Crystallization Kinetics in an Immiscible Polyolefin Blend

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ABSTRACT: Motivated by the problem of brittle mechanical behavior in recycled blends of high density polyethylene (HDPE) and isotactic polypropylene (iPP), we employ optical microscopy, rheo-Raman, and differential scanning calorimetry (DSC) to measure the composition dependence of their crystallization kinetics. Raman spectra are analyzed via multivariate curve resolution with alternating least-squares (MCR-ALS) to provide component crystallization values. We find that iPP crystallization behavior varies strongly with blend composition. Optical microscopy shows that three crystallization kinetic



regimes correspond to three underlying two-phase morphologies: HDPE droplets in iPP, the inverse, and cocontinuous structures. In the HDPE droplet regime, iPP crystallization temperature decreases sharply with increasing HDPE composition. For cocontinuous morphologies, iPP crystallization is delayed, but the onset temperature changes little with the exact blend composition. In the iPP droplet regime, the two components crystallize nearly concurrently. Rheological measurements are consistent with these observations. DSC indicates that the enthalpy of crystallization of the blends is less than the weighted values of the individual components, providing a possible clue for the decreased iPP crystallization temperatures.

INTRODUCTION

Polyethylene (PE) and polypropylene (PP) are the two most abundantly produced polymers today, accounting for over half of all plastic production worldwide.^{1,2} Products made from high-density polyethylene (HDPE) and isotactic polypropylene (iPP) are frequently found together in mixed-waste streams, and their similar hydrocarbon backbone and densities make them difficult to separate at industrial scale.^{3–6} As a result, strategies to combine the two materials in recycled products are of great interest for sustainability and economic reasons. Unfortunately, the two polymers are immiscible, leading to phase separation with poor interfacial adhesion.^{4,7,8} Composites formed from PP/PE blends often have poor mechanical properties such as brittleness and low peel and impact strength.^{3,9–11}

Efforts to improve the mechanical properties of polyolefin blends have centered around the control of molar mass distribution and the addition of compatibilizers.^{3,5,11,12} Notably, Eagan and co-workers¹¹ have utilized tetrablock compatibilizers to achieve tensile properties comparable to those of the individual homopolymers at low compatibilizer concentrations. In uncompatibilized blends, recent work by Macosko et al.¹³ has shown that elongation at break comparable to that in pure homopolymers can be achieved by blending metallocene homopolymers with more tightly controlled molar mass distributions. Interfacial structure and adhesion between immiscible domains is believed to play an important role in these systems. These efforts indicate important progress toward the goal of polyolefin recyclates with improved properties.

While the melt-processing of such blends can influence mechanical properties, the relationships between melt domain structure, rheology, and crystallization kinetics are still not well understood. The internal microstructure of PE-iPP blends is set by a wide variety of factors, including blend composition,¹⁴ molecular architecture, viscosity ratio,^{15,16} mechanical and melt processing,^{5,17} imposed flow,^{18–20} and additives such as compatibilizers.^{3,12,21} These in turn affect the crystallization kinetics and the final properties of a blended product.

In previous studies of crystallization kinetics in PE-iPP blends, there have been conflicting reports of the crystallization behaviors, which are often more complex than the sum of the kinetics of the pure components. Nucleation at the interface between the two components has been observed via thermal methods. Some studies have shown that HDPE retards the crystallization of the iPP,²²⁻²⁴ but other studies have found little influence of added HDPE on the crystallization of iPP.^{6,14,24} This discrepancy may be due to several interrelated phenomena. Teh and co-workers^{25,26} have postulated that finite-size effects cause suppression of nucleation in discrete droplets because of fractionated crystallization,²⁷ whereby there are more droplets than active nucleation agents, suppressing crystallization until lower temperatures, or even causing homogeneous crystallization. Bartczak et al.²⁸ as well as Carmeli et al.²⁹ have postulated that active nucleation agents migrate from the iPP phase to the PE during the mixing process, thus delaying iPP crystallization. Finally, Li and

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Shanks et al.^{24,30} have invoked partial miscibility to explain suppression of nucleation of iPP in linear low-density polyethylene (LLDPE).

We argue that a multimodal approach capable of capturing both melt state and crystallization behavior is needed to address these phenomena. The workhorse methods in the literature for kinetic studies of multicomponent crystallization are differential scanning calorimetry (DSC) and polarized optical microscopy. A critical gap is the determination of crystallization of each individual component during the process. A second gap is the measurement of the melt domain structure prior to the crystallization process, and a third is the general need to integrate across measurement modalities.

