

MAR06-2005-001300

Abstract for an Invited Paper
for the MAR06 Meeting of
the American Physical Society

A Lattice Model for Segmental Dynamics of Miscible Polymer Blends¹

RALPH H. COLBY, Materials Science and Engineering, Pennsylvania State University

Thermally-driven concentration fluctuations make local regions (at the scale of monomers) have a wide range of local compositions for weakly interacting miscible blends of long chain polymers. These fluctuations remain important hundreds of degrees from the critical temperature because the entropy (and hence free energy) of mixing is small in polymer mixtures. The connected nature of the chain biases the local composition distribution, making the range of effective compositions surrounding a given monomer extend from the self-composition to environments very rich in that type of monomer. These two polymer physics issues make blends of polymers vastly more interesting than mixtures of small molecules. Time-temperature superposition can fail and motions can persist far below the glass transition temperature of the blend; both of these results are enhanced as the glass transition contrast between the two components increases. A simple lattice model is used to describe the segmental dynamics of miscible polymer blends. Concentration fluctuations and chain connectivity effects are calculated at the scale of the Kuhn length, by considering a central monomer to be surrounded, out to the second shell of monomers, by 24 lattice sites. Including the central monomer, fraction $5/25 = 0.2$ of the lattice sites are part of the central monomer's chain (the self-composition) and the other 20 sites are occupied stochastically, while preserving connectivity of all chains. The resulting concentration distributions are mapped onto segmental relaxation time distributions for each blend component using the composition dependence of the glass transition and dynamic scaling. The predicted distributions are compared with experimental dielectric data on miscible polymer blends using three methods: (1) A Debye (single exponential) relaxation of each composition predicts dielectric loss peaks for each blend component which are too narrow because the lattice model ignores density fluctuations. (2) The empirical Havriliak-Negami distribution can be fit to the dielectric loss of each pure component and then assigned to each composition in that component's distribution in the blend. (3) The pure component data can be modeled with a Gaussian distribution of density fluctuations with times related to free volume using the Doolittle equation, and subsequently this distribution is assigned to each composition in that component's blend distribution. The relative merits of these three approaches will be discussed in detail.

¹with Jane E. G. Lipson, Dartmouth College