New materials from multiscale modelling procedures: properties prediction and customisation of polymeric nanocomposites

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In this work we aim at describing procedures and potentialities arisen from multiscale molecular modelling procedures. These relatively new techniques are now opening unexplored frontiers in the fields of material sciences. Nowadays nanocomposite materials are growing up in interest, due to their improved characteristics for industrial applications. This is the case of nanoengineered polymers, which offer better performances in terms of thermal, mechanical and barrier properties. We will show a representative study about molecular simulations potentiality for polymer-clay nanocomposites. Multiscale calculation has been performed with the task of obtaining mechanical, thermodynamic and structural properties by the use of *ab initio* and *totally-in-silico* procedures.

1. Introduction

In the last decades molecular simulation techniques have been recognised as a powerful tool to investigate and predict materials morphologies and behaviour. Moreover, progressive improvements in CPU performances and new algorithms to overcome the limits of atomistic and quantum-mechanics calculations have now opened new possibilities to couple different length and time scale simulations (Charpentier, 2002). In this way, multiscale procedures allow to study thermodynamic, structural and mechanical properties with *totally-in-silico* procedures.

Today, the interest about polymer-clay nanocomposites is considerably increasing, due to the improved performances they may offer (Utracki, 2004). In this work, we will show how to project a nanocomposite of industrial interest with the exclusive use of multiscale molecular simulation techniques.

Multiscale simulations are based upon the principle that the set of outputs from lower length and/or time scale calculations shall be used as input data for higher scale simulations. These procedures allow determining characteristic behaviours, such as:

-   the structure and partial charge of nanocomposite constituents (quantum-mechanics)
-   the proper procedures to choose the nanocomposite surfactants, which enlarge clay layers and favour polymer to exfoliate platelets (atomistic level)
-   the characteristics of the exfoliation/intercalation of the clay platelets (atomistic level)

- the morphology of the polymer matrix (atomistic or/and mesoscale level)
- the mechanical properties of polymer blends and/or nanocomposite (finite elements simulations)

In Figure 1 a chart with time and length potentialities of modules employed in multiscale simulations is exposed.
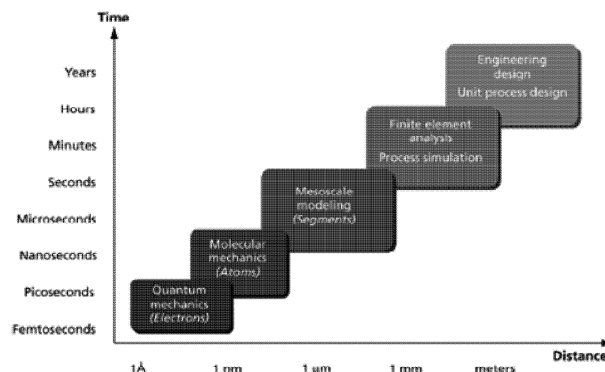

Figure 1: multiscale simulation levels.

We will refer to the system ABS-MMT, which is constituted by a polymer blend (acrylonitrile-butadiene-styrene) and by exfoliated platelets of montmorillonite (MMT) clay. We consider of this system as emblematic, because its study groups some of the typical problems encountered both in polymer blends and in nanocomposite preparation. ABS is a polymeric blend of industrial interest; its mechanical properties may be greatly enhanced by a small quantity of MMT (2% in our case).

In following pages we show how each main modulus will be used to simulate the exfoliation process, the morphology of blends and nanocomposite, and then the mechanical properties. In the results and discussion section we also show experimental validation obtained against literature data.

2. Methods

2.1 Quantum-mechanics

Quantum mechanics methods are used to predict molecule partial charges, bonds and angles. These data can be easily imported to atomistic molecular mechanics and dynamics.

2.2 Molecular mechanics and dynamics

Molecular simulations of surfactant (quats) intercalation between MMT layers, and MMT exfoliation, can be performed with molecular mechanics and dynamics (MM/MD). We aimed at choosing the best quat in terms of MMT spacing and thermodynamic behaviour of the exfoliated ternary system (MMT-quat-polymer), examining binding energies of the systems.

