Many-scale molecular simulation for ABS–MMT nanocomposites: Upgrading of industrial scraps

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Abstract

An innovative many-scale molecular modeling procedure has been developed and applied to study possible ways to improve and recycle automotive reinforced acrylonitrile–butadiene–styrene (ABS) scraps by their conversion into organoclay nanocomposites.

In this work, we simulated modified organoclay exfoliation and intercalation at an atomistic level, thus providing information about the rational choice of compatibilizers and polymer insertions behavior. Phase morphology and segregation domains have then been obtained resorting to mesoscale simulation techniques. Finally, finite element calculations at micrometric level have been performed, considering the whole structure of the nanocomposite (i.e., mineral filler and polymer blend), to calculate the corresponding improvement in the mechanical properties. Output data, such as phase morphologies and mechanical properties, have been validated against experimental data available in literature, finding good agreements.

The proposed procedure relies solely on input data obtained by molecular simulations, exception made for the experimental value of the Young modulus of the filler. Accordingly, our computational recipe constitutes a sort of innovative, atomistic-based, step-by-step procedure, in which each level calculations yield information necessary to perform simulation at the next, higher level length/time scale.

Keywords: Molecular simulations; Multiscale simulation; ABS nanocomposites; Recycling

1. Introduction

Many industrial scraps based on polymeric materials cannot be reused in an advantageous way, mainly because of their degradation. When possible, rejects of industrial scraps are added to the virgin material for new molding, although the amount of recycled polymer cannot exceed 15% of moldable material to obtain good final performances. For this reason, post-industrial rejects constitute a major problem both from the standpoint of the European legislation and policy and from the economic side where enterprises are involved.

Concerning automotive industry, EU directive 2000/53 states that, before 2015, 95% of vehicle scraps have to be recovered, while 85% have to be recycled [1]. Nowadays, the total amount of recycled industrial scraps is about 75% [2]. Even if automotive enterprises are not so far from this limit, a major effort is required; although plastic components constitute a relatively small amount of motor cars wastes, it has increased from about 5% to 12% by weight in 30–35 years [2].

As recycling of industrial plastic scraps would not offer best performances, due to polymer degradation after re-processing, different ways to improve mechanical properties are necessary, the use of polymer blends for reinforcement being a prime example. In the last decade, however, nanotechnologies have opened new avenues in this field, which are not yet fully explored. Accordingly,
in this paper we focus our attention on the procedure of embedding nanoparticles, such as montmorillonite layers (MMT) modified by quaternary ammonium organic salts (quats) in the recycled polymer matrix, a technique which yields a considerable improvement of physical and mechanical properties of the scrap, ultimately increasing life cycles and versatility of such materials [3,4]. In details, we have applied a multiscale simulation approach to study the nanostructure morphology of recycled ABS (acylonitrile–butadiene–styrene polymer blend), which is a polymer of special interest in the automotive industry, with MMT layers intercalated into the blend. To date, there are only a few publications dealing with the synthesis and characterization of ABS nanocomposites [5–7], upon which we based some of our theoretical assumptions and which we used for validation of the calculated morphologies and mechanical properties.

According to our computational ansatz, starting from quantum-mechanical and atomistic-based molecular mechanics/molecular dynamics (MM/MD) simulations, we developed and applied a procedure to choose the more appropriate clay compatibilizers (i.e., quats) for MMT layers exfoliation, in terms of interaction/binding energy and basal spacing values. We then performed mesoscale level (10–100 nm) simulations to determine ABS blend morphology, and evaluate blend density distributions of domains. Lastly, this information has been imported into finite element methods calculations (FEM), so as to obtain the mechanical properties of the final nanocomposite (ABS–MMT).

The proposed procedure relies solely on input data obtained by molecular simulations, exception made for the experimental value of the Young modulus of the filler. Accordingly, our computational recipe constitutes a sort of innovative, step-by-step procedure, in which each level calculations yield information necessary to perform simulation at the next, higher level length/time scale.

