to more sophisticated and innovative processes.

Acknowledgements

The authors thank, Marco Ferrone, Paolo Cosoli, Giulio Scocchi, Letitia Toma, Paola Posocco, Radovan Toth and Marek Maly for the support in the calculations.

Table 4

<table>
<thead>
<tr>
<th>Thermo-physical property</th>
<th>Molecular modeling methods used</th>
<th>Average deviation from exp. data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octanol–water partition coefficient</td>
<td>QSAR, COSMO-RS</td>
<td>14.22%</td>
</tr>
<tr>
<td>Life time</td>
<td>SAR</td>
<td>21.37%</td>
</tr>
<tr>
<td>Reaction rate with ozone</td>
<td>SAR</td>
<td>25%</td>
</tr>
<tr>
<td>Reaction rate with hydroxyl</td>
<td>GCM, QSAR</td>
<td>22%, 20%</td>
</tr>
</tbody>
</table>

References


