Modeling of polymer blends for automotive industry by multiscale molecular simulations

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Industrial scraps cannot be reused in an advantageous way, mainly because of their degradation. When it is possible, rejects are added to the virgin material for new molding, although the amount of "non virgin" polymer cannot exceed 15% of moldable material to obtain good final performances. The remaining amount of scraps then follows two different routes: i) employment in very poor applications, and ii) land filling. 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 concerned. In this work we have applied the mesoscale simulation approach to study the equilibrium morphology of blends consisting of both virgin and recycled polymers of special interest in the automotive industry. The main goal was the definition of the possible causes leading to incompatibility between virgin and non-virgin materials. In particular, starting from atomistic-based simulations we derived a procedure to 1) describe in appropriate fashion the polymer chains in terms of the relevant Gaussian models; 2) determine the appropriate Flory-Huggins interaction parameters; 3) determine the bead self-diffusion coefficients, necessary to convert the mesoscopic dimensionless time step to an effective time scale.

Key words: mesoscale, blends, beads, phase segregation, recycling

1 INTRODUCTION

The design and production of car lights often involve the mandatory choice of a given techno polymeric material, characterized by high thermal resistance, to be employed in small working areas and/or in the proximity of a light source. Further, these materials should possess enhanced performances with respect to impact resistance. A typical example is constituted by the so-called high-impact poly(methyl methacrylate), or PMMA. The drawback of these choices is, quite often, the elevate cost of such materials, mainly ascribable to the lack of market alternatives. Accordingly, the price difference between conventional and specialty polymers can constitute a vital problem for those industries which operate with highly restricted margins, as the automotive sector. A valid alternative, therefore, could be recycling of PMMA industrial scraps, its addition to the virgin polymer (in amounts not exceeding 15%) and further engineerization, by blending with polycarbonate (PC) in order to enhance its impact resistance and reduce costs deriving from additives.

In this work Aim we applied a mesoscale simulation approach to study the equilibrium morphology of methacrylate blends of special interest in the automotive industry. To this purpose, we developed a procedure, based on atomistic molecular dynamic simulations, to derive the necessary input parameters for the successive mesoscale calculations, such as the architecture of the Gaussian chains, the Flory-Huggins interaction parameters and the bead self-diffusion coefficients.

2 COMPUTATIONAL DETAILS

2.1 Blend systems

The systems under consideration were mixtures of virgin PMMA (molecular weight (MW) 40000 g/mole) and non-virgin PMMA, having MW in the range 6000 to 80000 g/mole. The amount of non-virgin material in each mixture was kept constant

and equal, approximately, to 15% (weight fraction). Further, two mixtures of virgin PMMA and polycarbonate (MW = 30000 g/mole), characterized by a weight fraction of PPMA of 0.8 and 0.9, respectively, were also considered. The compositions of all systems studied are summarized in Tables 1 to 2.

Table1. Virgin-non virgin PMMA mixture compositions

MW (g/mol)	Volume fraction
PMMA6-40	
PMMA 6000	0,130
PMMA 40000	0,870
PMMA24-40	
PMMA 24000	0,146
PMMA 40000	0,854
PMMA60-40	
PMMA 60000	0,091
PMMA 40000	0,909
PMMA80-40	
PMMA 80000	0,125
PMMA 40000	0,875

Table 2. PMMA-PC mixture compositions

PMMA80PC20	Weight fraction	Volume fraction
PC	0,202	0,200
PMMA	0,798	0,800
PMMA90PC10	Weight fractions	Volume fractions
PC	0,113	0,111
PMMA	0,887	0,889

2.2 Polymer chain parametrization

To reduce computational time to reasonable limits, the molecular weight of each chain was scaled by a factor of ten. The resulting polymer chains were 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_b) and the length (α_b) of the Gaussian chain segments were estimated by the following relationships:

$$N_b = \frac{N_{mon}}{C_\infty} \qquad (1)$$

$$\alpha_b = \alpha_{mon} C_\infty \qquad (2)$$

where N_{mon} is the polymerization degree, α_{mon} is the monomer unit length, and C_∞ is the characteristic ratio of an infinite length chain. The C_∞ and monomer length values for PMMA and PC were estimated with the Synthia program of Cerius^2 (v. 4.9 Accelrys, San Diego, CA, USA). This semiempirical method, developed by Bicerano at Dow Corporation [1], uses connectivity indices to describe the topology of the polymer. The number of

Kuhn segments (beads) and their lengths were calculated from eqs (1) and (2).

