MANY-SCALE MOLECULAR MODELING OF PET/PEN BLENDS

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INTRODUCTION

Properties of polyethylene terephthalate (PET)/polyethylene 2,6 – naphthalate (PEN) blends have been widely investigated in this decade, due to the improved PEN capacity of food packaging and preservation. Enhanced mechanical properties, heat stability and barrier properties have made PEN much competitive with respect to PET (1). However, as long as PEN resins continue to be expensive, there will be a considerable commercial interest among researchers for PET/PEN blends, as valid alternatives to many–layer expensive food packaging.

PET and PEN homopolymers are known to be essentially immiscible at any temperature at any composition (2). Anyway, miscibility near and above melting temperature is increased by transesterification. This reaction always occurs, if not inhibited, influencing blends properties as the transerestified copolymers induce miscibility. The entity of transesterification depends upon processing temperature, annealing time, PET/PEN weight distribution and shear. The reaction can be controlled by aptly tuning those parameters.

In case the short blending time before extrusion does not allow the system to create long random copolymers, few block copolymers (with a low degree of randomness) would be generated in the blend. In the first phase of the transesterification reaction, polymers do not break bonds, but link together to create longer, block copopolymers, as evidenced experimentally (3). As transesterification proceeds, polymers become more random in nature; past some critical level of the degree of randomness, blend properties become constant, varying only with the composition of the blend (4). Therefore, along the entire transesterification pathway, many different species of different block copolymers are present in the blend; they continue to react and link together improving the randomness of the system and the miscibility of the blend. It has been demonstrated that the system starts to show miscibility only above 10% transesterification: this should be granted by a longer annealing time, or by multiple extrusions (5,6).

In this work different molecular many–scale simulations have been performed, in which the transesterification degree has been gradually increased. As the composition of PET/PEN was fixed at 80–20 %, we decided to improve transesterification till the maximum degree of transesterification theoretically achievable. This implies that, in the last simulation, PEN has been completely included in the block copolymer. In this paper, however, we will compare the results for an immiscible system without transesterification, and for the totally mixed system with complete transesterification.

Many–scale molecular simulations have been performed to characterize the systems considered in this work. Data obtained from quantum mechanics (QM) and atomistic molecular dynamics (MD) simulations have been used as input parameters for mesoscale simulations (MS), where the characteristic dimension is about 10-100 nm.

Results will carry better miscibility predictions for alternative and cost–saving technological features, as they can also be used to predict physical properties with finite-difference simulations.

SIMULATION METHODS AND COMPUTATIONAL DETAILS

In this first stage of the research, PET/PEN homopolymer blends have been modeled in order to compare homopolymer blends miscibility with more realistic block/random copolymer blends. An 80% PET–20% PEN w/w composition has been chosen, as an acceptable compromise for industrial applications. The characteristics of the examined systems in the 2 set of simulations discussed in this work are listed in Table 1.

Table 1 – Characteristics of the examined systems in the two set of simulations.

	T [K]	Transesterification [%]	PET MW (g/mol)	PEN MW (g/mol)	PET/PEN (% w/w)
System 1	583	0	18000	18000	80/20
System 2	583	40	18000	18000	80/20

Extrusion temperature has been chosen according to (7), while 18000 g/mol is a typical value for the molecular weight of industrially employed PET and PEN polymers. As in some cases low shear rates can be applied during extrusion, at a rough first approximation PET/PEN systems can be modeled at zero-shear rate (7). In the case of the complete transesterification, randomness degree calculation and PET/PEN sequence length estimation in the transesterified copolymer have been provided by previous publications (8,9). In this simulation, the content of the hetero sequence in the whole blend is about 40%, as all PEN monomers ideally migrate from the PEN homopolymer into the copolymer.

The software modules Mopac, Amorphous Builder, Discover, and MesoDyn, as implemented in the commercial platform Materials Studio (v. 3.1, Accelrys, San Diego, CA, USA), were employed to perform the simulations. In the many-scale simulation framework, the input parameters for higher scale simulations (e.g., MS) are obtained by performing calculations at lower scales (e.g., QM and MD). The first, key parameter of the MS calculations - the Flory-Huggins interaction parameter χ - was obtained via the solubility parameter δ of the two polymers, following the procedure described in (10), and based on the derivation of the cohesive energy through MD.