In this work, we use the rheo-Raman microscope in addition to the above two methodologies. The ability to carry out simultaneous measurements of rheology and Raman spectroscopy has proven useful in development of crystallization models in single component homopolymers.³¹ Raman spectroscopy is a well-established, noninvasive method of estimating the crystallinity of semicrystalline homopolymers.^{32,33} More recently, Raman spectroscopy was used to measure the crystallization kinetics of single-component systems.^{31,34,35} However, there are no reports of quantitative crystallization measurements in blends where two (or more) components crystallize.^{36–38} The challenge here for traditional peak-fitting analyses of Raman spectra is the simultaneous measurement of partially overlapping peaks. Here, we propose a measurement of the crystallization kinetics through multivariate curve resolution with alternating least-squares (MCR-ALS).^{39,40}

Rheological measurements are a useful tool for probing crystallization because the modulus increases by orders of magnitude as molten polymer solidifies.⁴¹⁻⁴³ In the context of processing, knowledge of the transient modulus at any point in a process line is critical to design and control. In the case of recyclate processing with multiple crystallizing species, such knowledge may be more critical, as industrial processes are typically designed for crystallization to occur at a single location in the line. In the two-component system of HDPE and iPP, Teh et al.^{25,26} successfully measured modulus increase, though without concomitant measure of crystallinity. Rheo-Raman can provide the needed information on crystallization. In single component systems, rheo-Raman has been used to show that the increase in modulus during crystallization occurs via percolation,^{31,35} and later in iPP it was shown via simultaneous rheology and microscopy that the percolation is caused by impinging spherulitic superstructures.44

We utilize the above multimodal techniques to examine the composition dependence of crystallization of an HDPE-iPP blend during fixed-rate cooling. We observe a multitude of phenomena, maintaining attention on the changes in crystallization across the composition space. By combining insights from the four measurement modalities, we consider several arguments in the literature that have been advanced to explain such results. Melt domain morphology, along with an additional compositional effect in the melt state, emerges as the primary driver behind these effects.

EXPERIMENTAL SECTION

Sample Preparation. The HDPE used in this study is NIST SRM 1475, a linear HDPE with a mass-average molar mass of 53 000 g/mol and dispersity (D) of 2.9, with pentaerythritol tetrakis(3,5-

ditert-butyl-4-hydroxyhydrocinnamate) (Irganox 1010) present as an antioxidant. Melt processing did not alter this to a significant extent. The iPP used in this study was manufactured by Braskem and is commercially known as F1000HC, a high-crystallinity iPP. It does not contain externally added nucleating agents, though residual catalyst and additives are known to nucleate crystallization.⁴⁵ The polymer was received in pellet form with added antioxidants, and the massaverage molar mass measured via gel permeation chromatography (GPC) was 143 300 g/mol with D = 5.4. However, after melt processing, an extruded sample of 100% iPP (F1000HC) was measured via GPC to have a mass-average molar mass of 93 300 g/ mol and D = 3.9. Molar masses were determined through gel permeation chromatography measurements on the polymer dissolved in 1,2,4-trichlorobenzene, to within an uncertainty of 10%. Samples were prepared from HDPE and/or iPP by mixing in a twin-screw compounder manufactured by Daca Instruments. Pellets of HDPE and iPP were blended in the compounder at 210 °C and 300 rpm $(10\pi \text{ rad/s})$ for 5 min and then extruded as a long fiber that was cut into short segments. Blends were prepared at a full range of HDPE/ iPP compositions in 10% increments.

Rheology and Raman Spectroscopy. The primary instrument used in this study is the rheo-Raman-microscope (Thermo-Fisher), which is capable of simultaneously measuring rheology, optical microscopy, and Raman spectroscopy. Sample segments were melted in the rheo-Raman-microscope at 200 °C. The 8 mm parallel-plate upper geometry was lowered to 600 μ m, the sample was trimmed, and the gap further lowered to a measurement height of 500 μ m. The sample was sheared at a rate of 1 s^{-1} at 200 $^\circ C$ for 5 min to provide a consistent shear history to all samples while annealing. After annealing, the sample was (a) cooled at 5 °C/min to 160 °C, (b) cooled at 1 °C/min to 80 °C, (c) heated at 5 °C/min to 120 °C, and (d) finally heated at 1 °C/min to 180 °C. Oscillatory shear rheometry was performed during steps (a) and (b) at frequency 1 s^{-1} and amplitude $\gamma = 0.01$; when the elastic modulus exceeded a threshold value of $G' > 10^6$ Pa, the amplitude was reduced to $\gamma = 0.0025$ to prevent separation from the parallel plate. The temperature data during cooling were corrected via comparison with temperatures measured by a digital thermometer (Fluke 51 II, temperature uncertainty within 0.3 °C) during cooling of polyphenylmethylsiloxane (PPMS) from 200 to 80 °C. Concurrently with the rheological measurements, Raman spectra were measured (spectral resolution = 4 cm⁻¹) with a 532 nm excitation laser at a power of 10 mW, at an interval of 16 s.

The shear step at 200 °C deserves additional comment. In a typical single-component crystallization experiment, one typically holds the sample well above the melting point without shear in order to erase melt memory. However, in the case of a two-component immiscible blend, the situation is more complex. One must consider the multicomponent blend morphology, which undergoes coalescence during annealing. Shearing flow tends to counter droplet coalescence. Additionally, one desires a consistent starting morphology from run to run and a consistent protocol between compositions. We thus impose a shearing step at high temperature, near the point where temperature can erase flow-induced crystallization, as a balance between the need for a consistent morphology without undue coalescence and the need for minimal flow-induced crystallization. We further note that we observe no flow-induced crystallization at these shear rates, though flow-induced crystallization is beyond the scope of this manuscript.