2. Methods

All simulations were carried out on an Intel bi-processor XEON 32 bit workstation, using software modules implemented in the commercial platform Materials Studio (v. 4.0, Accelrys, San Diego, CA, USA), in-house developed software, and the FEM Palmyra software (MatSim, Zürich, CH).

Atomistic simulations of quat intercalation between MMT layers, and MMT exfoliation by polymer insertion have been performed following a well-established procedure, already described in details in our previous papers [8–11]; accordingly, it will only be briefly reviewed here. The force field used in the atomistic calculations was COMPASS force field which has been validated on the systems of interest for this investigation in previous papers [8–11].

We built a simplified MMT structure, in which the chemical structure is derived from the mineral pyrophyllite by random substituting Al ions by Mg ions. The principal building element MMT are 2D arrays of aluminum–oxygen–hydroxyl octahedra sandwiched between two 2D arrays of silicon–oxygen tetrahedra, overall forming a three-layered platelet.

Typical ammonium quaternary salts have been considered to modify MMT layers, with the final goal of rendering them less hydrophilic, and ultimately facilitating polymer intercalation (i.e., compatibilizers). Given the experimental values of the ion exchange capacity of commercial MMTs, in the relevant, 3D model building we assumed a complete ion exchange process in which all Na ions present over MMT surface were quantitatively exchanged with quats.

Polymer chains constructions have been performed by the use of the rotational isomeric state (RIS) method [12,13], while quats 3D model building and charge calculations have been obtained by standard quantum-mechanics methods [14].

After each component was modeled (MMT platelet, quat and polymer) the overall, ternary system was built. The bond between the quaternary nitrogen and the methylene group of each quat was oriented perpendicularly to the xy-plane of the mineral, and the same N atoms was positioned just above the corresponding magnesium ion; this procedure ensures that the dispersive term of the van der Waals forces are favored over the repulsive one.

The lattice constant of the MMT cell with five quat molecules on one side was extended to 125–150 Å, depending on the length of quats and polymer molecules, to simulate an exfoliated structure. Further, this guarantees that the polymer chain is attracted to the quat–MMT surface by favorable nonbonded interactions, but is still far away enough, so that its initial conformation hardly affects the equilibrium states of the system [9].

The first set of MD simulations has been performed on ternary systems MMT–quat–polymer in the canonical (i.e., NVT) ensemble, to evaluate the interfacial strength between the supposed already-dispersed clay platelet, the quat and the polymer chain (see Fig. 1). This information can be obtained by calculating the binding energies between the system components which, in turn, are the negative of the MD interaction energies for the corresponding binary and ternary systems, as given below [8–11]:

\[
E_{\text{pol–MMT–quat}} = E_{\text{pol}} + E_{\text{MMT}} + E_{\text{quat}} + E_{\text{MMT–quat}} + E_{\text{MMT–pol}} + E_{\text{pol–quat}}
\]  

(1)

where the first three terms represent the energy of polymer, MMT and quat (consisting of both valence and nonbonded energy), and the last three terms are the interaction energies between each of two component pairs, made up of nonbonded terms only. In a straightforward fashion, the binding energies of binary systems (MMT–polymer, MMT–quat, and polymer–quat) can be defined as follows:
Moreover, the results of these MD simulations allowed us to explore the ABS interlayer structure in the corresponding nanocomposite, and to evaluate the most favored polymer chain for gallery intercalation. Indeed, ABS blends are extremely complex systems; they are mainly constituted by acrylonitrile–styrene block copolymers chains (SAN) – the most rigid phase and butadiene branched with SAN lateral chains (polyB–SAN) constituting the “rubbery” phase.

