Dynamic Heterogeneity in Fully Miscible Polymer Blends through Molecular Simulations

Manolis Doxastakis,[3] Vagelis Harmandaris[1,2,*]

[1]Department of Mathematics and Applied Mathematics, University of Crete, GR-71409, Heraklion, Crete, Greece.
[2]Institute of Applied and Computational Mathematics (IACM), Foundation for Research and Technology Hellas (FORTH), GR-71110 Heraklion, Crete, Greece.
[3]Department of Chemical and Biomolecular Engineering, University of Houston, Texas, USA &
Argonne National Lab, USA
* E-mail address of presenting author: vagelis@tem.uoc.gr

ABSTRACT SUMMARY:

The effect of self-concentration and intermolecular packing on the dynamics of polymer miscible blends is examined by extensive atomistic simulations. Direct information on local structure of the blend system allows a quantitative calculation of self- and effective composition terms at various length scales that are introduced to proposed models of blend dynamics. Through a detailed statistical analysis, the full distribution of relaxation times associated with re-orientation of carbon-hydrogen bonds was extracted and compared to literature experimental data. A direct relation between relaxation times and local effective composition is found using a composition-dependent length scale. The pertinent dynamic length scale that best describes the slow segmental dynamics in miscible blends relates to both intra- and intermolecular contributions.

INTRODUCTION:

The dynamics of polymer mixtures remains an area of intense research for nearly two decades due to their complex dynamical and rheological behaviour.[1,2] It is well established that even thermodynamically miscible blends, can retain distinct individual mobilities in the mixed state that are separate from the pure components.[1-4] A critical parameter in the observed behaviour is the dynamic asymmetry, controlled by the difference in the glass transition temperatures (T_g) of the constituent homopolymers. In this aspect several open questions pertaining to linking molecular details to model parameters; see refs. 1-6 and references within.

Several models combine concentration fluctuations and contributions from chain connectivity to provide a framework that rationalizes the observed experimental behavior.[1-2] Concentration fluctuations are expected to be present in mixtures and depending on their lifetime they can promote a distribution of segmental relaxation times. Besides that the effect of self-concentration can also be of great importance for describing the dynamics of miscible polymer blends. According to this concept (Lodge-McLeish, LM, model), each segment of a specific component *A* is experiencing an environment that is enriched to *A* due to chain connectivity.[2]

In the present work, we examine whether the dynamics in fully miscible polymer blends as described by atomistic simulations, can be predicted by employing the concept of self-concentration combined with composition fluctuations which lead to a distribution of relaxation times. Two different binary systems were examined: (a) Oligomers of polyisoprene (PI)/polystyrene (PS), and (b) Blends of polystyrene with oligostyrene.

SIMULATION METHODS:

Detailed atomistic molecular dynamics (MD) simulations were performed in the *NPT* ensemble maintaining a pressure of 1 bar at four different temperatures T: 413, 443, 473, and 503 K. All bonds were kept constant and the time step in the integration of the equations of motion was 1*fs*. For mixtures at least 200*ns* trajectories were generated, far beyond the relaxation time of these oligomers. More details about the all atom MD simulations employed in this study and the equilibration procedure are given elsewhere.[3]

The (atactic) PS model is based on a fully atomistic description that is described in the literature.[7,8] We verified that the conformational and thermodynamic properties are reproduced faithfully in agreement to available experimental data. PI oligomers are also modeled using an all-atom model.[4] The chain dimensions as well as the structure of PI bulk systems are in good agreement with available experimental data. Note also that the molecular lengths of both PI and PS were chosen in order to be very similar to PI/PS blends studied before through experiments. Blends with longer PI or PS chains will lead to strong miscibility problems.

RESULTS AND DISCUSSION:

Structure and Self Composition. We first discuss how components distribute within the oligomer melts. The LM model employs self, φ_{self}, and effective, φ_{eff}, local volume, or mass, fractions to correlate compositions around a polymer segment to the observed dynamic behavior.
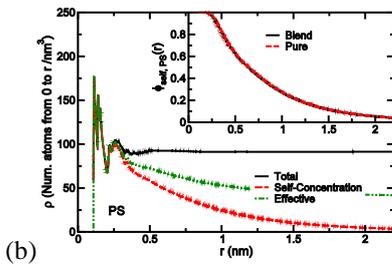

