

Should we keep choosing nano-sized particles to kinetically stabilize co-continuous blends?

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ABSTRACT

Filling co-continuous polymer blends with solid particles has proven to improve their structural stability. Such composites further demonstrate improved functionality, making them an attractive choice of material in a wide range of applications. These objectives are achieved by trapping and percolating the particles either in one of the polymer phases or at the polymer-polymer interface. Localization is dependent on the thermodynamics and geometric properties of the particles, polymers and processing conditions employed. It has been widely reported for spherical particles that particles with smaller sizes are the most effective in preventing the coarsening of co-continuous structures. However, processing composites with nanoparticles is not trivial due their tendency to aggregate, caused by colloidal interactions. As such, they require chemical surface modification to be effective. Tuning surface properties often involve complex, costly, toxic treatments and are usually useful on a case-by-case basis. Another crucial factor considered in reported studies is the requirement of monodisperse particles, which again is not trivial to achieve on an industrial scale. To tackle these issues, we approach this study with two critical questions in mind: How is microstructural stability dependent on the size of pristine particle? How does particle size distribution affect it? We perform in-situ high-temperature confocal rheology studies to assess the effect of particle size on the extent of particle agglomeration, particle migration across the interface, and its consequence on coarsening of polymer blends filled with pristine silica particles. This enabled characterization of coarsening kinetics by relating the evolving 3D microstructure to the time dependence of the macroscopic flow behavior with rheological measurements.

We began by investigating the dynamics of five different silica particles with diameter ranging from 5 nm to 490 nm filled polypropylene (PP) and poly(ethylene-co-vinyl acetate) (EVA) co-continuous blend which is known to breakdown into droplet-matrix blend during coarsening when not filled with particles. While particle size does not play a role on blend stability when particles are thermodynamically driven to their preferred polymer phase, a striking effect is achieved when particles are kinetically trapped at the interface. We find that the interparticle interaction, driven by smaller interparticle distance governs their extent of agglomeration and consequently their ability to stabilize co-continuous morphology. Strikingly, the largest (490 nm) particles are more effective in suppressing coarsening than 5 nm and 60 nm particles, while 140 nm and 250 nm particles are

most effective. Furthermore, we demonstrate that migration of primary particles of any size is influenced by the interplay of interfacial folding during melt blending and Laplacian pressure exerted by a highly curved, newly created, interface. On the other hand, the large agglomerates localized in the thermodynamically preferred polymer phase.

In the second part of the study, we introduce the most effective particles (140 nm and 250 nm) in the blends under different loading ratios to simulate polydispersity in four different blends based on PP (or polyethylene, PE) and EVA. Different grades of PP (or PE) and EVA are carefully chosen as model polymers blends with different properties, viz., zero shear viscosity, interfacial tension, and viscosity ratio between components under processing conditions and at rest. As such the driving force (ratio between interfacial tension and viscosity, Γ/η) for coarsening in these blends is different. We find that polydispersity in particle size do not negatively affect the blend stability, it can be used as an additional tuning parameter. The efficacy of the particles to suppress the coarsening is dependent on the zero-shear viscosity of the blends. Lower viscosity blends can coarsen to a greater extent before particles can percolate at the interface. Further, the increase of elasticity in blends has a dependence on final blend morphology, and Γ/η ratio. Blend with lowest Γ/η ratio has higher interfacial area and hence the corresponding network of particles formed on the interface are weaker yielding a lower growth in elasticity. As such, the blend elasticity is determined to be more susceptible to the morphology of blends than component properties. Blends of medium interfacial tension and viscosity achieved optimal structural stability and enhancement in elasticity. These results extend our fundamental understanding of the stabilization of co-continuous morphology in polymer blends by particles, providing promising new avenues for fundamental studies and applications alike.