Optical Microscopy. To visualize domain morphology and crystallization at the μ m to mm length scale, we use transmission optical microscopy with simultaneous phase contrast and crossed polarization optics. (This approach necessitates measurements with a separate optical microscope—not the one on the rheo-Raman microscope.) The measurements were conducted in a shear cell (Linkam Scientific Instruments, CSS 450): samples were heated to 200 °C, cooled to 160 °C at 5 °C/min, and cooled to 100 °C at 1 °C/min. The phase contrast optics provide optical contrast between the two polyolefin components due to the difference between their refractive indices while in the melt state. The polymers are birefringent in the crystalline state, so polarization optics provide a



Figure 1. Raman spectra in the (700 to 1600) cm⁻¹ wavenumber range, at temperatures ranging from 140 to 100 °C, for (a) 100% iPP, (b) 100% HDPE, and (c) a 50% HDPE–50% iPP blend.

means to visualize crystallization: we use a first-order retardation plate (530 nm) that provides information on the local alignment of the polymer. The retardation plate plays a second role. In the melt state, when the sample is optically isotropic, the crossed polarizers alone would block transmission of the light. The retardation plate rotates polarization of the light, causing the red and blue hues to pass through the crossed polarizers and allowing imaging of the melt state structure in a magenta hue. For the phase-contrast images presented, the sample thickness is 20 μ m. This is considerably thinner than the sample width used in the rheo-Raman microscope. We choose this thickness because it allows for more facile visualization of the domain structures, although there may be some thickness-dependent effects. For the nucleation density measurements, the sample thickness is 200 μ m.

Differential Scanning Calorimetry (DSC). DSC measurements were performed on a TA Instruments DSC2500 calorimeter equipped with a mechanical intracooler under a nitrogen atmosphere purge. Samples were (a) heated to 200 °C and held at temperature for 5 min, (b) cooled to 160 °C at 5 °C/min, (c) cooled to 40 °C at 1 °C/min, (d) heated to 120 °C at 5 °C/min, and then (e) heated to 180 °C at 1 °C/min. Calibrations were performed according to manufacturer specifications.

Raman Analysis through Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS). The percent crystallinity of each component is determined through multivariate curve resolution with alternating least-squares (MCR-ALS) of Raman spectra. Figure 1 shows Raman spectra for iPP (panel a), HDPE (panel b), and a 50/50 by mass fraction HDPE-iPP blend (panel c) at various temperatures as they are cooled from 140 to 100 °C. All three samples show significant change in their Raman spectra as the polymers crystallize. In the iPP sample, the (780 to 860) cm⁻¹ region changes from a broad peak to two narrow peaks as the temperature drops from 135 to 130 °C (highlighted in the red box). This is associated with the formation of helical chains^{33,47} as iPP crystallizes. In the HDPE sample, prominent changes are seen in the (1025 to 1150) cm⁻¹ (C–C stretching), (1250 to 1350) cm⁻¹ (CH₂ twisting), and (1400 to 1500) cm⁻¹ (CH₂ bending) regions, associated with the formation of an orthorhombic crystal structure, as highlighted in the blue boxes. The CH₂ twisting peak shifts to a sharper peak at lower wavenumbers, and the C–C stretching and CH₂ bending peaks split into peaks representing in-phase and out-of-phase vibrational modes.³² In the blended sample (Figure 1c), crystallization peaks from each sample are visible. Between 130 and 125 °C, one sees growth of peaks associated with iPP (red rectangles), while, between 125 and 120 °C, one can see peaks associated with HDPE crystallization (blue rectangles). While peak fitting methods can be used to establish the percent crystallinity of the pure components, there is significant overlap between peaks in the spectra of HDPE and iPP, particularly in the (1400 to 1500) cm⁻¹ region, where strong peaks that change upon crystallization occur in both the HDPE and iPP spectra. It is therefore not possible to apply this method directly to analyze the Raman spectra of HDPE-iPP blends.

We instead determine percent crystallinity of each component in the blend by deconvoluting the blend spectra into their individual components through multivariate curve resolution with alternating least-squares (MCR-ALS) using a publicly available toolbox developed by Jaumot et al.^{39,40} for Matlab. In this method, we first apply a background correction to remove contributions from artifacts such as fluorescence via asymmetrically reweighted penalized least-squares smoothing (arPLS).⁴⁸ Next, we normalize the spectra using the standard normal variate (SNV) method, where each spectrum is normalized with respect to its standard deviation, to remove multiplicative effects from changes in light scattering due to phase changes. The normalized, baseline-corrected spectra from a single cooling experiment are then input into the toolbox over the range of temperatures where crystallization occurs, typically from 150 to 80 °C. We further input four experimentally measured single-component spectra: (i) HDPE in the molten state at 150 °C; (ii) HDPE in the semicrystalline state at 80 °C; (iii) molten iPP at 150 °C; (iv) semicrystalline iPP at 80 °C and specify the output to contain 4 component spectra. MCR-ALS is able to identify these singlecomponent spectra as the four basis spectra, and for each input spectrum, it determines the relative weightings (abundance) of the basis spectra. The accuracy of this method for estimating crystallinity

was compared with measurements from DSC melting experiments; final crystallinity measured via DSC was 59.1% with an uncertainty of $\pm 0.1\%$ for iPP and 66.9% $\pm 0.1\%$ for HDPE. This compares similarly to the final crystallinity determined via MCR-ALS and subsequent peak-fitting, which yielded 59% crystallinity for pure iPP and 72% crystallinity for pure HDPE.

