

The component miscibility evolution during polymerization of the polybutadiene containing styrene solutions

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Abstract In situ graft copolymerization of polystyrene (PS) on polybutadiene (PB) during polymerization of PB solution in styrene monomer was investigated to determine the performance of grafting process, chain structure of generated copolymers, and their effectiveness as compatibilizing agents for incompatible PS-rich and PB-rich phases. The amount of copolymers and their chain structures at different stages of polymerization were determined by gel permeation chromatography (GPC) curves of the reactive blends (taken directly from the reaction) and physical blends (physically prepared based on total composition of reactive blends). It was demonstrated that copolymer formation started from the early stage of polymerization and continued up to the phase inversion stage. In addition, PS grafting on PB occurred initially via single-chain attachment and then converted to a double-chain scenario later on. Compatibilizing efficiency of the copolymers was evaluated by Huggins coefficient (k_H) obtained by performing dilute solution viscometry (DSV) on samples taken at different stages of conversions. The effect of molecular weight of PB on the grafting process and the effectiveness of copolymers generated were also studied. It was found that while compatibilizing role of the copolymers produced from high molecular weight PB (HPB) increases as conversion goes further, the compatibilizing efficiency of the copolymers produced from low molecular weight PB (LPB) shows a very sharp variation in a small range of conversion. Plotting k_H of physical blends against weight fraction of PB molecules in solid content of the

solutions (w_{PB}) showed negative deviation from mixture law with a W-like pattern containing two minima with a maximum in between. While a negative deviation was assumed as indication of immiscibility of the components, upward deviation at middle values of w_{PB} was attributed to molecular segregations that reduce the interface between the incompatible PS-rich and PB-rich phases.

Keywords Miscibility evolution · Styrene solutions · Polybutadiene · Graft copolymer · Polymerization

Introduction

One of the possible strategies to disperse a polymer into another polymeric material is to polymerize homogeneous solution of the former in monomer of the latter [1]. The procedure may, however, leads to a homogeneous dispersion or a totally phase separated system depending on the miscibility between the involved components. Therefore, in situ block or graft copolymer formation in the reactive blend components and its interfacial localization is the main objective of many compatibilization tasks. Apparently, a copolymer formation enhances the component miscibility leading to changing their state of assembly toward the least free energy [2]. In this way, free energy decline of the system enhances the stability of developed solid state morphology, which usually results in improved mechanical properties [3]. High impact polystyrene (HIPS) is a multiphase heterogeneous material, which is formed by dispersing rubber particles in polystyrene (PS) matrix via a reactive mixing process [4]. During styrene polymerization, PS macroradicals are grafted on polybutadiene (PB) chains leading to the component miscibility improvement [5]. The compatibility improvement between the PS-rich

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