2.3 Flory-Huggins interaction parameter calculation

The tendency of the polymers to mix at a specific composition was estimated via the cohesive energies of the mixtures and of the pure components. Subsequently, the Flory-Huggins (F-H) χ parameters were estimated as

$$\chi = \left(\frac{\Delta E_{mix}}{RT}\right) V_{mon} \qquad (3)$$

where Vmon is the monomer unit volume, and ΔE_{mix} is defined as:

$$\Delta E_{mix} = \Phi_1 \left(\frac{E_{coh}}{V}\right)_{pure1} + \Phi_2 \left(\frac{E_{coh}}{V}\right)_{pure2} - \left(\frac{E_{coh}}{V}\right)_{mix} \qquad (4)$$

in which Φ is the volume fraction, and the subscripts pure and mix denote refer to the pure components and the binary mixture, respectively.

In general, the cohesive energy density is defined as the ratio of the cohesive energy E_{coh} and the molar volume V at a given temperature; E_{coh}, in turn, is defined as the increase in internal energy per mole of substance if all intermolecular forces are eliminated. In our simulated systems, 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_{coh} at different temperatures can be obtained, both for mixtures and pure components, from simulation by calculating the difference between the nonbonded energy of the periodic structure and the corresponding value of an isolated parent chain in vacuum:

$$E_{coh} = E_{nb}^{isolated} - E_{nb}^{periodic} \qquad (5)$$

All simulations were performed on a bi-processor Intel Xeon The commercial software Materials Studio (v. 3.0) from Accelrys was used for both MM and MD simulations. The generation of accurate model amorphous structures of virgin PMMA, non-virgin PMMA at different MWs, and PC was conducted as follows. For each polymer, the constitutive repeating unit (CRU) was first built and its geometry optimized by energy minimization using the COMPASS force field [2]. Energy was minimized by up to 5000 Newton-Raphson iterations. Following this procedure, the root-mean-square (rms) atomic derivatives in the low energy regions were smaller than 0.05 kcal/mole Å. Long-range nonbonded interactions were treated by applying suitable cut-off distances, and to avoid the

discontinuities caused by direct cutoffs, the cubic spline switching method was used [3]. Van der Waals distances and energy parameters for nonbonded interactions between heteronuclear atoms were obtained by the 6th-power combination rule proposed by [4].

Each CRU was polymerized to its scaled degree of polymerization (DP) Different 3D periodic cells were generated for each mixture and pure components with the Amorphous Cell program of Materials Studio. This program makes combined use of an algorithm developed by Theodoru and Suter [5] and the scanning method of Meirovitch [6]. According to this procedure, initially, a proposed structure is generated via the Rotational Isomeric State (RIS) theory .at a proper process temperature (550 K). To avoid excessive overlaps between the chains, modified conditional probabilities are used that account for the nonbonded interactions between the atom to be placed and the rest of the system. The initial density for each chain, at the process temperature, was determined via the Synthia module, in order to minimize discrepancies in the final density values obtained from (NPT ensemble) MD simulations [7] The structures were then relaxed using the conjugate-gradient method. In each case, the Ewald technique was employed in handling nonbonded interactions. Such a straightforward molecular mechanics scheme is likely to trap the simulated system in a metastable local high-energy minima. To prevent the system from such entrapments, the relaxed structures were subjected simulated annealing (5 repeated cycles from 550 K to 1000 K and back) using constant volume/constant temperature (NVT) MD conditions. At the end of each annealing cycle, the structures were again relaxed via FF, using a rms force less than 0.1 kcal/mole Å for the polymer and 0.1 kcal/mole $Å^3$ for the stresses on the periodic boxes as convergence criteria. Both convergence criteria were simultaneously satisfied for the system to be relaxed completely. The simulation box was allowed to vary in size and shape during energy minimization, in order to find the equilibrium density for each structure. The conformations of the chains are assumed to resemble those of the unperturbed (from excluded volume interactions) chains that are found with significant probability in the bulk. From the fully relaxed models of the corresponding polymeric chains, isothermal-isobaric (NPT) MD experiments were run. The Newton atomic equations of motion were integrated numerically by the Verlet leapfrog algorithm [8], using an integration step of 1 fs. For the NPT dynamics simulations, the relaxation time τ= 0.1 ps and a cell mass prefactor for the mass-like