We demonstrate this method on a 50% HDPE-50% iPP blend; the spectra from a cooling experiment performed on a 50–50 blend, with the four single-component spectra appended, were analyzed via MCR-ALS, which generated the four basis spectra displayed in Figure 2a.



Figure 2. (a) Input basis spectra: contributions from semicrystalline HDPE, amorphous HDPE, semicrystalline iPP, and amorphous iPP. (b) Raman spectrum of 50/50 HDPE-iPP blend at 126 $^{\circ}$ C (dotted line), overlaid with MCR-ALS fit (solid line).

Through visual inspection, one can match each spectral component to one of the four primary single composition spectra of Figure 1(a–b) (corresponding to molten and semicrystalline HDPE and iPP); the spectral components are so labeled. In Figure 2b we graph the experimental spectrum at 126 °C and list the relative weightings determined by MCR-ALS for the basis spectra. The weightings show that at this temperature, the iPP has largely solidified, but the HDPE in the blend remains molten. The weighted, summed contributions of the basis spectra are plotted in red in panel (a), nearly overlapping with the original experimental spectrum and demonstrating the applicability of MCR-ALS in fitting Raman spectra of HDPE-iPP blends to ascertain the amorphous and crystalline contributions of each component. The crystallinity (crystalline mass fraction) of the HDPE phases are then determined by summing the weighted semicrystalline and molten HDPE spectral contributions and computing the ratio of the intensity of the crystalline peak at 1416 cm⁻¹ to the total intensity of the twisting vibration peaks near 1300 cm⁻¹, following the method of Strobl and Hagedorn.³² Similarly, the crystallinity of the iPP phases was determined by combining the weighted semicrystalline and molten iPP spectra and computing the intensity of the 808 cm⁻¹ peak relative to the total integrated intensity from 780 to 880 cm⁻¹.³³ Performing this analysis on each input spectrum from a cooling run allows monitoring of crystallinity within each phase as a function of temperature.

RESULTS

In this section, we show the results of our cooling experiments, where we heat our blended samples to 200 $^{\circ}$ C, cool the samples at 5 $^{\circ}$ C/min to 160 $^{\circ}$ C, and subsequently cool at 1 $^{\circ}$ C/min to 80 $^{\circ}$ C to induce crystallization, as described in the Rheology and Raman spectroscopy subsection. At all blend compositions and temperatures, the HDPE and iPP are immiscible, and the size and shape of the melt domains are a function of composition and melt processing (i.e., compounding during blend preparation and coalescence during subsequent melting). These composition- and processing dependent factors strongly impact the crystallization kinetics, as we will show.

Rheo-Raman and DSC. In Figure 3, we show the complex modulus, the crystallinity of each component, and the normalized heat flow for the case of a 20% HDPE-80% iPP blend. The crystallinity is determined from the Raman spectra by the methods described above. Note the clear separation in temperature between the onset of crystallization in the iPP phase and that of the HDPE. Two separate crystallization processes are clearly reflected in the DSC results as well, though a priori one cannot ascertain if a given peak is from iPP or from HDPE. On the other hand, the transient modulus seems to show a single increase that is associated with the iPP crystallization-there is little sign of an upturn associated with the HDPE crystallization. We thus additionally plot $tan(\delta) =$ G''/G', which shows a weak upturn near the point of HDPE crystallization. The dashed line at a temperature of T = 133 °C shows that the upturn in iPP crystallinity is observed before that of modulus; we return to this point later. Because the rheo-Raman measurements are performed in a different apparatus than the DSC, and there are inevitable differences in sample thickness, wall surface chemistry, and thermal lags, we do not compare exact transition temperature between the methods. Given the above caveats, there is very good agreement between the three modalities.

In Figures 4–6, we show the evolution of crystallinity, rheology, and heat flow with temperature over the full range of compositions. Figure 4 shows crystallinity measured from Raman spectra for the iPP, HDPE, and the mass-averaged crystallinity over all phases, $X_{c,tot} = x_{PE} X_{c,PE} + x_{iPP} X_{c,iPP}$, where x_{PE} is the mass fraction of HDPE within a mixture and x_{iPP} is the mass fraction of iPP. The total crystallinity, $X_{c,tot}$, is shown in the bottom panel of Figure 4 to provide a sense of when the process can be viewed as a one- or two-step process. In the range of 10% to 30% HDPE, there exist two distinct upturns in crystallinity as temperature decreases, separated by plateaus. For the cases of 40% and 50% HDPE, we observe an increase



Figure 3. Blend of 20% HDPE-80% iPP cooled at 1 °C/min. Top: Rheology $|G^*|$ and tan δ as a function of temperature. Middle: masspercent crystallinity of PE and iPP phases, measured from Raman spectra. Error bars omitted for clarity; uncertainty is ±0.05. Bottom: DSC trace (separate experiment); the endotherm direction is up.

in crystallinity associated with the iPP crystallization, followed by a shoulder at the point of the HDPE crystallization. Additionally, the iPP crystallization temperature plateaus briefly before decreasing again as HDPE content is increased to 60%. Finally, for HDPE concentrations of 70% and above, $X_{c,tot}$ by itself does not indicate two separate processes.

