PVC/LDPE incompatible blends for industrial applications: a computational multiscale approach

M. Fermeglia[1], A. Coslanich[1], M. Ferrone[1], T. Humar[1], M.S. Paneni[1], S. Pricl[1], E. Paglione[2]

[1]*Computer-aided System Laboratory – MO.S:E., Department of Chemical, Environmental and Raw Materials Engineering, University of Trieste – Piazzale Europa 1, 34127 Trieste, Italy;*
[2]*Adriaplast S.p.A. – Solvay Group, Via Timavo 59, 34074 Monfalcone (GO), Italy.*

Introduction

With a today's worldwide annual production capacity of approximately more than 30 million to poly(vinyl chloride) (PVC) is the second largest volume thermoplastic only to polyethylene as volume leader in the plastics industry [1]. Its ability to be compounded with many additives to a wide range of flexible and rigid products constitutes the major factor responsible for the versatile application of PVC. Because of the low cost and the processability by a wide variety of techniques (e.g. calendering, extrusion, injection molding, and plastisol techniques) combined with good physical, chemical and weathering properties, PVC has become a universal polymer, with many applications, e.g. for pipes, profiles, floor coverings, cable insulation, roofing sheets, packaging foils, bottles, and medical products.

At the end of the service-time of these articles, as well as along the pathway of their production processes, large amounts of scrap arise. Therefore, the question of the disposal of used PVC 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. On the other hand, the plastics industry continually looks for cost savings. In some cases, where an expensive polymer may be over-engineered for an application, blending with a less expensive polymer or filler using a corresponding compatibilizer or coupling agent reduces cost. Another solution is to modify a less expensive polymer like PE, using additives or blend components, so that it can compete with higher end materials.

A further, topical solution to cost saving is internal recycling. The material recycling is already practiced in plastics industry over many years with postmanufacturing waste. These experiences can be used to develop new concepts for material recycling of both post-consumer waste and of production scrapes. 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. In-plant scrap use is routine for thermoplastics processing. If the waste stream includes incompatible polymers, such as in a multi-layer structure, the incompatible portion will move to the outside of the extrudate and result in die build-up. 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.

In this work we present the results obtained from the application of the mesoscale simulation approach to the study of the morphology of poly(vinyl chloride)/low density poly(ethylene) (PCV/LDPE) immiscible blend systems, with and without compatibilizer, of special interest in the packaging industry. In particular, starting from atomistic-based

simulations, we applied 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 [2].

MODELING DETAILS

The model systems

The following systems of practical industrial importance were considered: a) PVC/LDPE at 10% by weight of LDPE; b) PVC/LDPE at 3% by weight of LDPE (a value of practical interest for the packaging industry); c) PVC/LDPE at 1% by weight of LDPE. All polymer blends were simulated both at room temperature (298 K) and at 393 K, a temperature corresponding to the extrusion process of these materials for food and pharmaceutical packaging.

Polymer chain parameterization

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 (a_b) of the Gaussian chain segments were estimated by the following relationships:

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

$$a_b = a_{mon} \, C_\infty \qquad (2)$$

where N_{mon} is the polymerization degree, a_{mon} is the monomer unit length, and C_∞ is the characteristic ratio of an infinite length chain. The C_∞ and monomer length values for PVC and LDPE and PC were estimated with the Synthia program of *Cerius²* (v. 4.9, Accelrys, San Diego, CA, USA). This semi empirical method, developed by Bicerano at Dow Corporation [2], uses connectivity indices to describe the topology of the polymer. The number of the corresponding Kuhn segments (beads) and their lengths were calculated from eqs (1) and (2).

