Many-Scale Simulation of ABS/PC Blends for the Automotive Industry

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Abstract. Industrial scraps cannot be reused in an advantageous way, mainly because of their degradation. When possible, rejects are added to the virgin material for new molding, although the amount of recycled block copolymer cannot exceed 15% of moldable material to obtain good final performances. The remaining amount of scraps then follows three different routes: i) employment in very poor applications, ii) land filling, and iii) thermal treatment. 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 a multiscale simulation approach to study the nanostructured equilibrium morphology of blends consisting of mainly recycled block copolymers of special interest in the automotive industry. The main goal was the definition of the possible causes leading to incompatibility due to 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, and 2) determine the relevant Flory-Huggins interaction parameters. Finally, we coupled mesoscale model with finite elements codes to obtain a quantified structure-property relationship for mechanical modulus and coefficient of thermal expansion.

Introduction

The world's annual consumption of plastic materials has increased from around 5 million tons in the 1950s to nearly 100 million tons today [1]. At the end of the service-time of plastic wares, as well as along the pathway of their production processes, large amounts of scrap arise. Therefore, the question of the disposal of used plastics has gained increasing importance in the public discussion because of the environmental problems resulting from the rapid growth of the plastic waste during the last years.

A further, topical solution to cost saving is internal recycling. The major problem in the recycling of used plastics is connected to a great inhomogeneity of the polymers present in the waste. The eventual incompatibility of these components is the most important reason of the difficult processing and inferior mechanical properties of the resulting products from mixed, chemically different polymers. The detailed knowledge of the microstructure of the systems, coupled with the operative process parameters and the eventual effects of a compatibilizer can reduce or prevent this die build-up, and can allow recycling of laminated film scrap.

Nowadays, alternative destinations for industrial scraps are studied to reduce the percentage of plastic materials to be landfilled or incinerated; European legislation foresees that, in case of automotive components, within 2015 the percentage of recycling should rise up to 95 % [2].

At a molecular level, the requalification of plastic materials involves a material-process-product integrated pathway which combines different molecular simulation techniques - from an atomistic

scale up to finite elements - to calculate morphologies, thermal and mechanical properties of the recycled blends under simulated pressing conditions (e.g., high temperature and under the application of a shear rate). These results are then in turn used to predict material behavior during production.

In this article we discuss the results obtained from the application of a many-scale molecular simulation strategy to the determination of morphological and thermophysical properties of polycarbonate and acrylonitrile–butadiene–styrene blends (PC-ABS) at different compositions. Such blend systems are currently used in the production of automotive lights, where the excellent mechanical and optical properties of PC polymers are coupled with the better workability of ABS blends.

Materials and methods

All simulations have been performed on Intel Xeon bi-processor workstations, using the commercial software platform Materials Studio (v.3.2, Accelrys Inc., San Diego, CA, USA).

The ABS material is a two phase polymer blend. The continuous phase of styrene-acrylonitrile copolymer (SAN) confers to this material its well known rigidity, hardness, and heat resistance. The toughness of ABS is instead the result of submicroscopically fine polybutadiene rubber particles uniformly distributed in the SAN matrix. The structure is eventually reinforced by the formation of crosslinks. Given the complexity of this material, we decided to adopt an approximated molecular model for it, constituted of three molecular species: i) a butadiene homopolymer (polyB); ii) an acrylonitrile-styrene block copolymer (SAN), and iii) a ramified macromolecule having a butadiene main backbone and styrene-acrylonitrile copolymer branches (B-SAN). In the case of PC, to comply with the mesoscale simulation requirement of similar bead dimensions, the entire constitutive repeating unit (CRU) was divided into two separate structural units, PC01 and PC02.

In the spirit of the many-scale simulation approach, lower scale molecular simulations (e.g., atomistic molecular dynamics (MD) or Monte Carlo (MC) calculations) are performed to obtain input parameters for higher level calculations (e.g., mesoscale (MS) simulations). Thus, the first, key parameter of the MS calculations carried out in this work - the Flory-Huggins interaction parameter χ - was obtained for each system via the solubility parameter δ of the polymers, following the procedure based on the derivation of the cohesive energy density e_{coh} through MD simulations, and described in details by Fermeglia and Pricl [3,4]. The theory underlying the methodology for the calculations of the next set of MS input parameters - the number N_{meso} and the bond length a of the MS beads - is similar to the classical dynamic random phase approximation (RPA) [5,6]. The polymer chains are modeled as Gaussian chains consisting of beads, each bead representing a number of monomers of the real polymer. The mapping of the real polymer chains onto Gaussian chains can be obtained via the characteristic ratio C_∞, by imposing the mean-square end-to-end distance $<r^2>$, and the length of the freely-jointed chain to be equal for the real and the Gaussian chain. In this work, the two quantities $<r^2>$ and C_∞, necessary to the estimation of N_{meso} and a, were obtained from atomistic Monte Carlo calculations following the procedure reported in [7].