To perform this set of simulations, after simulated-annealing MD [8–11] to relax the structures, NVT MD experiments were run at 550 K. A high temperature was chosen for fast system equilibration. During these simulations, the positions of the MMT and K⁺ atoms/ions were fixed, but the polymer molecule and the quats were allowed to move accordingly. System equilibration was monitored by recording the instantaneous values of total, potential and nonbonded energy. After reaching equilibrium, the MD data collection phase was extended up to 300 ps. To calculate each binding energy values of Eq. (2), the following procedure was adopted, here illustrated only for the first line of Eq. (2) for the sake of brevity. We first created an ABS–MMT system deleting the quat molecules from an energy minimized conformation of the ternary ABS–MMT–quat system, and calculated the corresponding potential energy $E_{\text{pol-MMT}}$ without further minimization. Next, again from the ternary system we deleted the MMT platelet and the quats, leaving the ABS system components alone; this yields the $E_{\text{pol}}$ term in Eq. (2). Similarly, we deleted the ABS components and the quats from the ternary system, and calculated the $E_{\text{MMT}}$ term. The same procedure is then repeated straightforward to obtain the values of the terms of the other two lines in Eq. (2).

Basal spacing of intercalated quats into MMT layers has been evaluated using isochoric-isothermal (NPT) MD simulations of the MMT–quat under 3D periodic binary conditions. In this case, whilst the $x$- and $y$-cell dimensions are kept fixed, constraints on $z$-axis (normal to MMT layers) are removed, in order to reach the equilibrium distance between the layers. During each MD, both montmorillonite layers were treated as rigid bodies, while all atoms in the interlayer space including K⁺ cations were allow to move [9]. The ultimate information afforded by these calculations is then the available space for polymer insertion after MMT modification by a given quat (see Fig. 2).

The exfoliation process for this kind of composite blend is difficult to be evaluated by MM/MD techniques if treated with a single, conventional scaled polymer in a ternary periodic system. To overcome problems related to complex copolymer chains introduction and orientation, we performed a plethora of different simulations of the exfoliated structure, in order to analyze binding energies and chain orientations; each polymer structure was properly re-scaled to few monomers, however still maintaining the proportionality between main and side chains. Overall, the systems considered for this task were the following:

- MMT, quat and butadiene (B), styrene (S), acrylonitrile (AN) single homopolymers;
- MMT, quat and SAN, the last component oriented both with AN and S towards the MMT surface;
- MMT, quat and polyB–SAN, the last component oriented either parallel or normal to the MMT surface along this B chain.

All results in terms of basal spacing and block copolymer insertion and interaction with the inorganic framework have been averaged and analyzed, with the dual purpose of formulating a criterion for the choice of the best
compatibilizer, and to gather preliminary information on the system morphology.

A more, in-depth investigation of blend morphology, segregation at the mesoscale and density distributions was attained by performing simulations of the ABS structure at the mesoscopic level using mean-field density functional theory (MFDFT). The starting point of any mesoscale simulation is a coarse grained model for the diffusive and hydrodynamic phenomena in phase separation dynamics [15]. Generally speaking, the familiar atomistic description of a molecule is lumped into beads of material (representing the collective degree of freedom of many atoms). These beads interact through pair-potentials which capture the underlying interactions of the constituent atoms.

The simulation procedures we employed here are fully reported in our previous paper [16], whilst the details of MFDFT and the relevant computer code employed in our calculations, i.e., MesoDyn, is extensively described by Fraaije and coworkers [15,17–19]. Accordingly, here we will only briefly summarize both the procedure and the underlying theory to the benefit of all readers.

The mesoscale molecular model used by MesoDyn consists of beads of various types $I, J, \ldots$. The intramolecular interactions among the beads are described by harmonic oscillator potentials in a Gaussian chain (ideal interactions), $F_{\text{id}}[\rho]$. Intermolecular interactions between the chains (nonideal interactions) are introduced by a mean-field potential $F_{\text{nid}}[\rho]$ of the form:

$$F_{\text{nid}}[\rho] = \frac{1}{2} \sum_{IJ} \int \int \epsilon_{IJ}(|\mathbf{r} - \mathbf{r}'|) \rho_I(\mathbf{r}) \rho_J(\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}'$$  \hspace{1cm} (3)

in which $\rho_I(\mathbf{r})$ is the density of bead type $I$ at $\mathbf{r}$ (local bead concentration), and $\epsilon_{IJ}(\mathbf{r} - \mathbf{r}')$ is a cohesive interaction between beads $I$ at $\mathbf{r}$ and $J$ at $\mathbf{r}'$, chosen to have a Gaussian form:

$$\epsilon_{IJ}(\mathbf{r} - \mathbf{r}') = \epsilon_0^{ij} \left( \frac{3}{2\pi a^2} \right)^{3/2} e^{-3/2(a^2)(r-r')^2}$$  \hspace{1cm} (4)