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 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 V_{mon} 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 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, Accelrys, San Diego, CA, USA) was used for both molecular mechanics (MM) and molecular dynamics (MD) simulations. The generation of accurate model amorphous structures of PVC and LDPE 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 [3]. 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 [4]. Van der Waals distances and energy parameters for nonbonded interactions between heteronuclear atoms were obtained by the 6th-power combination rule proposed by [5]. 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 [6] and the scanning method of Meirovitch [7]. According to this procedure, a proposed structure is generated via the Rotational Isomeric State (RIS) theory .at a proper process temperature (393 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 process temperature was determined via the Synthia module, in order to minimize discrepancies in the final density values obtained from isothermal-isobaric (*NPT*) MD simulations [8]. 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 metastable local high-energy minima. To prevent the system from such entrapments, the relaxed structures were subjected simulated annealing (5 repeated cycles from 393 K to 1000 K and back) using constant volume/constant temperature (*NVT*) MD conditions [9]. At the end of each annealing cycle, the structures were again relaxed via force field, 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, 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 with coupling constant τ_T = 0.01ps, whereas pressure was kept constant by coupling to a pressure bath with relaxation time τ_P = 0.1 ps [10]. Each *NPT* MD run was started by assigning initial velocity for the atoms according to a Boltzmann distribution at 2×*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 nonbonded energies were calculated, for both the pure components and the mixtures, as the mean total potential energy of intermolecular nonbonded interactions. For each 3D periodic system, the mean nonbonded 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 nonbonded 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

Self-diffusion coefficient calculations

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

$$\tau = \beta^{-1} M h^{-2} \Delta t \tag{6}$$

is the equation that relates the adimensional time step τ used in the MesoDyn calculation algorithm [11], 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, equivalent 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. 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.

Interaction parameter scaling and mesoscopic simulations

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. The phase separation dynamics at the mesoscopic level was simulated by MesoDyn using the parameter sets obtained with the procedure described in the foregoing paragraphs. 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*.

RESULTS AND DISCUSSION

Figure 1 shows, as an example, the isodensity surfaces obtained from the mesoscale simulations for the PVC/LDPE systems at 3% and 10% by weight at 298 K and in the absence of shear, respectively.
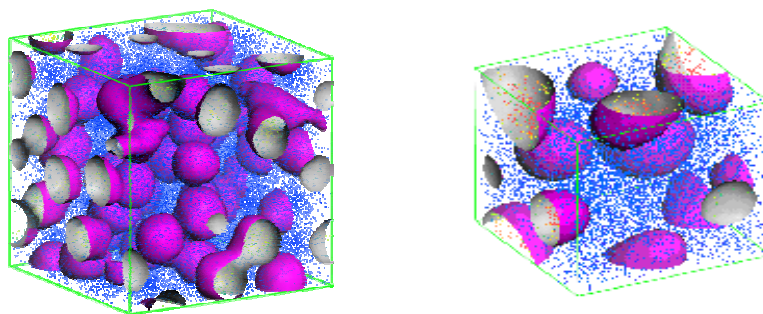

Figure 1. Isodensity surfaces for the PVC/LDPE system at 3% (left) and 10% (right) by weight of LDPE obtained from mesoscale simulations at 298 K and in the absence of shear.

In both cases, we can detect the formation of spherulitical domains of LDPE within the PVC matrix; this predicted morphology has been confirmed by the corresponding experimental evidences resulting from scanning electron microscopy (SEM) [12]. The domain dimensions resulting from the phase separation process can be quantified by mapping the density of the B-type beads (LDPE) on a plane intercalated within the 3D cell, as reported in Figure 2.
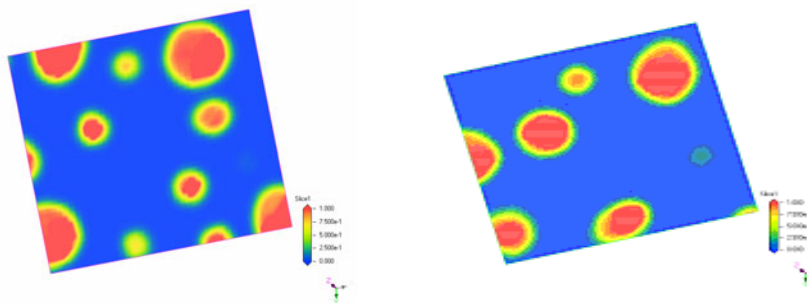

Figure 2. Mapping of B-type beads (LDPE) onto a plane intercalated in the 3D cell for the system PVC/LDPE system at 10% by weight of LDPE at 298 K and in the absence of shear. Right: after 5000 simulation steps; left: after 10000 simulation steps.