Next, the number N_{meso} and the bond length a of the MS beads (Kuhn segment) can be calculated, under the hypothesis of a Gaussian chain, from the characteristic ratio C_∞ of the two polymers, as:

$$C_\infty = \frac{\langle r^2 \rangle_0}{Nl^2} \qquad [1]$$

with:

$$l^2 = \sum_{i=1}^{N_l} l_i^2 \qquad [2]$$

where N is the number of monomers, l the monomer length and $\langle r^2 \rangle_0$ the chain mean-square end-to-end distance. C_∞ has been calculated by performing MD simulations on polymer chains generated by the modified RIS method (11). The RIS generates a given number of configurations, each of which is simulated independently by a procedure with molecular mechanics (MM) minimization and annealing before running NVT (MD) simulations. Once the MD is performed, the chain end-to-end distance is estimated, and C_∞ is calculated according to equation [1]. The procedure is repeated for each configuration at different chain length until a constant value of C_∞ is obtained. The true value of C_∞ is estimated by averaging over all configurations considered.

The core of this work is the use of mesoscale simulations with MesoDyn. The starting point for each MS simulation is a coarse-grained model for the diffusive and hydrodynamic phenomena in phase-separation dynamics (12). The thermodynamic forces are obtained via a mean-field density functional theory, assuming a Gaussian chain as a molecular model. 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. For industrially relevant polymer systems, these calculations are highly resource consuming (CPU, memory and bandwidth between CPU and memory). This makes the use of high performance computing (HPC) tools, especially many-processor systems with distributed memory, almost mandatory.

RESULTS AND DISCUSSION

Calculation of characteristic ratios C_∞ gave values close to the ones given in (1), as shown in Table 2. The same agreement was found for the solubility parameter δ of PET (13) (see Table 2). Both these evidences can be taken as a validation of the computational procedure adopted to calculate these molecular parameters. The entire set of MS input parameters obtained from lower scale molecular simulations are listed in Table 3. It should be noticed that bead self-diffusion coefficient *D* was appropriately estimated in order to avoid the simulation dimensionless time step (i.e., the product of the time step and the bead diffusion coefficient, divided by the square of the grid spacing) to exceed the recommended limit. It has been seen, however, that the self-diffusion parameter does not have an appreciable effect on the final results of the MesoDyn simulation. The compressibility parameter *K* was left at its default value of 10, as it is suited for our dynamic simulation. A typical MS simulation was performed using the following operative settings: grid dimensions = 32 nm, grid spacing = 2.305 nm, noise factor = 75, time step = 50 ns, number of steps = 15,000, maximum number of iterations per step = 100.

The bead number N_{meso} and length a for the Gaussian chains in the simulation were estimated through the following expressions (14):

$$N_{meso} = \frac{M_P}{M_M \cdot C_\infty} \quad [3]$$

where M_P is the polymer molecular weight, M_M is the monomer weight, and:

$$a = C_\infty l \quad [4]$$

$$l = \sqrt{\sum l_i^2} \quad [5]$$

where l_i are the monomer unit lengths.

Table 2 – Comparison between simulated and literature C_∞ and δ values.

	C_∞ PET	C_∞ PEN	δ PET [MPa$^{1/2}$]
Simulated value	4.02	5.27	21.93
Literature value (ref.)	4.11	5.33	21.54
Error	2.2 %	1.1 %	1.8 %

Table 3 – MS input parameters obtained from lower scale molecular simulations.

	C_∞	δ [MPa$^{1/2}$]	D [cm^2/s]	K [m^{2}kgs^{-2}]	χ	V_{mol} [cm^3/mol]
PET	4.02	21.93	2×10^{-7}	10	0.523	143
PEN	5.27	18.19	2×10^{-7}	10	0.523	219