In Eq. (4), $a$ is the Gaussian bond length, and $\epsilon_0^{ij}$ is the constant cohesive interaction between beads $I$ and $J$ which can be taken equal to the Flory–Huggins parameter $\chi$ (see below).

The total free energy of the system is then defined as

$$F[\rho] = F_{\text{id}}[\rho] + F_{\text{nid}}[\rho]$$  \hspace{1cm} (5)

More details about the method are reported in [16].

The dynamics of the model are described by the following set of diffusion equations (generalized time-dependent Ginzburg–Landau model):

$$\frac{\delta \rho_I(\mathbf{r}, t)}{\delta t} = \sum_{J=1}^{N} \int D_{IJ}(\mathbf{r}, \mathbf{r}', t) \frac{\delta F}{\delta \rho_J}(\mathbf{r}', t) \, d\mathbf{r}' + \eta_I(\mathbf{r}, t)$$  \hspace{1cm} (6)

with the diffusion operator $D_{IJ}$, and noise $\eta_I$; correlations are reported in [16].

The corresponding Flory–Huggins parameters were estimated as

$$\chi_{1,2} = \frac{(\delta_1 - \delta_2)^2}{RT} V_{1,2}$$  \hspace{1cm} (7)

where $V_{1,2}$ was considered as the average molecular volume of the different polymer constitutive repeated units (CRUs) present in the system, weighted over the corresponding volume fractions. The appropriate solubility parameter $\delta$ values were thus obtained as

$$\delta = \sqrt{E_{\text{coh}}} = \sqrt{E_{\text{coh}}/V}$$  \hspace{1cm} (8)

where $E_{\text{coh}}$ is the cohesive energy and $V$ the molar volume of single species. $E_{\text{coh}}$, in turn, is obtained by performing atomistic NVT MD simulations, as reported by us in details in [20]. Considering the chain architecture and applying the procedure described in [16], we finally get the relevant expressions for the mesoscale input parameters $N_{\text{meso}}$ and $a$, the so-called bond length:
In our case, blend composition (polyB–SAN phase and SAN phase, respectively) and molecular weight have been taken from typical, commercial ABS blends [21]. All other mesoscopic simulation input data – the Flory–Huggins interaction parameter \( \chi \), self-diffusion coefficients \( D \), characteristic ratio \( C_\infty \), and molar volumes \( V \) – were obtained from lower-scale simulations [16]. Tables 1–3 list the most important parameters for our systems.

One of the main output parameter of mesoscale simulations is the so-called order parameters \( P_I \), defined for each species \( I \) as the deviation from the mean bead density at homogeneity [16]:

\[
P_I = \frac{1}{V} \int_V \left( \bar{\theta}_I(r) - \bar{\theta}_I^0 \right) \, dr
\]

where \( \theta \) 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. Again, the phase morphology obtained by mesoscale calculations is then compared with the one obtained experimentally by Stretz et al. [7].

We also evaluated beads density distributions in our 3D periodic cell. Files containing these distributions were then exported as input data for the FEM calculations to determine ABS mechanical properties (i.e., Young modulus).

Two sets of simulations have been performed at the mesoscopic level. One maintained the visualization of AN, B, S species for each AN–S AN–B S–B blend composition and architecture.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Mesoscale beads interaction parameters</th>
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<tr>
<td></td>
<td>AN–S</td>
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<td>( X )</td>
<td>2.002</td>
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<th>Table 2</th>
<th>ABS composition and architecture</th>
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<tr>
<td></td>
<td>Architecture</td>
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<tr>
<td></td>
<td>polyB–SAN</td>
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<tr>
<td></td>
<td>SAN</td>
</tr>
<tr>
<td></td>
<td>[AN 6 S 6] B 2</td>
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</table>

Branching chains are enclosed in squared brackets.