In Figure 5, we examine G^* and $tan(\delta)$ during crystallization over the range of compositions and we observe several of the same trends as seen in the crystallization measurements via Raman-in particular, an overall decrease in the temperature at which the samples transition from viscoelastic liquid to viscoelastic solid. This can again be divided into three distinct kinetic behaviors that depend on the initial blend composition: (1) from 0% to 30% HDPE, there is a steady decrease in the transition temperature, (2) between 40% and 50% HDPE, the curves nearly overlap, and (3) at higher HDPE concentrations, there is a plateau at lower temperatures. The onset of crystallinity from the Raman measurements precedes that of the rheological transition across the range of concentrations. Previously, it was remarked that the $tan(\delta)$ curve for the 20% HDPE blend shows a weak upturn at the HDPE crystallization point; now that effect is seen from 20% to 60% HDPE and most strongly for the 50% blend.



Figure 4. Crystalline mass fraction X_c of iPP (top), HDPE (middle), and mass-averaged total crystallinity (bottom), measured from Raman spectra of sample cooled at 1 °C/min. Uncertainty of Ramandetermined crystallinity X_c is ±0.05 for HDPE and up to ±0.1 for iPP; error bars have been omitted for clarity.

The relationship between crystallinity and transient modulus can be understood by considering the nonlinear relationship between these two parameters during crystallization of single component systems, such as iPP and PCL.^{31,44,49} In these systems, the largest upturn in modulus occurs during the percolation transition when discrete crystallizing entities such as spherulites impinge on each other. In the curves with 10% to 50% HDPE, the HDPE begins to crystallize after the primary rheological upturn, thus after percolation. The ensuing crystallization of HDPE causes only a modest increase in the log of the modulus and, thus, is not easily discerned. The second phenomenon noted above regarding the upturn of crystallinity before modulus is also seen in the singlecomponent cases and can also be ascribed to the nonlinearity of this relationship as well. In this case, it occurs during the prepercolation stage, where there is significant crystallinity, but the crystallizing entities are discrete and thus contribute little to the log of the modulus.

The DSC crystallization curves in Figure 6 reinforce the trends seen in the Raman spectra and rheology concerning the depression of crystallization for the iPP and the weaker effect for the HDPE. A primary advantage here of DSC over Raman spectroscopic measurements of crystallinity is its superior signal-to-noise ratio allowing for smaller effects to be measured. For the lower HDPE concentrations, two separate peaks are observed, and we associate the higher temperature



Figure 5. (Top) Complex modulus, $|G^*|$, and (bottom) damping factor, tan δ , versus temperature, during cooling.



Figure 6. DSC traces during 1 °C/min cooling ramps of HDPE-iPP blends. The endotherm direction is up.

one with the iPP and the lower with HDPE. For the HDPE concentrations from 0% to 30%, one again observes the depression of iPP crystallization with increasing concentration. For the intermediate range from 40% to 60%, we observe a transitional behavior: the iPP and HDPE crystallization exotherms merge, with the iPP crystallization peak visible as a shoulder to the right of the sharp HDPE crystallization peak. In this intermediate composition range, the downward trend in iPP crystallization temperature stops. As the HDPE content is increased to 70%, a phase inversion occurs; in this majority-

HDPE composition range, the iPP crystallization exotherm suddenly shifts farther left and can no longer be discerned from that of HDPE. The crystallization behavior in these three separate composition ranges can be directly correlated with the domain structure, which we will show later through polarized optical microscopy.

For the pure components, we note a consistency in the results between the Raman and the DSC. The DSC results show an asymmetric extended tail in the HDPE peak of the heat flow trace at temperatures below the peak, while the iPP shows a more symmetric peak without such a tail. An analogous effect is seen in the Raman-derived crystallinity for the two pure components where the iPP crystallinity is flat after the initial rise, whereas the HDPE shows a continued increase with decreasing temperature. These suggest that secondary crystallization effects are much slower or weaker in the iPP than HDPE.

Optical Microscopy. In this section, we show and discuss the phase-contrast polarized optical microscopy images taken during cooling of HDPE-iPP blends, in the manner described above in the Optical Microscopy subsection of the Experimental Section. As previously noted, the sample thickness is reduced to 20 μ m to visually distinguish the different liquid domains of HDPE and iPP, although we note this thickness may lead to confinement effects on the domain morphology and crystallization kinetics. We also performed optical microscopy experiments with a sample thickness of 200 μ m to measure spherulite concentration during cooling; these images are shown later, although the larger sample thickness means the liquid domains are not clearly distinguished. More phase-contrast optical microscopy images taken over the full range of compositions are further included in the Supporting Information.

