DIBLOCK COPOLYMERS FOR THE AUTOMOTIVE INDUSTRY: THE MESOSCOPIC APPROACH

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In this work we have applied the mesoscale simulation approach to study the equilibrium morphology of linear (A_mB_n) methacrylate diblock copolymer systems of special interest in the automotive industry. In particular, starting from atomistic-based simulations, we derived a detailed procedure to determine the mesoscale input parameters, such as correct Gaussian chain architectures, appropriate Flory-Huggins interaction parameters and bead self-diffusion coefficients, necessary to mesoscopic scale calculations.

1. INTRODUCTION

Block copolymers are polymer chains consisting of segments with different chemical composition. The preference of the different polymer blocks to phase-separate from one another on the nanometer scale can lead to dramatically distinct physical and chemical properties in materials made from block copolymers. Due to their increased flexibility and toughness, these materials could potentially be less costly substitutes for existing materials.

The design and production of car lights often involve the mandatory choice of a given technopolymeric 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 resorting to the engineerization of standard PMMA, by copolymerization with, for instance, *n*-butyl methacrylate(NBM) or acrylonitrile (AN).

Aim of this work is the application of the mesoscale simulation approach to study the equilibrium morphology of linear (A_mB_n) methacrylate diblock copolymer systems 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. The Gaussian chain model

The systems under consideration were four methacrylate block copolymers made of PMMA, PNBM and PAN blocks of different compositions. These were selected to obtain specific ratios between the two block segments for the corresponding representations of the Gaussian chains, expressed in terms of Kuhn segments (0.5 and 0.3, respectively). We developed our Gaussian chain models from comparison of Random Phase Approximation (RPA)[1] and Molecular Dynamics (MD) structure factors.

2.2. Structure factors determination

To determine the structure factors via MD simulation, different 3D periodic cells were generated for each of the four copolymer systems. After initial construction and optimization, the amorphous phases were checked for filling space regularly and eventually refined by short dynamics simulations (20 ps). The interatomic interactions were modeled with COMPASS force field[2]. The amorphous cells contained a number of atoms ≥2000, which is usually sufficient for avoiding finite size effects. The box length was between 27 and 30 Å. For each configuration, MD simulations in the under constant temperature (298 K) and density (NVT ensemble) were conducted. Preliminary runs of 200-250 ps were carried out in order to bring the system to the target temperature. After equilibration, main runs of 100 ps followed, during which trajectories were stored, periodically, for later postprocessing. For each copolymer studied, five to seven trajectories were generated, starting from different initial configurations. The structure factors were calculated as the average over the frames stored in the trajectory files obtained for each copolymer system. The structure factor maxima, obtained by MD, were fitted to the relevant maxima obtained by RPA for Gaussian chains, and expressed by the following relationship:

$$S(q) = N/[F(x) - 2\chi N]$$

as a function of the Flory-Huggins interaction parameter χ, the number of segments *N* and a function of the chain segment length F(x). For each system considered, the fitting procedure was applied to three types of Gaussian chains: the first having a number of segments equal to the number of polymer monomers, the second featured a number of segments equal to the number of Kuhn segments, and the third was characterized by a number of segments smaller than the Kuhn segment number. Since for Gaussian chains the height of the maxima is dependent on the number of particles in the chain, in order to determine the optimal model for each copolymer, the structure factors of the single Gaussian chains were multiplied by the ratio between the number of particles in the corresponding MD simulation and the number of Gaussian chain beads.

2.3. F-H interaction parameter determination

The χ parameters were estimated as:

$$\chi = V_{\text{mon}} \frac{\Delta E_{\text{mix}}}{RT}$$

where V_{mon} is the average molecular volume of the two species making up each copolymer weighted over the volume fractions, and ΔE_{mix} is the mixing energy of a binary mixture composed by the same volume fraction of the A and B species present in the diblock copolymer. This parameter is given by the difference between the cohesion energy of the pure components, weighted with respect to their volume fractions in the mixture, and the cohesion energy of the mixture. The pure components cohesion energies were calculated from NVT simulations as the mean total potential energy of intermolecular interactions. For each oligomer, the mean cohesion energy density (CED) resulted as the arithmetic average of the CED values obtained from NVT simulations of different initial configurations, as described above. Successively, MD runs were carried out to determine the cohesion energies of the mixtures. 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.