All MS simulations have been performed with MesoDyn, a coarse grained model for the diffusive and hydrodynamic phenomena in phase-separation dynamics [8]. The thermodynamic forces are obtained via a mean-field density functional theory, assuming a Gaussian chain as a molecular model. The main element for the chain architecture is represented by "beads", which group a homogeneous series of monomers. The melt dynamics are described by a set of stochastic partial differential equations (functional Langevin equations) for polymer diffusion. Noise sources, with correlations dictated by the fluctuation-dissipation theorem, introduce the thermal fluctuations. The numerical calculations involve the time-integration of functional Langevin equations, given an implicit Gaussian density functional expression for the intrinsic chemical potentials. All the details of these simulations are similar to those previously performed on other, similar systems [4,7].

The simulated polymer molecular weights, temperature, and applied shear rate have been set equal to processing material and conditions used by CRP. The main characteristics of the simulated systems are reported in Tables 1 and 2. As can be seen, both PC and ABS molecular weight was fixed at 30000, while the systems were characterized by different PC/ABS ratios.

Table 1. Main characteristics of the mesoscale simulations.

a [nm]	Cell dimensions [nm]	Time steps	T [K]	Shear rate [s^{-1}]	PC/ABS ratio (%w/w)
1.909	53×53×53	4000	548	25000	15/85, 35/65, 55/45, 85/15

Table 2. Characteristics of the structural architectures for mesoscale simulations.

Molecular species	MW fraction in chains	MW fraction in ABS	Bead sequences
PC	1		(PC01PC02)15
polyB	1	0.31	B50
B-SAN		0.20	B3B[AN9S3]B2B[S2AN9]B3
AN	0.46		
B	0.16		
S	0.38		
SAN		0.49	AN12S10
S	0.7		
AN	0.3		

Finally, density distributions obtained from MS simulations have been imported in the finite elements MesoProp software [9], in order to calculate the Young modulus, shear modulus, Poisson modulus, bulk modulus, and thermal expansion coefficient of these systems.

Results and discussion

One of the essential results yielded by MS simulations is the morphology of a given polymeric system. Figure 1a, b and c shows, as an example, the three-dimensional slice visualization, the density distribution, and the order parameter of an equilibrated structure corresponding to the 55/45 PC/ABS system. The order parameter P [10], defined for each bead species i as:

$$P = \frac{1}{V} \int_V \left[\theta_i^2(\mathbf{r}) - \theta_{i,0}^2 \right] d\mathbf{r}. \tag{1}$$

