

Rheology during Cascading Crystallization in Mixed Polyolefins: Implications for Mechanical Recycling

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The low recycling rates of post-consumer polyolefins has its origins in thermodynamics. Polyolefins typically enter the recycling stream in mixed form and are subsequently melt processed as blends. Due to thermodynamic incompatibilities, they form micro-domains and upon subsequent cooling, crystallize in a cascading fashion, frequently with poor interfacial adhesion - causing brittleness. While such cascading crystallization is critical to the final mechanical properties, it is poorly understood. For example, in an immiscible blend where both components are crystallizable, the effects of shear on the relative crystallization rates are little studied.

Here we employ multi-modal methods (rheology, Raman, x-rays and calorimetry and optical microscopy) to study the crystallization kinetics and associated rheology in immiscible blends of high-density polyethylene and isotactic polypropylene, under both quiescent and shear conditions. For interpretation of crystallization kinetics through Raman spectroscopy, we utilize multivariate curve resolution with alternating least-squares (MCR-ALS). We find strong differences in polypropylene crystallization as a function of the primary experimental variables: molar mass, composition and shear – with domain morphology playing a major role.

In the case of low molar mass compositions, we find that the quiescent iPP crystallization behaviour varies strongly with blend composition. Rheology and optical microscopy show that three crystallization kinetic regimes correspond to three underlying two-phase morphologies: HDPE droplets in iPP, the inverse, and co-continuous structures. In the HDPE droplet regime, iPP crystallization temperatures decrease sharply with increasing HDPE composition¹. We show that partial melting rheology is a powerful method to assess domain continuity of the high melting point component (polypropylene).

In the case of higher molar mass compositions, the crystallization temperatures of each component is less affected by composition, but more strongly affected by shear. We find unexpected composition dependence to the shear-induced crystallization behavior of the polypropylene which we attribute to domain structure and micro-flow fields.

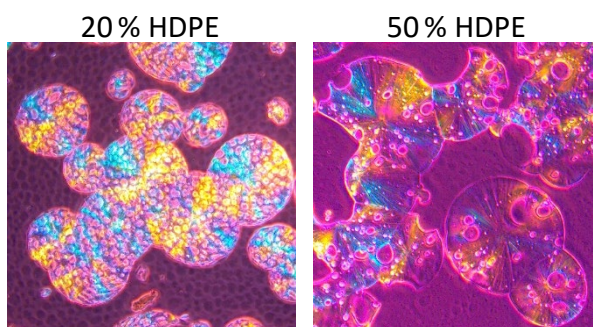


Figure 1: Optical microscopy observations of crystallization of polyethylene-polypropylene blends for two compositions. The associated rheological transformations are strongly influenced by the micro-domain kinetics.

¹ D.E. Huang et al., *Macromolecules*. **55**, 10921 (2022).