parameter W equal to 1.00 were used. Temperature was controlled via weak coupling to a temperature bath [9] with coupling constant $\tau_T = 0.01$ps, whereas pressure was kept constant by coupling to a pressure bath [10], with relaxation time τ_P = 0.1 ps. Each NPT MD run was started by assigning initial velocity for the atoms according to a Boltzmann distribution at $2\times T$. It consisted in an equilibration phase of 10 ps (i.e., 50,000 MD steps with time step = 1 fs), during which system equilibration was monitored by recording the instantaneous values of the total, potential and kinetic energy and the time evolution of the volume, and in a data collection phase, which was extended up to 300 ps. From the NPT simulations the nonbond energies were calculated, for both the pure components and the mixtures, as the mean total potential energy of intermolecular nonbond interactions. For each 3D periodic system, the mean nonbond energy resulted as the arithmetic average of the values (from the retained frames of the trajectory files) obtained from NPT simulations of different initial configurations.

For the nonbond energies of the isolated chains, six parent chains for each polymer were generated and their energy minimized according to the procedure described above. The simulated annealing method was again applied as described above to these systems to provide thermal energies to cross energy barriers between conformation local minima. Finally, NVT MD simulations were performed on the single chains (again the six best relaxed chains for each polymer) in vacuum at the same temperature conditions applied for the simulations of the relevant periodic systems. The estimation of the molar volumes, required for the determination of the cohesive energy densities, were obtain from the specific volumes of the 3D periodic cells

2.4 Self-diffusion coefficient calculations

Bead self-diffusion coefficient is necessary to convert the mesoscopic dimensionless time step to an effective time scale. Accordingly:

$$\tau = \beta^{-1}Mh^{-2}\Delta t \qquad (6)$$

is the equation that relates the adimensional time step τ used in the MesoDyn calculation algorithm [11,12], as implemented in the Materials Studio platform, to the effective time step Δt via the bead self-diffusion coefficient. For each mixture under study, a proper set of atoms, corresponding to the number of the constitutive repeating units making up a bead of the corresponding chain, was selected in the trajectory file of the relevant mixture 3D periodic NPT simulations. Diffusion coefficients

were calculated from the mean square displacement (MSD) of such a set by means of the Einstein equation [13]. In the present study, the MSDs for each set were calculated as averages over the different 300 ps trajectories, from different initial configurations, used previously for the cohesive energy density calculation. Finally, the self-diffusion coefficients of the beads were estimated from the linear portion of the corresponding MSD vs. time curves.

2.5 Interaction parameter scaling

The F-H χ parameters obtained with the procedure outlined above were scaled from the atomistic dimension to the mesoscale, ensuring the constancy of the segregation parameter χN.

2.6 Mesoscopic simulations

The phase separation dynamics at the mesoscopic level was simulated by MesoDyn using the parameter sets obtained with the procedure outlined above. We performed different simulations, one for each mixture at the process temperature. All simulations were started from a homogeneous density distribution with instantaneous quench. The phase separation dynamics was monitored by the time evolution of the order parameter P.

3 RESULTS AND DISCUSSION

In figure 1 we report, as an example, the MSDs versus simulation time for the PMMA pure component.
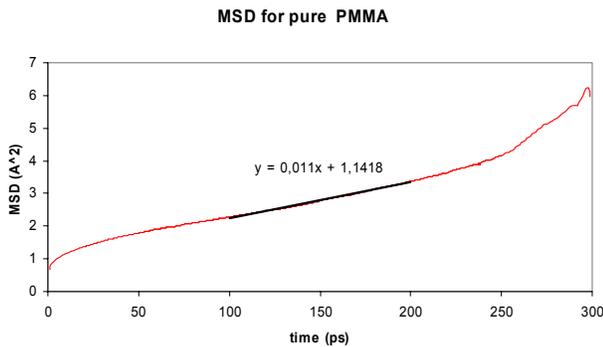
MSD for pure PMMA

Fig. 1. MSD vs simulation time for PMMA pure component.