2.4. Bead self-diffusion coefficient determination

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

$$\tau = \beta^{-1} M h^{-2} \Delta t$$

is the equation that relates the adimensional time step τ, used in the MesoDyn

calculation algorithm[3,4] to the effective time step Δt via the bead self-diffusion coefficient. For each of the 3 species constituting the copolymers, an ensemble of 3D periodic cells was constructed and optimized, following the same procedure described previously. Each cell contained a suitable number of oligomers (≥ 2000 atoms), and the oligomers were constituted by a number of constitutive repeating units (CRU) equal to the number of CRU making up a bead. Diffusion coefficients were calculated from the mean square displacement (MSD) of the molecules composing each cell by means of the Einstein equation[5]. In the present study, the MSDs for each of the three species were calculated as averages for five different 300 ps trajectory runs from different initial configurations. The MD simulations (NVT conditions) were run at 298 and 400 K, and at the corresponding densities, obtained by NPT simulations at the same temperatures. Finally, the self-diffusion coefficients of the beads were estimated from the linear portion of the corresponding MSD vs. time curves, and further weighted over the volume fractions of each block for each copolymer.

2.5. 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 four simulations, one for each copolymer. All simulations were started from a homogeneous density distribution with instantaneous quench without any shear applied. The equilibrium condition reached was used as a starting configuration for the application of shear. A shear rate of 0.001 ns^{-1} was applied, and the systems were further evolved towards equilibrium. The phase separation dynamics was monitored by the time evolution of the order parameter *P*.

3. Results and discussion

In Table 1 we report the Gaussian chain architectures from RPA, the mesoscale χ parameter values and the bead self-diffusion coefficients obtained by the procedure outlined above. It is interesting to note that 1) the number of segments of each Gaussian chain resulting from RPA is smaller than the corresponding chain based on Kuhn segments (results not shown) and 2) the best fit was attained by reducing the number of segments and increasing their length. Two goals then were achieved simultaneously: 1) the computational times involved in the successive mesoscale simulation have been drastically reduced (as they scale linearly with the number of beads of the Gaussian chain), and 2) the accuracy of the model representation has been noteworthy enhanced.

Copolymer	Gaussian Chain	Bead length (nm)	D (10^{10}cm^2/s)	χRT (kJ/mol)
PMMA-PNBM (1)	A5B5	2.59	2.34	10.6
PMMA-PNBM (2)	A3B7	2.74	2.56	9.24
PMMA-PAN (1)	A5B5	2.04	2.04	10.4
PMMA-PAN (2)	A3B7	1.91	2.24	11.3

TABLE 1
Input parameters for mesoscale simulations derived from atomistic MD procedures

Furthermore, even though the fitting operation implies that the wavelength of the fluctuations in the Gaussian chain and the model derived from MD simulations are the same, the amplitude in the Gaussian chain is overestimated. This has an important consequence for the noise expansion parameter Ω, which represents the number of particles in a grid cell of size h^3. For such a reason the noise values for the copolymer systems were estimated on the basis of the PMMA, PNBM and PAN densities (calculated by NPT MD simulations as previously described) weighted over their volume fractions in each copolymer and successively scaled by a proper factor, in order to account for fluctuations of the same amplitude. For mesoscale calculations, we have simulated the time evolution of the four systems in a cubic box with 323 cells corresponding to a cell length of 43 nm, 42 nm, 39 nm and 39 nm, respectively, determined on the basis of the mean length of the beads weighted over the volume fractions of each block in the copolymer. The self-diffusion coefficients allowed us to convert the mesoscopic dimensionless time step (0.5) to an effective time scale which was of the order of the microseconds in the four mesoscale simulations we performed.
As a fist example, consider system PMMA-PNBM (1) which, starting from the configuration reached in the absence of shear, characterized by the presence of several defects, has been evolved under shear towards a lamellar morphology, reaching a plateau of the order parameter in 59.1 ms. Subsequently, upon shear removal, the system has progressed toward a new equilibrium configuration, in which the partial lamellar morphology evolved to completion, in 39.8 ms from shear removal (see Figure 1).

Another meaningful example is given by system PMMA-PAN (2). Figure 2 shows the morphology of the A4B9 and A3B7 (right) systems after 2000 steps of simulation under

shear, corresponding to 53.0 and 67.5 ms, respectively.