When the transterification reaction is not inhibited, pure homopolymers are progressively substituted by block copolymers that became more random in nature as long as the reaction proceeds. The following equations for the estimation of the average sequence lengths of ethylene terephthalate and naphthalate units - L_T and L_N, respectively - have been proposed by Patcheak and Jabarin (8):

$$L_T = \frac{1}{(1 - X_T)DR} \qquad L_N = \frac{1}{(1 - X_N)DR} \quad [6]$$

where X_T and X_N are the molar fraction of PET and PEN, respectively, and DR is the degree of randomness. DR can be defined as the sum of the probabilities of finding a naphthalate unit next to a terephthalate unit (P_{tn}) and a terephthalate unit next to a naphthalate unit (P_{nt}) (15). Ihm et al. (5) examined the extent of transesterification in 50/50 PET/PEN blends as a function of the annealing time: the longer the annealing time, the higher the DR and the shorter the block sequence length into the copolymer. In our case, an ideal complete transesterification was supposed, so the block copolymer structure construction implies short repeating units. The bead number for each repeating unit in the copolymer was then calculated as:

$$B_{N_i} = \frac{r}{C_\infty} \qquad [7]$$

where r is the number of repetitions of each repeating unit in blocks, and B_{N_i} the bead number for each block. We decided to simply alternate PET and PEN beads, maintaining the weight fraction of 50% PET/50% PEN in the copolymer. Copolymer weight was arbitrarily fixed at 36000 g/mol, which corresponds to the fusion of one chain of PET and one of PEN. As previously remarked, all PEN homopolymer has been incorporated into the copolymer. Accordingly, the bead numbers of the molecule types differ in the two simulations, as shown in Table 4.

Table 4 – Bead number used in MS simulations.

	Bead number (PET)	Bead number (PEN)	Bead number (copolymer)	*a* [nm]
Pure homopolymers	23	14	0	2,661
Complete transterification	23	0	14 + 23, alternate	2,661

RESULTS AND DISCUSSION

PET/PEN blends without transesterification

As the first case, PET/PEN homopolymer blends miscibility in the absence of a transesterification reaction has been examined. As previously demonstrated by experimental data (3), such blend systems show a complete segregation phase at the melting temperature considered. Due to the low PEN concentration, in the PET 80% - PEN 20% blend the system shows a slow convergence towards a free energy stable condition. This can be evaluated by controlling the order parameter, which represents a measure of the system segregation state in the blend, as showed in Figure 1a. From this Figure we can infer that a little amount of immiscible PEN homopolymers will slowly find a way for aggregation in separated clusters. Moreover, it can be noticed that the smaller the quantity of species, the longer the way they have to cover to aggregate each other. Figure 1b shows the 3D – bead volumetric density distribution of the phase segregation. Finally, in Figure 1c the density field distribution of the 2 species is shown. It should be noticed that densities of PET and PEN have two (small) peaks at different densities, which is a clear indication that segregation occurs. PET and PEN are both present at densities close to 0 and close to the maximum.