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. We then decided to model the ternary system following the procedure described, for example, by (Tanaka et. al., 2002) and (Toth et.

al., 2004), as a whole system, and in parts, in order to separate and evaluate significant contributions to binding energies. Moreover, we have also taken into account different copolymers position between MMT layers. Binary binding energies (MMT-polymer, MMT-quat, and polymer-quat) in a ternary system can be defined as follows:

$$E_{MMT-pol} = E_{(MMT+pol)} - \left(E_{MMT} + E_{pol}\right)$$
$$E_{MMT-quat} = E_{(MMT+quat)} - \left(E_{MMT} + E_{quat}\right)$$
$$E_{pol-quat} = E_{(pol+quat)} - \left(E_{pol} + E_{quat}\right)$$

Negative values show a good thermodynamic compatibility between pairs.

2.3 Mesoscale simulations

We used MesoDyn simulation method, based upon the mean field density functional theory (Altevogt et. al., 1999), to predict the phase behaviour of the ABS blend. The mesoscale molecular model consists of beads of various types, each of which represents a group of monomers in the chains. The size of the bead (e.g the number of monomers contained in each bead) depends on chain flexibility and is related to the polymer characteristic ratio C_∞, previously obtained by sets of atomistic simulations.

The method relies mainly upon the determination of the Flory-Huggins parameters χ_{ij} which have also been obtained via atomistic simulations, by the calculation of solubility parameters δ_{ij} between examined polymer chains (Flory, 1974).

Simulations results are given in terms of bead local densities; the so-called order parameters P_I, defined for each species I as the deviation from the mean bead density at homogeneity [16]:

$$P_I = \frac{1}{V} \int_V \left[\theta_I^2(r) - \theta_{I,0}^2\right] dr$$

Where θ is a dimensionless density (volume fraction) for bead species I, and the index 0 denotes average values at homogeneity. Order parameters with large values indicate strong phase segregation. Conversely, very small values of P_I correspond to homogeneous systems.

2.5 Finite element simulations

Finite element simulations methods (FEM) for polymer blends assume density distributions from mesoscale calculation and, thus, have been used to find ABS mechanical properties (Young's modulus). FEM softwares, MesoProp and Palmyra (Gusev, 1997), use mechanical properties of pure systems, which are available from a database, or calculated with previous simulations. In our case, Young's modulus, Poisson's ratio and densities have been calculated with Synthia modulus, which uses linear regression of a set of experimental data available from a database to calculate polymer properties for atomistic models (Bicerano, 2002).

Then we used the Palmyra software to simulate into two separate phases the nanocomposite structure. To model this structure, we used morphological information obtained from mesoscale and atomistic simulations mechanical properties previously

calculated and MMT Young's modulus given by literature data (Stretz et. al., 2005). Finally, we obtained Young's modulus for the entire structure, and we compared results with literature data.

3. Results and discussion

Atomistic simulations allowed us to choose the best quat. In Figure 2 a 3D periodic cell for ternary simulations is shown, while Table 1 contains binding energies for the best quat, which is the quaternary, double-tailed ammonium salt Cloisite 20A® (C20); these are also significant to suppose the nanocomposite morphologies for further, higher scale simulations.

Table 1: binding energies and spacing for C20. SAN: polymer oriented with S next to MMT surface. ANS: polymer oriented with S next to MMT surface. PolyB-SAN: main chain of B oriented parallel to MMT surface. PolyB-SANa: main chain of B oriented normal to MMT surface; all binding energy are favourable (negative values).