Figure 7 shows how phase contrast with simultaneous polarization optical microscopy provides crucial structural information at μm to mm length scales. For the case of a 30% HDPE in 70% iPP, we expect by volume fraction arguments that the morphology consists of HDPE droplets in an iPP matrix, the size of which is dictated by the polymers' melt viscosity and processing factors such as compounding and later coalescence. At T = 140 °C, we see the melt-state structure, consisting of darker HDPE droplets in the lighter matrix. At T = 128 °C, crystallization has commenced. We observe an engulfment phenomenon whereby the iPP crystallizes around molten HDPE, leaving behind spherulites that are filled with droplets of molten HDPE; these molten droplets are the circular purple objects in the spherulites. Eventually, the spherulites impinge and form a space-filling superstructure. At lower temperatures, the HDPE crystallizes-while the images at this point lose clarity, it can be observed in the T = 120 °C image that the droplets from the two higher temperature images are no longer purple; some show up as white. This is consistent with crystallization of the HDPE.

The 50% HDPE–50% iPP blend is expected to consist of more complex cocontinuous and hierarchical structures. The melt-state images at T = 140 °C show this complexity (Figure 7): the overall domain size is significantly larger than in the droplet state. A primary reason for the increase in domain size comes from coarsening. Recall that our procedure is to slowly ramp down the temperature at zero shear rate from the initial temperature of T = 200 °C. It is observed (not shown here) that coarsening (i.e., droplet coalescence) due to interfacial tension effects occurs during this time, and that this effect is

Figure 8. Three leftmost images show crystallization of a 50–50 blend during cooling to T = 120 °C. The rightmost image shows subsequent heating to T = 150 °C. Sample thickness: 20 μ m.

more pronounced in these complex morphologies. Also, droplets of HDPE (darker) in iPP (lighter) are visible, and vice versa. As crystallization proceeds, we observe engulfment of HDPE droplets as before, but also that the larger HDPE domains cause large-scale distortions of the overall shape of the spherulites. This effect can be anticipated when the size of a spherulite and the size of a domain become comparable. (Figure 8 explores the kinetics at 50% HDPE–50% iPP in

further detail.) The 60% HDPE-40% iPP blend shows a hybrid structure—examining the T = 140 °C melt structure shows that parts of the sample consist of iPP droplets in HDPE while other parts show extended iPP domains. At T = 125 °C, we observe that iPP domains are beginning to crystallize; the HDPE is also showing the first signs of crystallization. These extended domains do not fully crystallize before the HDPE crystallization event.

Figure 9. Left: Spherulite density as a function of temperature. Right: Polarized optical microscopy images of iPP, 20% HDPE, 50% HDPE, and 70% HDPE during cooling as iPP spherulites grow. Sample thickness: 200 μ m.

Finally, the HDPE 70%-30% iPP blend shows a phase inversion over the full sample; in the melt state, HDPE (darker) becomes the major component with suspended iPP droplets. The images at T = 125.5 °C show the overall suppression of the iPP crystallization when in its droplet state, consistent with observations from rheology, Raman, and DSC. However, note the single white circular object at these temperatures. Video observation shows that this is a single iPP droplet which has crystallized (it appears as white due to saturation of the digital image). The crystallization of this droplet is likely attributable to a large nucleation site present in that droplet. In this morphology, the iPP is confined to discrete droplets and so the crystallization cannot extend beyond the droplet that crystallized. Such droplet individuality has been observed previously where the droplet was crystallizable and the matrix was not.^{27,50}

The 50% HDPE-50% iPP blend images demonstrate the relationship between liquid domain morphology and crystallization kinetics. Figure 8 shows a region of the sample where there is a large, irregular HDPE droplet on the left side of the image (black arrow), containing smaller iPP droplets within. The remainder of the image shows a continuous iPP region which contains HDPE droplets. As the temperature decreases, there are several points of iPP nucleation, and the spherulitic crystals from these nucleation sites surround the irregular HDPE droplet. While most of the iPP from the continuous region has crystallized by T = 127 °C, none of the iPP inside the irregular HDPE droplet has crystallized. We subsequently cool the sample to 120 °C before heating to 150 °C, as shown, which melts the HDPE while maintaining the iPP in its crystalline state. The purple corresponds to the molten HDPE, and the other colors to the iPP; this confirms the stated assignments within the images and also shows that the iPP droplets do crystallize, but at lower temperatures than the continuous regions. This demonstrates in one sample that iPP in a continuous phase can nucleate spherulites that then propagate through the sample, whereas iPP in droplet domains does not crystallize until lower temperatures.

The cause of the retarded iPP crystallization can be further studied by examining the nucleation density. The images in Figure 7 show fewer spherulites as HDPE concentration increases, and the growth in spherulite concentration can be estimated through visual inspection by counting the number of spherulites within the known volume within each image. We quantify this effect in the left panel of Figure 9, where we plot the density of the spherulites during the crystallization process as a function of temperature for four selected compositions. The discrete steps at the lower densities are not physical; this is a counting artifact that occurs when there are fewer than roughly 5 spherulites in a given image. As the mass fraction of iPP is reduced from 100% to 50%, the final density of iPP spherulites is reduced by 2 orders of magnitude. In the right panel of Figure 9, we show more polarized optical microscopy images of iPP and HDPE-iPP blends midway through the cooling process; the dramatically lowered density of spherulites as HDPE content is increased means that each iPP spherulite must grow to a much larger size before it encounters other crystalline domains to form a space-spanning network.