(a)
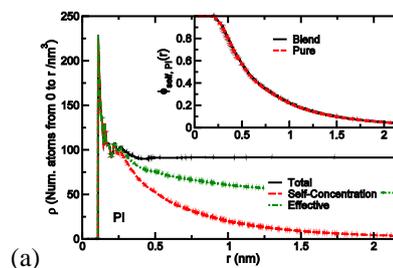
Fig. 1: *(a) Number density of atoms within a sphere r starting from a PI atom. (b) Number density of atoms within a sphere r starting from a PS atom. The insets provide the ratio $\varphi_{self,i}(r)$ compared to pure PI and PS.*

Calculation of mass fractions from the simulation data is straightforward. Figures 1a and 1b present the cumulative radial density of atoms, for a spherical volume extending from an atom to *r*, over the total volume for both components, for the 50/50 blend at 443 K. As it is observed, the local effective concentration calculated directly from the simulation is higher than the bulk and converges to the latter value as the self-concentration term approaches zero. The inset in these plots, presents the normalized fraction of self-concentration for the blends as well as for the pure components. As it is evident, no significant deviation from the pure components exists.

Segmental Dynamics. Then we discuss dynamics of polymer melts through atomistic simulations. In MD simulations, the segmental dynamics of polymer melts can be studied by calculating time-autocorrelation functions of a vector along the monomer, of the type:
$$P_2(t) = \frac{3}{2}\langle \cos^2 \theta(t) \rangle - \frac{1}{2}$$
where, $\theta(t)$ is the angle of the vector under consideration at time *t* relative to its position at *t*=0. Here we report data for the carbon-hydrogen, *CH*, vector. A quantitative comparison among the different systems is based on a fit of $P_2(t)$ with mKWW stretch exponential functions; example of such fits are shown in Figure 2a.[3] It is clear that both PI and PS dynamics is quantitatively described by the above expression.
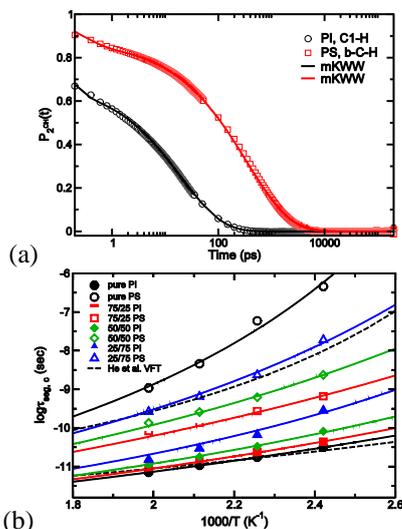

Fig. 2: *(a) Averaged orientation autocorrelation functions of unit vectors along CH bonds for PI and PS at 443 K and 50/50 wt.%. Lines represent best fits with the mKWW function. (b) Mean correlation times*

provided by the mKWW description of simulation data (symbols, filled for PI and open for PS). Dashed lines are the VFT fits on experiments of pure systems. Continuous lines are VFT representations of our data.

Fig. 2b presents the extracted mean correlation times associated with segmental dynamics (area below the curves shown in Fig. 2a) from all simulations with symbols. We can quantitatively compare our results to experimental measurements represented by the dashed lines reproduced only for the pure components (for clarity). It is apparent that pure PI dynamics is captured by our model quantitatively. Despite deviations for PS, we clearly observe a significant acceleration of the slower component and a minor deceleration of PI, a feature well-established in such blend dynamics. Continuous lines in the same figure are the results of a first attempt to employ the LM model.

In the next stage we extend the analysis of the atomistic simulations by a comprehensive statistical approach that involves independent fits over thousands autocorrelation functions of CH vectors for each component. This method allowed us to directly access the underlying distribution of relaxation times providing unique information from detailed all-atom MD simulations for the first time to the best of our knowledge. In the next stage the local environment was considered by calculating the self-, φ_{self}, and effective, φ_{eff}, local composition for each vector at various length scales. Then a direct coupling between the local environment for a specific CH vector, at different length scales, and its actual segmental relaxation time was performed. More details can be found elsewhere.[3]

As a final remark, we should state that the monomer structure of a specific polymer can play a crucial role in the dependence of its segmental dynamics on its local environment. Current work extends the above analysis onto different polymer miscible blend systems.

CONCLUSIONS:
In conclusion, binary miscible polymer blends (PI/PS and PS/oligostyrene) display dynamic heterogeneity at the segment level. The self-concentration model describes the segmental dynamics through a composition-dependent length scale. The relevant dynamic length scale exhibits distinct concentration dependence, which is weaker as that of atom-to-atom correlations in the intermolecular pair correlation functions corresponding solely to the polymer. These results suggest that the pertinent length scale that best describes the slow segmental dynamics in miscible blends relates to both intra- and intermolecular contributions.

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