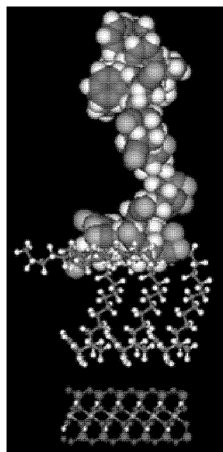| Polymer	$E_{MMT\text{-}pol}$[kcal/mol]	$E_{MMT\text{-}quat}$[kcal/mol]	$E_{pol\text{-}quat}$[kcal/mol]	Basal spacing [nm]
PS	-24	-1216	-32	3.108
PB	-7	-1266	-16	
PAN	-41	-1248	-100	
SAN	-9	-1165	-36	
ANS	-15	-1102	-146	
polyB-SAN	-5	-1386	116	
polyB-SANa	-19	-1230	-71	

Figure 2: 3D periodic system of a ternary (MMT-quat-polymer) system.

Examining the values of the $E_{pol-quat}$ component, we find that the most polar AN homopolymer is more affine to both quats than all other ABS chain components. In an analogous way, B homopolymer binding energies are smaller. Finally, if we take into account 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 we compare 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 led us to consider the smaller, rigid and less ramified SAN block copolymer into MMT layers, as the most probable mode of insertion.

This assumption will be later confirmed by ABS mesoscale modeling and by literature data: rubbery phase (polyB-SAN) seems to separate, forming round islands. This can be also seen in Figure 3, a 3D mesoscale volumetric visualisation.
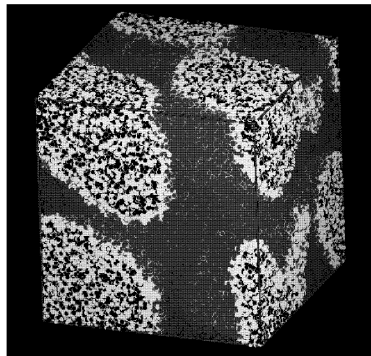

Figure 3: ABS mesoscale simulation. PolyB-SAN tends to form black-and-white islands.

Once again, binding energies and literature data (Stretz et.al., 2005) confirm that 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 Figure 4, a scheme of our 2-phases Palmyra simulations is presented: the MMT stack with SAN intercalation (where overall Young's modulus has been calculated with the 1st Palmyra simulation), and the whole system with MMT stacks and rubbery phases. Polymer bulk properties have been obtained from previous simulations.
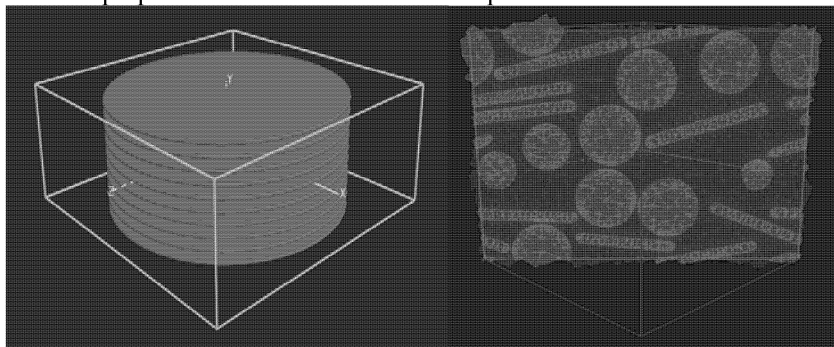

Figure 4: 3D cell visualisation of Palmyra simulations.

Table 2 shows overall results for ABS and nanocomposite Young's modulus; 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 range of compositions. For this reason, we also compare G/G_0 ratio between nanocomposite and pure ABS Young's modulus obtained by simulations and experimentally.

Table 2: Young's modulus for ABS-MMT nanocomposite and comparison with Stretz et.al, 2005.

Overall properties	% MMT	Calculated	Experimental
G_0 [GPa]	0	2.42	2.20
G [GPa]	2	3.15	2.75
G/G_0	2	1.30	1.25

4. Conclusions

In this work, we have shown how multiscale simulation may be helpful to investigate material science practical problems, reducing time and costs of experimental analysis. Flexible procedures here developed have been nicely validated against experimental data, confirming their potentialities as powerful tools in material design and property predictions.

5. References

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