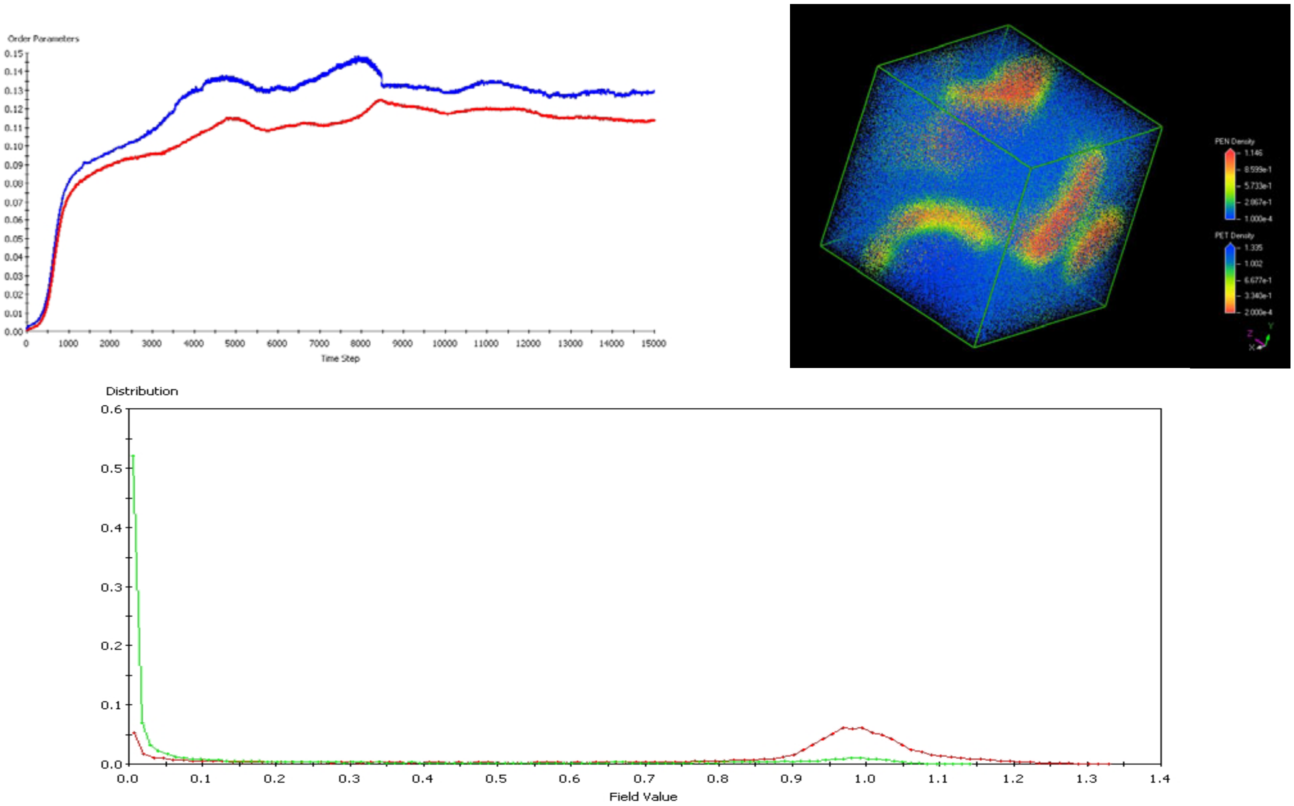

Figure 1 – Characteristics of the 80% PET/20% PEN blend MS simulation without transesterification (a), top left: PET/PEN blend order parameter (blue line: PET, red line: PEN); (b), top right: segregation of PET and PEN in the 3 D – bead volumetric density distribution; (c), bottom center: PET/PEN field distribution density for the blend (red line: PET, green line: PEN).

PET/PEN blends with transesterification

As discussed in the previous paragraphs, a transesterification reaction, if not inhibited, always occurs during the melting, and extruding phases of PET/PEN blends; accordingly, we simulated the three-phase system: homopolymer PET, homopolymer PEN, block copolymer PET/PEN. We decided to simulate a complete transesterification (around 40%), as shown in Table 5. In order to visualize and emphasize the displacement of PET beads in the simulation grid, PET beads in the copolymer have been defined in a different way (i.e., PETCO), although they are obviously characterized by the same χ parameters of the PET beads in the PET homopolymer.

The results obtained from this MS simulation clearly differ from the previous case, as can be observed looking at the order parameter of the field distribution density, the 3D – bead volumetric density distribution and the field distribution density shown in Figure 2a, 2b, 2c respectively. Order parameters are at least 2 orders of magnitude lower than the case without transesterification. Density profiles show a single well-defined peak for each species; further, densities are narrowly distributed around the mean value.