Discussion. We focus our attention mainly on the iPP crystallization temperature, as it is observed to change by approximately 15 °C over the range of compositions whereas the HDPE crystallization temperature changes by approximately 1 °C. In order to understand the crystallization kinetics of the iPP, we invoke two separate phenomena, the first related to blend concentration and the second one related to blend morphology. The effects can be considered by constructing a map (Figure 10) of crystallization temperatures determined by the various modalities onto the three domain morphologies as shown in Figure 10. The crystallization temperature for the Raman-derived crystallinity is defined here as the value where the crystallinity is roughly half its value at T = 115 °C, that is $X_{c,PE} \approx 0.3$ and $X_{c,PP} \approx 0.3$. For the rheology, it is defined as the temperature at which tan $\delta = 1$. While there is some arbitrariness in these selections, the trends will be the same regardless of the particular selection of values. For the DSC

Figure 10. (a) Temperature of crystallization for iPP and HDPE, as measured by Raman spectra, and temperature at which tan δ drops below unity, as a function of composition. (b) Temperature at peak heat flow for HDPE and iPP, measured via DSC.

curve, the HDPE and iPP are shown separately in the lower HDPE concentration cases where they are separable.

At low HDPE concentrations-where the blend consists of HDPE droplets suspended in an iPP matrix-the iPP crystallization temperature drops sharply with HDPE concentration. Because iPP is the matrix, fractionated crystallization arguments are not applicable. As shown in Figure 9, there is a significant drop in iPP nucleation density from the 0% HDPE sample to the 20%. One factor in this drop is the simple fact that the concentration of iPP (and hence iPP nucleating agents) is reduced due to the presence of HDPE. From this argument, one would expect that at, say, 20% HDPE concentration, the nucleation density of the iPP drops by approximately that amount. However, the observed effect is much stronger. For example, in comparing the 0% HDPE with the 20% HDPE, there is a reduction in spherulite density by nearly 2 orders of magnitude, indicating a comparable drop in nucleation rate.

Clearly, a different mechanism must be invoked to explain this result. We consider two possible mechanisms, which can both result from considering the actual composition of each phase in the blend. The first mechanism considered nucleating agents originally present in the iPP phase that migrate to the HDPE phase during mixing.²⁸ Direct evidence of this migration was not presented. The second mechanism involves trace miscibility between the components, which has been invoked to explain reduced crystallization in related systems namely, iPP blended with LLDPE—but not with HDPE. Thermodynamically, HDPE and iPP are expected to be immiscible; their χ interaction parameter has been both measured and calculated to be 0.02 or greater,^{51–53} which indicates that the two components are immiscible at the molar masses used in this study. In the present work, we confirm immiscibility by phase contrast optical microscopy in the melt state (Figure 7), which shows separate HDPE and iPP components. However, in an immiscible blend, each phase has a minority component and there is necessarily some trace HDPE in the iPP phase, and vice versa. Trace amounts of HDPE chains could inhibit the nucleation of iPP spherulites.

The second type of morphology is cocontinuous, occurring near 50-50 compositions. These cocontinuous morphologies are set by melt processing (both initial compounding and later coarsening) and are highly complex-one observes HDPE domains in iPP and vice versa, and elongated domains-and this complexity is reflected at the microscale in the crystallization process as seen in Figures 7 and 8. The morphology hinders the propagation of the spherulites that emanate from the reduced number of nucleation sites. Thus, in this case, the HDPE serves to both reduce nucleation and hinder growth through morphological complexity. In terms of the macroscale measurands of heat flow, Raman based crystallinity, and modulus, they represent averages over this microscale complexity. The end result is a reduction of crystallization temperature compared to those of HDPE droplet morphologies, as well as a plateau of the iPP crystallization temperatures as a function of composition in cocontinuous morphologies. This plateauing of the iPP crystallization temperature appears in both rheo-Raman (Figure 5) and DSC (Figure 6), and it may be due to increased local variance in composition when HDPE and iPP are cocontinuous, and therefore less dependence of crystallization kinetics on the overall composition in this cocontinuous region. It was noted above that the 60% HDPE-40% iPP blend is a hybrid microstructure, and this seems to be represented here by its intermediate temperature transition values.

The third morphology occurs at higher HDPE concentrations and consists of iPP droplets in an HDPE matrix. Here, the iPP crystallization temperature drops by several more degrees (Figure 10). In the literature, the crystallization of polymer droplets has been associated with fractionated crystallization, whereby there are more droplets than active nucleating agents, and so crystallization is suppressed. In many cases, it is suppressed until it occurs at much lower temperatures via homogeneous nucleation.^{27,50} In the current work, the iPP does not crystallize by homogeneous nucleation because the temperature of iPP crystallization is too high. For example, in the case of iPP/PCL blend crystallization where fractionated crystallization of iPP is believed to occur, the iPP crystallizes at temperatures as much as 70 °C lower than found here.⁵⁰ The much smaller reduction in crystallization onset temperature we observe suggests that nucleation sites exist in high enough concentrations to induce heterogeneous crystallization at most compositions, and for suspended-iPP morphologies, crystalline HDPE may also act as a nucleation site for iPP droplets.

