Chemistry and Mechanical Properties of Epoxy-Based Thermosets Reinforced by Reactive and Nonreactive SBMX Block Copolymers

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ABSTRACT: Polystyrene-*block*-polybutadiene-*block*-poly[(methyl methacrylate)-*stat*-(methacrylic acid)] (SB(MA)) block copolymers incorporating acid-reactive functionalities in the last block have been synthesized and studied as modifiers for epoxy thermosets based on the diglycidyl ether of bisphenol A (DGEBA). Different techniques including differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), and transmission electron microscopy (TEM) have been used to demonstrate the effectiveness of the reaction-induced modification compared to that with the nonreactive or slowly reacting polystyrene-*block*-polybutadiene-*block*-poly[(methyl methacrylate)-*stat*-(*tert*-butyl methacrylate)] SB(MT) triblock copolymer. Morphological characteristics revealed by TEM indicate that SB(MT) and SB(MA) are both miscible with the epoxy prepolymer. The kinetics of grafting, network formation, and possibly phase separation were quantified from FT-IR, DSC, and cloud point investigations of DGEBA/DDS (4,4′-diaminodiphenyl sulfone) as an epoxy−thermoset model system in the presence of poly[(methyl methacrylate)-*stat*-(methacrylic acid)] (HT121) or the block copolymers. The cure of the thermoset/block copolymer system has been explored using six different curing processes: 2-phenylimidazole (2-PI), alone or in the presence of methyltetrahydrophthalic anhydride (MTHPA) as comonomer, accelerated dicyandiamide (DICY), and three different diamines as comonomers without accelerator: 4,4′-methylenebis(3-chloro-2,6-diethylaniline) (MCDEA), 4,4′-methylenedianiline (MDA), and DDS. The use of reactive block copolymers instead of nonreactive ones permits a better control of morphology. The materials' performances are analyzed in terms of transparency, glass transition temperature, T_g, and linear elastic mechanics at break (critical intensity factor, K_{IC}).