<table>
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<th>Table 3</th>
<th>Mesoscale simulations input parameters and features</th>
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<tr>
<td></td>
<td>( a = \frac{C_\infty l}{\sin \frac{\theta}{2}} )</td>
</tr>
<tr>
<td>( N_{\text{meso}} )</td>
<td>( \frac{N}{C_\infty} \sin^2 \frac{\theta}{2} )</td>
</tr>
<tr>
<td></td>
<td>( D (\text{cm}^2/\text{s}) )</td>
</tr>
<tr>
<td></td>
<td>( T (\text{K}) )</td>
</tr>
<tr>
<td></td>
<td>Number of steps</td>
</tr>
<tr>
<td></td>
<td>Step length (ns)</td>
</tr>
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<td></td>
<td>Cell dimension (nm)</td>
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</table>
In the present study, we focused on the calculation of mechanical properties of composite materials. The elastic properties of a composite material are determined by the properties of its components and the geometry of the microstructure. The elastic energy of a tetrahedron is defined as

\[ E_t = \frac{1}{2} \sum_{i=1}^{n_{tet}} V_i C_{ik} e_i e_k \]  

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

The total elastic energy \( E \), which is a quadratic function of the displacements of the nodes, is defined as the sum over the element contributions:

\[ E = \sum_{i=1}^{n_{el}} E_i = \sum_{i=1}^{n_{el}} \frac{1}{2} V_i C_{ik} e_i e_k \]  

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

The local hydrostatic pressures \( P \) are calculated for each tetrahedron as the sum of the principal components of the stress tensor of that volume element:

\[ P = \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \]  

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

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

This value is listed in the output file for every applied deformation; the units are the same (GPa) as for the elastic constants. \( \tau \) typically controls the appearance of first inelastic events in metals and organic polymers. For example, in many organic polymers, the first inelastic events such as plasticity start occurring when the von Mises stress reaches a level of 50–100 MPa.

As mentioned before, mechanical properties and densities of single phases and MMT layers have to be determined a priori. To this aim, we used densities and mechanical properties of polymer chains calculated with Synthia, while MMT Young modulus and Poisson modulus were taken from [27]. Only the two phases, polyB–SAN and SAN, have been considered. Synthia calculates properties for homopolymers or random copolymers only; accordingly, its use is suitable for B main chain properties calculations. For SAN blocks in polyB–SAN and SAN copolymer, we averaged the mean values obtained with Synthia for S and AN, respectively. All obtained parameters, which have also been employed in MesoProp calculation, are shown in Table 4.

Although it might be possible to obtain reliable results about elastic constants and, then, mechanical properties from quantum-mechanical calculations [28,29], those are time-consuming (due to the presence of a relatively large MMT cell), and this kind of calculations, even if theoretically achievable, were out of the scope of our research.

The procedure for the calculation has been split in two parts, according to the morphology of the system: (i) partially exfoliated MMT layers are treated in a first simulation as a stack; and (ii) Young modulus and Poisson modulus obtained from (i) have then been used in a further simulation, in which the whole system is considered.

3. Results and discussion

In the first part of this work, we focused on the choice of the MMT compatibilizers; in particular, two commercial
quats, largely used in actual polymer–clay nanocomposite production, have been considered: cloisite 10 Å and cloisite 20 Å [30]. These two quaternary ammonium salts usually represent a good compromise between basal spacing between MMT layers and favorable binding energy interactions.