The values of the bead self-diffusion coefficients were obtained from the angular coefficient m of the trend lines as:

$$D = m/6N \qquad (7)$$

where N is the number of atoms making up each selected atom set in the periodic 3D cell (as outlined in the computational details section). The accuracy of the estimated values of D depends also on the force field used, on the simulation time, on the cutoff of the potential energy function for nonbonded interactions, and on other assumptions and approximations embodied in the MD simulations. Therefore, the absolute values of the calculated diffusion constants should not be considered for direct comparison with experimental values, due to the assumptions outlined above. However, the computed values can be used for comparison of relative self-diffusivities of the beads. In fact, a comparison in terms of time-to-equilibrium of different systems can be carried out on the bases of a common procedure for the determination of the self-diffusion coefficients, by which the simulation adimensional time step can be converted to an effective time step.

As a fist example, let us consider system PMMA 6000-PMMA 24000. For mesoscale simulation of such a mixture two Gaussian chain architectures were employed: the first one was constituted of 3 beads of type A (corresponding to the lower molecular weight chain), and the other made of 22 B beads. The mesoscale unit cell length h was obtained from the statistical segment length of PMMA. The 3D periodic grid was made up of 32 cells, in each spatial direction, corresponding to about 62.6 nm.

The adimensional time step was maintained to a value of 0.5 in order to ensure the stability of the integration algorithm. The calculated self-diffusion coefficient for this system led to an effective time step of 214.67 µs. The time evolution of the system has resulted into the equilibrium configuration reported in Figure 2.
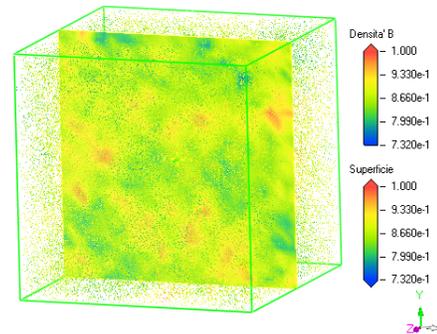

Fig. 2. Equilibrium morphology for the PMMA6000-PMMA24000 system.

It can be seen that the equilibrium morphology is characterized by a homogeneous distribution of the B22 chains around a relative density value of 0.9, which corresponds to the volume fraction of virgin

PMMA in the original mixture.

Another meaningful example is given by system PMMA-PC at a 0.8 volume fraction of virgin PMMA. The time evolution to equilibrium is reported in Figure 3.
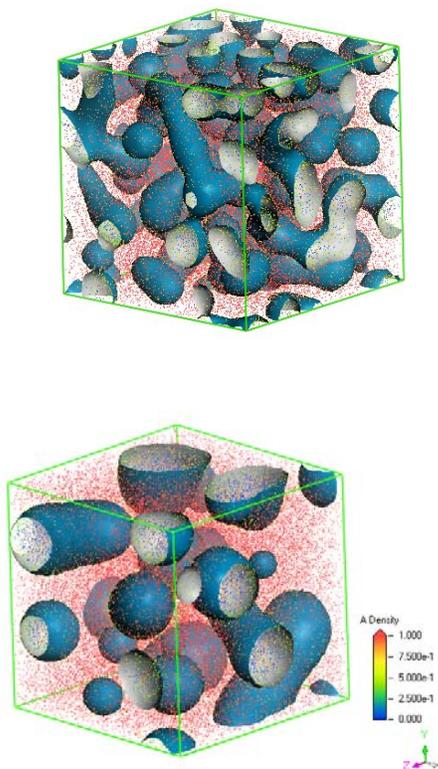

Fig. 3. (top) Early stages of phase segregation, and (bottom) equilibrium morphology of PMMA-PC blend (80% weight fraction of PMMA).

From Figure 3 we can see a macroscopic phase segregation, with the PC chains aggregating into spherical domains. The system progression toward equilibrium configuration, is dominated by a coarsening of the PC domains, due to the polymer diffusion from the smaller to the bigger ones.

4 CONCLUSIONS

In this work we have developed a procedure that, resorting to atomistic molecular simulations, allowed: 1) the apt description of polymer chains with Gaussian chain models made of a smaller number of segments than the monomer number; 2) the obtainment of specific Flory-Huggins interaction parameters for a blend at a specific temperature; 3) the determination of the bead self-diffusion coefficients for an estimation of the equilibration time of each, single system. All these information have been used as input parameters for mesoscale simulations, through which: 1) the equilibrium morphology of each system can be described; 2) a comparison, in terms of time-to-equilibrium of different systems (even under the action of an applied shear) can be carried out on the bases of a common procedure for the determination of the self-diffusion coefficients, by which the simulation adimensional time step can be converted to an effective time step.

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