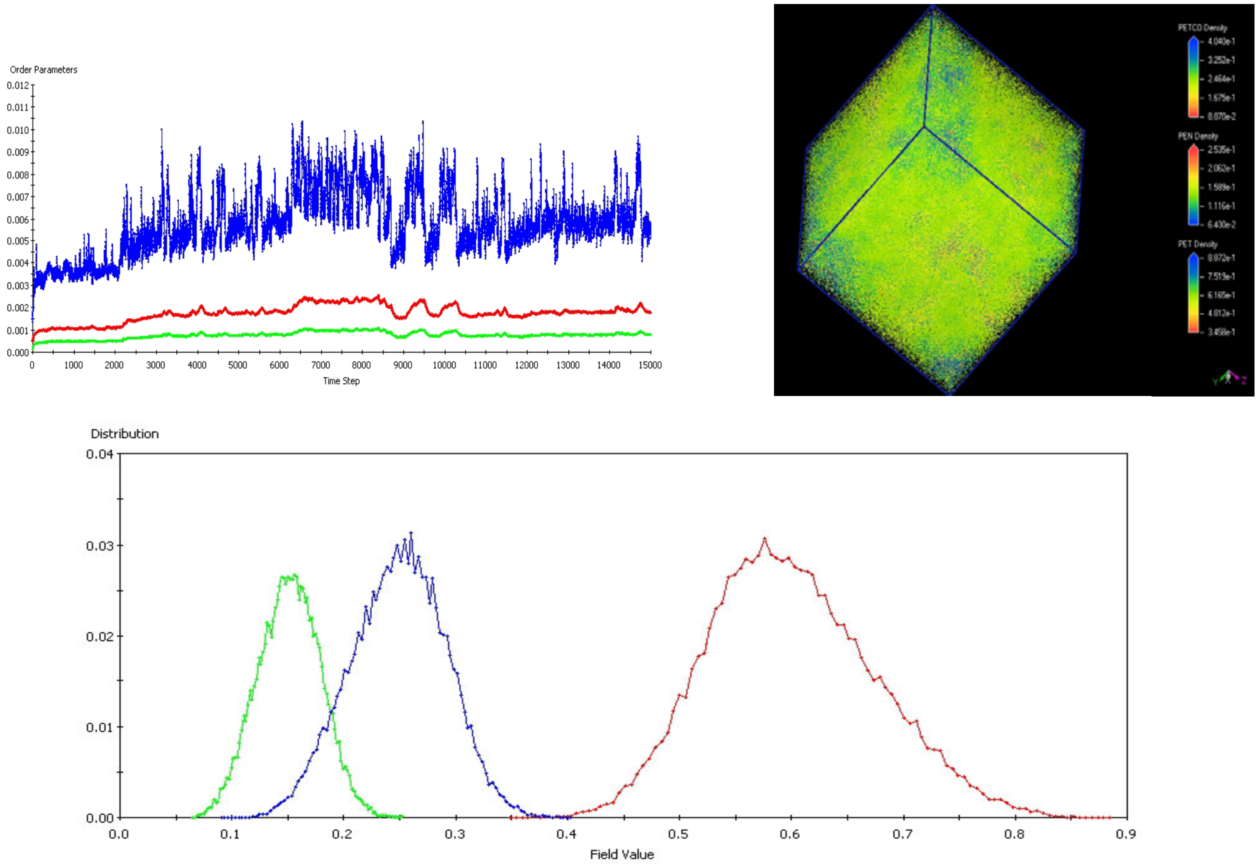

Figure 2 – Characteristics of the 80% PET / 20% PEN blend MS simulation with transesterification (40%) (a), top left: PET/PEN blend order parameter (blue line: PET, red line: PETCO, green line: PEN); (b), top right: segregation of PET and PEN in the 3 D – bead volumetric density distribution; (c), bottom center: PET/PEN/PETCO field distribution density for the blend (red line: PET, green line: PEN, blue: PETCO).

The sensible, rather obvious explanation for the improved miscibility envisaged in this system can be the compatibilization effect induced by the copolymer, which is able to compensate the repulsion between PET and PEN beads. Short blocks in the copolymer exert a “bridging” effect between the homopolymers, reducing the mean displacement of the beads, and avoiding phase segregation into bigger clusters.

As intermediate situations are more common in nature, different simulations should be performed in order to evaluate different extent of transesterification. Evaluation of miscibility for different degrees of transesterification at different temperatures and with a shear rate application may reveal some interesting feature from an industrial point of view, as transtesterification depends upon time, temperature and type of extrusion.

CONCLUSIONS

The mesoscale molecular modeling of PET/PEN blend performed in this work has revealed complete immiscibility for a 80% PET/20% PEN blend in the absence of a transesterification reaction, according to results provided by previous experimental tests (3). As transesterification usually occurs during the extrusion, simulations demonstrate that miscibility is slightly improved by a longer annealing process; in this case with an ideal complete transesterification, the system is completely mixed. Differences between the two systems are quite evident, as order parameters differ by two orders of magnitude, and, in the case of transesterification, density distributions are narrowly distributed around a single value. Imposing a higher degree of randomness favors miscibility, as at the end of the simulation bead density distribution vary weakly in each grid. The experimental trend that testifies a higher induced miscibility with a higher degree of transesterification has been fully confirmed by mesoscale molecular modeling. Further simulations could undoubtedly be helpful to predict the behavior of the blend at different levels of transesterification, shear rate and temperature.

In this work, the necessary MS input parameters have been obtained by a many–scale molecular modeling approach, revealing good accordance with experimental data, when available. In our opinion, the use of this “ab-initio” modeling approach constitutes a cost and time saving technique for predicting PET/PEN blending properties in a successful way. We also plan to perform further investigations with finite-difference simulations, in order to “close the circle” of the many-scale simulation, and being thus able to calculate physical properties of the blends.

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