The calculated binding binary energies for both quats obtained from NVT MD simulations are shown in Tables 5 and 6. These tables also list the corresponding basal spacing values, as obtained from NPT MD simulations. All binding energies are positive: this confirms the favorable interactions between all three system components (MMT, quat and polymer). If we carefully examine the binding energy values listed in these tables, we can clearly see that the energy values depend on the component relative orientation. Moreover, examining the values of the $E_{\text{pol-quat}}$ component (fourth column in both the tables), 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 (i.e., 91.0 kcal/mol for 10 Å and 76.5 kcal/mol for 10 Å, respectively) 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 for 20 Å and 83.5 kcal/mol for 10 Å, respectively), 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.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{\text{MMT-pol}}$</th>
<th>$E_{\text{MMT-quat}}$</th>
<th>$E_{\text{pol-quat}}$</th>
<th>Basal spacing</th>
</tr>
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<tbody>
<tr>
<td>PS</td>
<td>60</td>
<td>1565</td>
<td>22</td>
<td>2.343</td>
</tr>
<tr>
<td>PB</td>
<td>101</td>
<td>1537</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>PAN</td>
<td>7</td>
<td>1560</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>SAN</td>
<td>64</td>
<td>1566</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td>ANS</td>
<td>30</td>
<td>1562</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>polyB–SAN</td>
<td>96</td>
<td>1560</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>polyB–SANa</td>
<td>71</td>
<td>1561</td>
<td>62</td>
<td></td>
</tr>
</tbody>
</table>

SAN = Acrylonitrile–styrene copolymer oriented with S next to MMT surface; ANS = Acrylonitrile–styrene copolymer oriented with AN 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.
If we now compare the mean $E_{\text{MMT-quat}}$ values for the case SAN/ANS and cloisite 10 Å®, we see that they are slightly smaller than the one obtained for cloisite 20 Å®, more importantly, the corresponding basal spacing is much higher for 20 Å®, mainly ascribable to the presence two hydrocarbon tails on this quat. All the considerations developed above led us to conclude that, among the two, cloisite 20 Å® was the most effective compatibilizer for the ABS–MMT nanocomposite system.

The experimental paper by Stretz et al. [7] confirmed both our calculations and conclusion. In their work, in fact, these authors prepared and analyzed ABS/MMT nanocomposite systems. Their TEM images clearly show that exfoliation takes place only in part: only the SAN copolymers enter between MMT layers, creating stacks. The rubber phases, isolated in the shape of round islands, remain next to the stacks, as schematized in Fig. 3a, while SAN copolymer essentially constitute the matrix phase, as shown in Fig. 3b [7].

In order to estimate ABS morphology, and to import density distributions in MesoProp calculations to evaluate ABS Young modulus, we then performed and analyzed mesoscale simulations with MesoDyn. The relevant results, shown in Fig. 4a and b, clearly prove that a neat phase segregation take place at the nanoscale level. The extent of segregation can be quantitatively estimated considering the values of the order parameter $P_I$ (see Fig. 5) and the relevant density distributions (see Fig. 6). In particular, in Fig. 6, probability densities have more than one peak at different bead densities, which are a clear indication that segregation occurs. As we can see, the polar AN beads are shifted from the S and B beads. In particular, if we look at Fig. 4a, where only polyB–SAN and SAN structure are visualized, we can also observe that even in the sole ABS matrix there is a clear distinction between rigid and rubbery phases (islands).

From MesoProp simulations carried out using these morphological evidences, we obtained the mechanical properties of pure ABS in terms of the Young and Poisson moduli. The overall results are shown in Table 4, from which we can see that they perfectly match the range of a typical ABS [7,31]. We also noticed that there is a distribution of Young modulus values, exemplified in Fig. 7 (plane
cut normal to the \(x\)-axis, see Fig. 7a, and von Mises stress along the same axis, Fig. 7b), but, as expected, values along all three axes are very similar, as no shear conditions were applied; accordingly, the segregated phases appear as un-oriented spheroids.