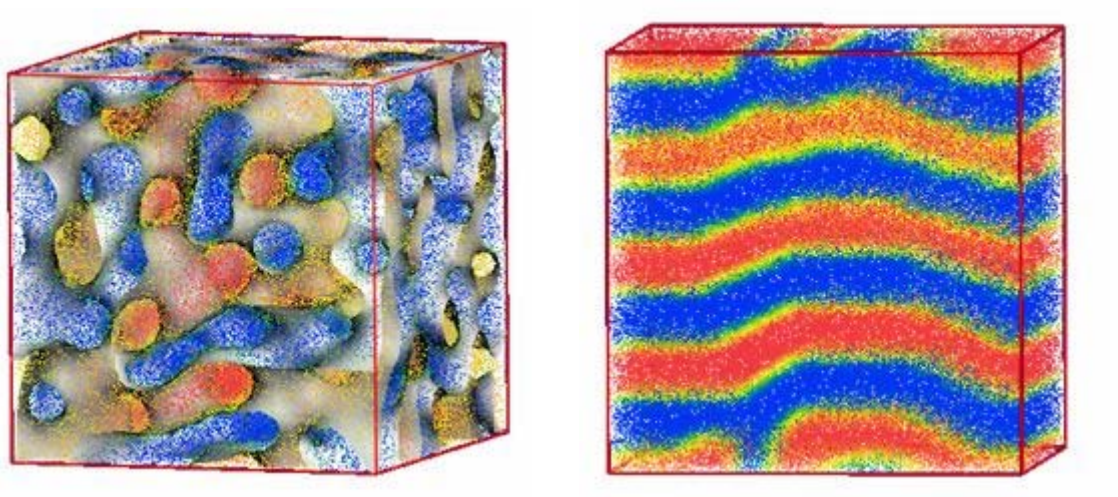

Figure 1
Pre-shear equilibrium configuration (left) and equilibrium configuration after shear removal (right) for system PMMA-PNBM (1).

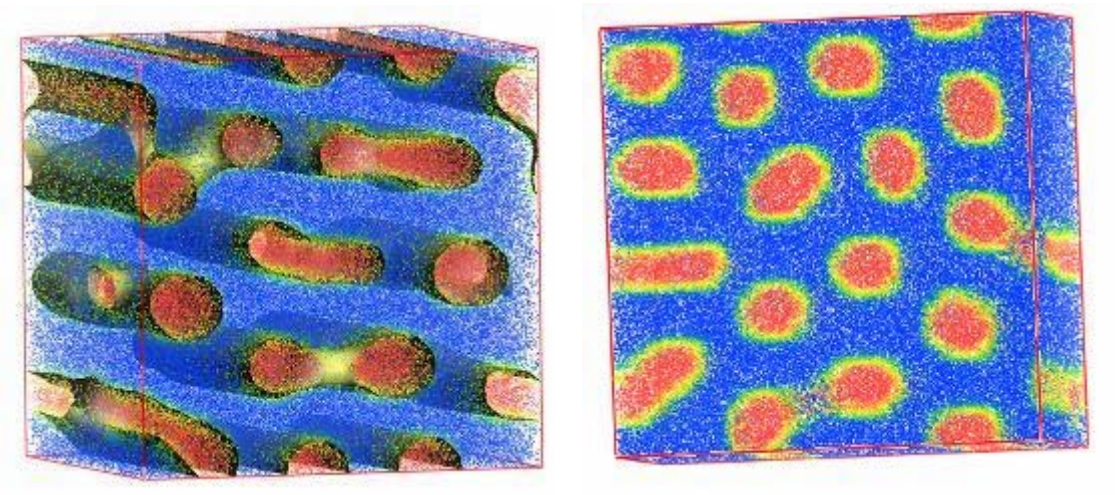

Figure 2
Morphology of A4B9 (left) and A3B7 (right) architectures for system PMMA-PAN (2) after 2000 simulation steps under shear.

During the mapping process, we observed that the Gaussian chain A3B7, resulting from

RPA, was more representative of the real chain than that obtained on the basis of Kuhn segments (A4B9). According to the self-consistent field theory (SCFT)[6], this choice reflects in a lower computational cost without affecting the final segregated morphology. As we can see for the A4B9 system, corresponding to a smaller effective evolutionary time, some necks between the tubes are still well present, whereas the tubes of the alternative, A3B7 system are completely formed and separated, being this system in an equilibrium configuration.

4. CONCLUSIONS

In this work we have developed a procedure that, resorting to atomistic molecular simulations, allowed: 1) the apt description of diblock copolymer chains with Gaussian chain models made of a smaller number of segments and more representative than those described on the basis of Kuhn segment length; 2) the obtainment of specific Flory-Huggins interaction parameters for diblock copolymers; 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 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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