From an analysis of Figure 2 we can see how, during the simulation, the smaller size domains tend to coalesce towards an equilibrium, homogeneous geometry, in which the domains are characterized by similar size and shape. Considering this Figure further, we can infer that the system presents a phase segregation characterized by a high degree of symmetry. Moreover, there is a neat difference in the density values across the interface, which is a symptom of a poor adhesion between the phases, and a consequent high interfacial energy. All these speculations are supported from the experimental evidence and constitute a further proof of the incompatibility of the two polymers at room temperature.

Figure 3 illustrates the isodensity surface obtained for a PVC/LDPE system at 3% by weight of LDPE at 393 K, coupled with the corresponding intercalation plane.
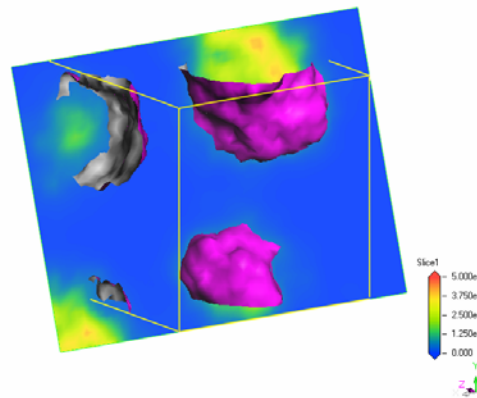

Figure 3. Isodensity surface and mapping of B-type beads (LDPE) onto a plane intercalated in the 3D cell for the systems PVC/LDPE system at 3% by weight of LDPE at 393 K and in the absence of shear.

We can observe how a phase separation is predicted by the mesoscale simulation also at 393 K, which is even more pronounced at this temperature and characterized by larger domains of lower symmetry. This clearly reflects in the practical industrial problems during the processing of these materials. If a shear rate is applied to this system with the purpose of better mimicking the processes conditions, the following equilibrium morphology is obtained (see Figure 4):
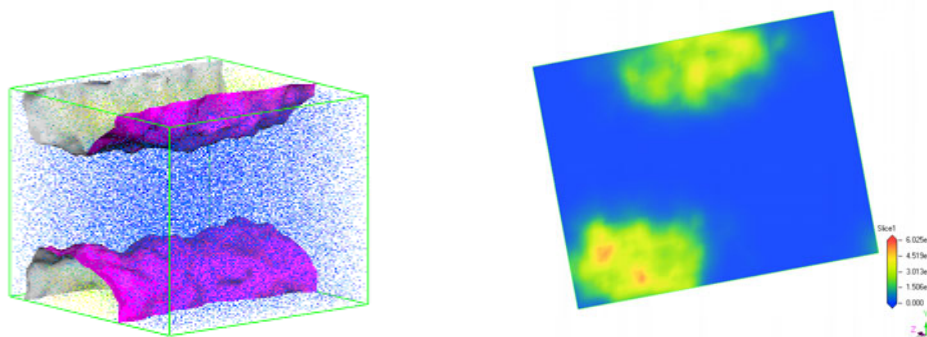

Figure 4. Isodensity surface and mapping of B-type beads (LDPE) onto a plane intercalated in the 3D cell for the systems PVC/LDPE system at 3% by weight of LDPE at 393 K under an applied shear rate of 100000 1/s.

We can clearly see how the applied shear rate results in an orientation of the

segregation domains in the direction of the applied field, giving rise to a cylindrical morphology utterly comparable to that observed for the same systems by SEM [12]. Obviously, this condition plays a critical role in the extrusion process of these materials, as it constitutes an initial step towards a crystallization process of LDPE under flow.

CONCLUSIONS

PVC/LDPE blends are materials which find extensive use in the plastic industry. The recycling of the production scraps of these polymeric systems is an economic must for these factories. Unfortunately, however, their incompatibility poses several, technological problems which result in production dead times with consequent maintenance costs.

This work constitutes a first step in the study of these polymer blends by means of a multiscale computational approach. Atomistic MD simulations are employed to calculate some molecular-based parameters which, in turn, constitute the input quantities for the subsequent mesoscale simulation.

According to the results obtained from the application of these simulation techniques, a PCV/LDPE system characterized by a 3% by weight of LDPE, such as that of interest in the food and pharmaceutical package industry, is characterized by a strong phase segregation under process conditions. On these bases, the optimization of the operative process parameters and the choice of an optimum compatibilizer to confine the phase segregation are currently under study in our laboratory.

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