FEM simulations with the Palmyra software, as mentioned before, have been carried out in two steps. To perform the calculations, we first fixed the total MMT content to 2\% w/w. The results from all our other simulations, validated by comparison with the experimental of Stretz et al. [7], led to the prediction of the morphology of the ABS nanocomposite, basically constituted by the presence of stacks of MMT layers (SAN intercalation) dispersed in a SAN bulk phase, in which rubbery islands (polyB–SAN) remain outside (but close to) the stacks. Then, we arranged the first set of simulations as follows: we considered a stack of 10 MMT parallel platelets (with 3\,nm spacing), intercalated with SAN copolymers. Mechanical properties of single phases were taken from our previous simulations or from literature [26]. Platelet aspect ratio \(p\), defined as

\[
p = \frac{d}{h}
\]

(15)

where \(d\) is the platelet diameter and \(h\) its thickness (1 \,nm), has been set to 100, a value which was compatible with the calculation (mesh construction) and reliable for MMT nanocomposites [4]. We also verified that simulations with increasing values of \(p\) do not show appreciable differences of the Young modulus \(G\) for \(p\) values above 70 (data not shown), a value after which \(G\) reaches a plateau.

In the second simulation set, we used the mechanical property values obtained from the first simulation set for larger platelets (MMT and SAN), which have been randomly dispersed in the matrix maintaining a proportionality between phases dimensions. The bulk itself has been modeled as a SAN matrix, in which polyB–SAN rubbery phases are represented as bubbles (\(d = 227\) \,nm) occupying 32\% of the total ABS volume (see Table 2).

Fig. 8a and b shows the 3D visualization of the results obtained in the first and second simulation set, respectively, confirming the similarity of our model to the real morphology, shown in Fig. 8c for comparison. The numerical results obtained with the proposed model are listed in Table 7. Table 8 reports a comparison between calculated and experimental values of the Young’s modulus. The first line of Table 8 shows the quantity for the pure ABS (\(G_0\)). The small discrepancy between the experimental and the calculated data is due to the slightly different formulation.

Fig. 7. (a) Plane cut normal to the \(x\)-axis (\(zy\)-plane) of MesoProp simulation showing Young modulus distribution of values, and (b) and von Mises stress along the \(x\)-axis for ABS.

Fig. 8. 3D visualization of the results obtained (a) in the first simulation set with Palmyra (MMT stack with SAN), and (b) in the second simulation set with the complete system (MMT–SAN stacks, SAN matrix and rubbery phase as spheres.)
Young’s modulus reported in [7], obtained with the best parallel stacks, comparison has been made with the highest since the model considers complete intercalation with par-
of Young’s modulus for ABS with 2% clay (G). In this case, it is interesting to consider the ratio ABS property, it is interesting to consider the ratio G/G0, thus normalizing the results with respect to ABS matrix. In this case (see line 3 in Table 8), the calculated results agree well with the experimental values.

As expected, effects of nanocomposite reinforcement allow a considerable improvement in Young modulus (more than 30% over mean value). In general, the agreement between experimental and calculated values is very good.

4. Conclusions

For the first time, a complete many-scale molecular simulation procedure has been developed and validated to afford polymer blend reinforcement design, from an industrial and environmental point of view. All higher-scale molecular simulations have been carried out on the basis of input data obtained from lower-scale calculations. Each step of molecular simulations procedure has been confirmed and validated by comparison with experimental data.

We simulated thermo-dynamic behaviors of MMT intercalation and exfoliation, obtaining useful indications about the most favorable MMT modifiers in the design of ABS-MMT nanocomposites, and ABS blend behavior after polymer insertion into the MMT galleries. Mesoscale simulation confirmed morphologies and phase segregation at the nanoscale level, yielding important information about the mechanical properties and structures of the blend. Finally, finite element simulations at the highest scale level (microns) have been performed to evaluate mechanical properties improvements for the nanocomposite.

In this way, we have developed a proof-of-concept for the possibility of (i) understanding structure, phase morphologies and mechanical properties of a rather complex polymer–clay nanocomposite system, (ii) formulating criteria leading to the correct choice of the best MMT modifier, and (iii) predict macroscopic properties improvements upon material nanosizing. Accordingly, molecular simulations techniques confirm once again their prime role as powerful tools in material design and property predictions.

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