represents the mean square displacement of the bead density from initial homogeneity, thus giving quantitative information about the phase segregations in the system.
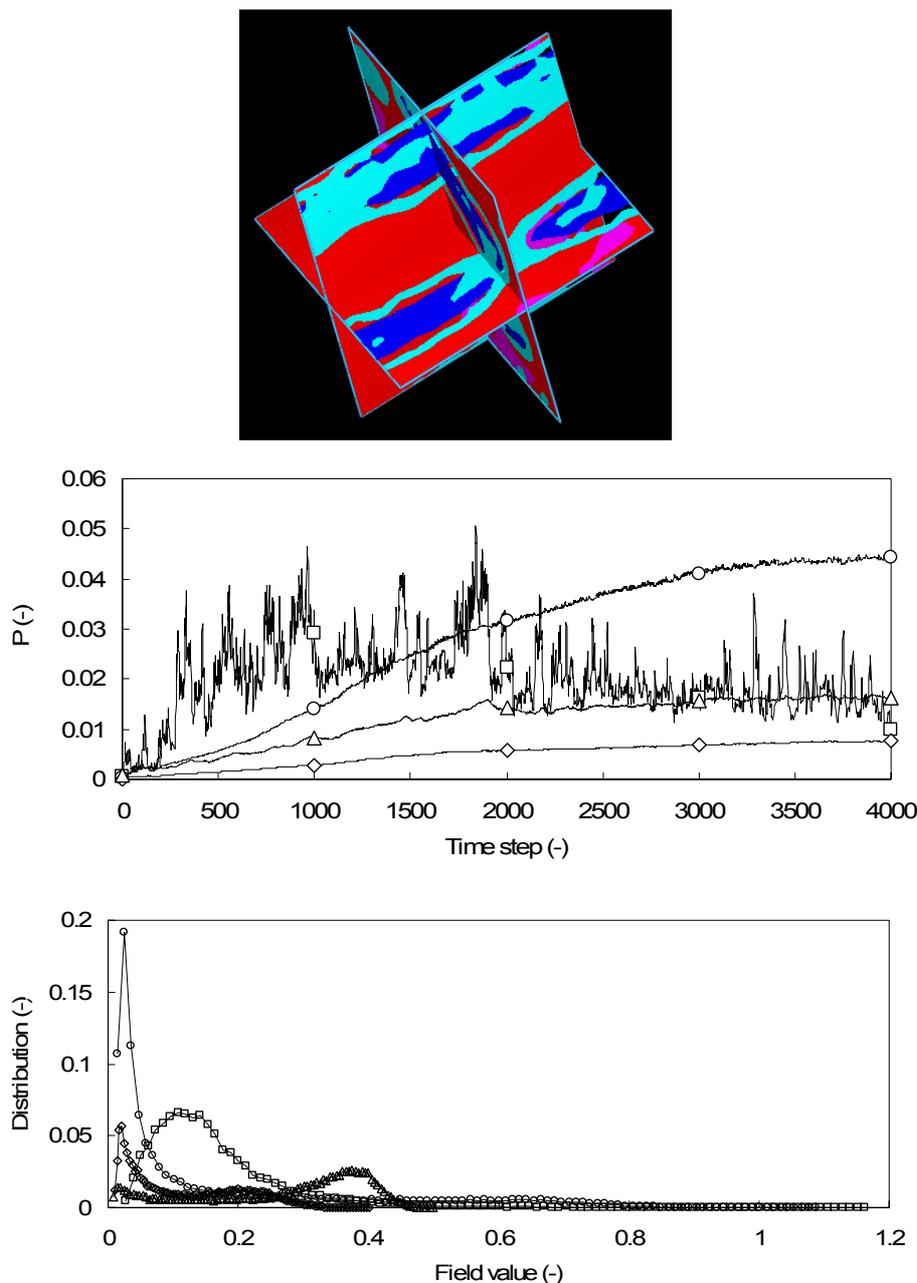
Figure 1. Slices of 3D bead distribution on xy, xz, zy planes (a, top; color coding: red: PC; blue: AN; cyan: S; purple: B), order parameter P as a function of simulation time (b, middle), and bead density distribution (c, bottom). Symbols: (□), B; (○), AN; (◇), S; (△), PC.

Utterly similar results have been obtained for all other simulated systems.

As explained in the previous section, the ABS used in this work contains three kinds of segments: a copolymer SAN, a homopolymer B and a terpolymer of grafted architecture, B-SAN. Let us now consider Fig. 1a, in which we can observe the detailed morphology of the system: the most polar acrylonitrile segments can be seen as islands, colored blue, surrounded by the styrene segments (cyan). The less polar component, B (purple) engulfs the PC segments (red), shielding them from unfavorable interactions with the polar AN beads. More precisely, the styrene and butadiene segments helps enwrapping the AN segments, thus attenuating the repulsion between its polar segments and the non-polar PC ones. AN repulsive behavior is also confirmed by its high P values (curve with circles in Fig. 1b). Moreover, quite evidently, the whole structure presents elongated features in the applied shear direction. The analysis of Figure 1c eventually reveals how bead distributions do not show a single, well defined peak around the initial value, but, especially in the case of PC and AN, two peaks appear close to 0 and close to the maximum value, respectively. This

clearly demonstrates that micro-phases of single bead type appear, characterized by micro-structure formation of approximately 10-20 nm in diameter.