Nevertheless, the iPP droplet morphology plays an important role in the further retardation of iPP crystallization relative to the cocontinuous and the HDPE droplet

Figure 11. (a) DSC traces during 1 °C/min heating ramps of HDPE-iPP blends after crystallization (Figure 6). The endotherm direction is up. (b) Enthalpy of melting as a function of composition. The uncertainty on all ΔH_m values is ±3%.

morphologies. This can be understood by comparing the density of iPP droplets to the density of iPP spherulites. The density of iPP droplets in the 70% HDPE sample at 140 °C can be estimated from Figure 7 to be on the order of 1×10^{-5} μ m⁻³. In comparison, the density of active nucleation sites at comparable concentrations and temperatures is seen from Figure 9 to be 2 orders of magnitude less. Thus, at temperatures above that of the HDPE crystallization, there are more droplets than active nucleation sites, and therefore, the crystallization of iPP is delayed. Furthermore, unlike the cocontinuous or iPP matrix morphologies, if the iPP nucleates in a droplet, the resulting spherulite cannot propagate throughout the sample.

While the crystallization of iPP is clearly retarded by increasing quantities of HDPE, we briefly consider the opposite case-the effect of iPP on the crystallization of HDPE. The crystallization as determined by Raman (Figures 4b and 10) shows that HDPE crystallizes at slightly higher temperatures for increasing amounts of iPP, with a total temperature increase of approximately 1.5 °C. As the iPP mainly crystallizes first, this is likely a templating effect whereby the iPP crystallization induces crystallization in the HDPE. Plausibility for this hypothesis comes from studies showing unit cell registration between iPP and HDPE.²⁸ This is consistent with previous work by Carmeli et al. $^{29}\ \rm who$ showed a small templating effect in HDPE when mixed with an iPP that contains a nucleating agent, but did not observe it in the absence of a nucleating agent and with a demonstration of epitaxy of HDPE on crystalline iPP.

To provide possible insight into the reduced nucleation density of the iPP component, we examine the DSC melting endotherms, as shown in Figure 11. The melting endotherms are well separated between the HDPE and the iPP over the full range of compositions, with complete HDPE melting below 137 °C and iPP melting via two peaks between 160 and 175 °C that indicate the presence of low molar mass or nonisotactic chain fractions.⁵⁴ Integration of the HDPE and iPP peaks allows for a quantitative comparison of the enthalpy of melting in each fraction as shown in Figure 11b. The primary observation is that the enthalpy of melting of the iPP

is slightly less than what would be expected by the linear mixing rule derived from that pure component melting curves. For HDPE, on the other hand, the mixing rule is followed. This indicates that the percent crystallinity of the iPP is reduced by the presence of the HDPE. While HDPE and iPP are thermodynamically immiscible, as discussed,^{51,52} there nevertheless will remain a small concentration of HDPE in the iPP that may act to lower the crystallization temperature. We do not quantify that in this work, but one expects it to be a function of molar mass distribution of the two components, as high-temperature blending reduces the molar mass of the iPP component in particular. The hypothesis is that it both retards the nucleation process (leading to a reduced nucleation density and rate at a given temperature) and disrupts the crystallization process, leading to lower overall crystallinity.

CONCLUSION

We have investigated the kinetics of crystallization of HDPEiPP blends through rheo-Raman, DSC, and polarized optical microscopy. MCR-ALS allows us to identify different polymer species within Raman spectra and determine their individual crystallinity, as well as the overall crystallinity of the sample. We find that the addition of even small quantities of HDPE inhibits crystallization of iPP, and we report three iPP crystallization behaviors arising at various compositions and show that these map onto three primary morphologies. We show that there are effects responsible for the retardation of iPP crystallization; the most important is the melt state morphology, which is set by the blend composition and can further vary with factors such as the polymers' melt viscosities and the blend processing history. In our study, the formation of cocontinuous or suspended iPP droplet domain structures determined whether iPP crystallizes before HDPE. The significant retardation of iPP crystallization, beyond that expected from geometric arguments, merits further study. We suggest two possible explanations for the impurity effect: the first is mixing-induced migration of nucleation sites from the iPP to the HDPE, and the second is the low concentration of HDPE in the iPP phase, which may act to raise the barrier for

iPP nucleation. Further work will be needed to understand either mechanism.

More broadly, this work shows that, in mechanical recycling, dramatic changes arise in structure and kinetic behavior with relatively small changes in chemical composition. The richness of the problem demands a multimodal kinetic approach. This work examined the effects of a single variable—composition on melt structure, and the downstream effects of this structure on crystallization kinetics. Moving forward, strategic slices through this phase space are needed, along with an understanding of their effects on the ultimate mechanical properties. In particular, melt-state processing, molar mass distribution, and additives that change the initial melt structure are expected to strongly influence crystallization kinetics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.2c01691.

Phase-contrast polarized optical microscopy images of HDPE-iPP blends during crystallization from melt (PDF)

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Notes

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