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PhD Dissertation Defense

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“Thermodynamic Interactions in Polydiene/Polyolefin Blends”

Abstract

Thermodynamic interactions in blends of polydienes and polyolefins were investigated using small angle neutron scattering (SANS). Model polydienes with controlled molecular weight, distribution, and precise chemical structure were synthesized using anionic polymerization and subsequently saturated with hydrogen or deuterium to form model polyolefins. The polydienes involved in this study include a series polybutadienes (PBD) with varying amounts of 1,2 and 1,4 microstructure units and 1,4-polyisoprene (1,4-PI); the corresponding polyolefins included are poly(ethyl ethylene) (PEE), polyethylene (PE), PE-*co*-PEE random copolymers with different compositions, poly(ethylene-*alt*-propylene) (PEP). Additionally, a model atactic polypropylene (aPP) prepared using a metallocene catalyst was also used in this study.

Near-critical melt blends were examined with SANS measurements in their single-phase region with varying temperatures. Scattering contrast was achieved through deuterium labeling of blend components. The SANS data were interpreted using the Zimm analysis and the Random Phase Approximation model to extract the Flory-Huggins interaction parameter, χ , and chain dimensions of the pure components. The thermodynamic interactions in blends of polydienes and polyolefins were demonstrated to be repulsive, quantitatively large, and strongly temperature dependent, where the isotope effect on χ is negligible. The chain dimensions of the components in these blends are in many cases expanded compared to those of the pure components.

The interactions in blends of polydienes and polyolefins were uncorrelated to the statistical segment length disparity between the components. The pure component PVT properties were found to qualitatively describe the relative trends of the measured χ parameters in various polydiene/polyolefin blends (with some exceptions), but failed to capture the magnitude of measured χ values. The Lattice Cluster Theory (LCT) which considers the effect of monomer shape was insufficient to describe the nonrandom mixing effect in the enthalpic part.

The interaction parameter in polydiene/polyolefin blends which include random copolymers consisting of polydienes and polyolefins were examined with random copolymer theory (RCT). RCT was found to be applicable for many polydiene/polyolefin blends based on model polydienes such as 1,2-PBD-*co*-PEE/PEE blends and 1,4-PI/1,2-PBD-*co*-PEE blends. The agreement of RCT to the data indicates the interactions were dominated by dispersive force without specific interactions. Sequence effect is relatively unimportant for model polydiene/polyolefin systems. We observed that RCT failed in some systems which contain complex random copolymer repeat units. The existing theories were unable to explain the departure from RCT, which indicates modified theories need to be developed.