MesoProp simulations have been then carried out to calculate mechanical and thermal properties of the blends; as described in the previous paragraph, density profiles obtained from MS simulations have been used as input data, while the mechanical and physical properties of single, pure components have been obtained experimentally in our laboratories. Figure 2a and b reports, as an example, the von Mises stress and stress distribution obtained for the 85/15 PC/ABS system.
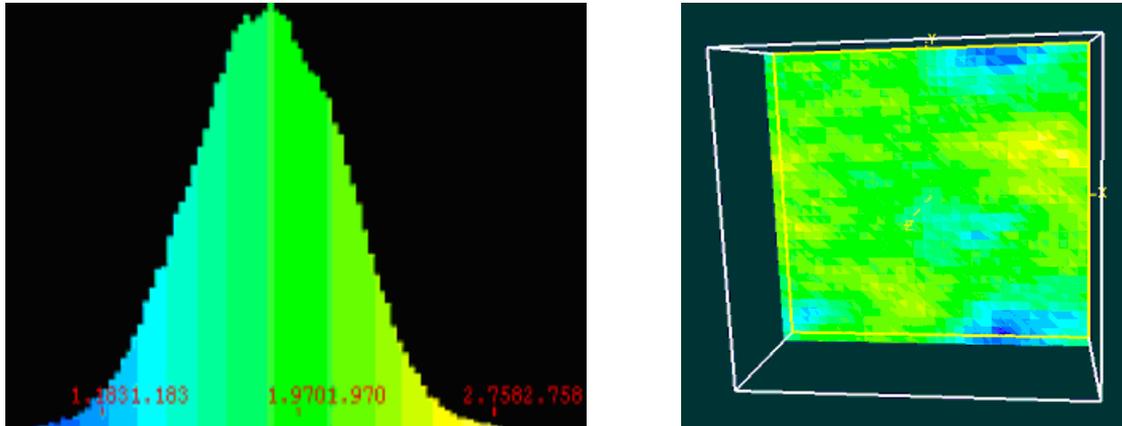

Figure 2. von Mises stress along the *z* axis (a, left) and von Mises stress distribution in the *xy* plane (b, right) for the 85/15 PC/ABS system.

From this Figure it can be noticed that, despite the rather evident phase segregation occurring in system testified by the MS simulations, the corresponding mechanical properties are homogeneous (e.g., the Gaussian distribution of the stress, Figure 2a). The same results have been obtained for all slices and for all systems considered. A sensible explanation for this might be there is not a neat separation between PC and ABS, as mesoscale simulations reveal only local incompatibilities, which can be more or less evidenced by AN presence. This component is present only in the free SAN copolymer or, grafted, in the B-SAN chain and, thus, it can not be able to segregate completely. This implies, in the evaluation of physical properties of the blend, a homogeneous (and intermediate) behavior between pure PC and ABS.

Table 3 lists all the properties calculated for the blend systems, whilst Table 4 compares the results obtained from simulation to the corresponding experimental values for the 85/15 PC/ABS system [11] as an example. As can be seen, the agreement is very good.

Table 3. Mechanical and thermal properties calculated by MesoProp.

Property	15/85 PC/ABS	35/65 PC/ABS	55/45 PC/ABS	85/15 PC/ABS
Young modulus [GPa]	2.40	2.39	2.35	2.34
Shear modulus [GPa]	$8.6 \cdot 10^{-1}$	$8.5 \cdot 10^{-1}$	$8.3 \cdot 10^{-1}$	$8.3 \cdot 10^{-1}$
Bulk modulus [GPa]	4.15	4.38	4.55	4.85
Thermal expansion coefficient [1/K]	$6.92 \cdot 10^{-5}$	$6.80 \cdot 10^{-5}$	$6.72 \cdot 10^{-5}$	$6.56 \cdot 10^{-5}$

Table 4. Comparison between simulated and experimental data for the 85/15 PC/ABS system.

	Bayblend® T 85 (Bayer)	85/15 PC/ABS
Young modulus [GPa]	2.30	2.34
Thermal expansion coefficient [1/K]	$7.5 \cdot 10^{-5}$	$6.56 \cdot 10^{-5}$

Conclusions

Molecular simulation is a useful tool for studying the microscopic structure and understanding the mechanism of physical processes on molecular/supramolecular levels. In particular, molecular simulations of polymeric structures have reached the stage where they are now helpful in gaining insights into the molecular origins of behavior of bulk polymers. In this paper we have investigated the phase behavior of PC/ABS blends produced from industrial scraps, and calculated some thermophysical properties in the light of possible utilizations of these materials in the automotive industry.

The application of the many-scale simulation approach to the study of PC/ABS blends has demonstrated that these systems show microphase segregation at all compositions; this phase morphology, however does not seem influence the mechanical properties of the resulting blends.

Acknowledgments

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