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Crystallization Behavior of Sheared Polyamide 66

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Abstract. The application of fast scanning chip calorimetry (FSC) for analysis of sheared polyamide 66 (PA 66) provided quantitative insight to the effect of shear flow and flow-induced formation of crystallization precursors/nuclei on the subsequent crystallization in a wide range of temperatures. In the high-temperature, heterogeneous-nucleation range, there is a direct relationship between the amount of specific work supplied to the melt and the acceleration of crystallization, presumably due in part to increased nucleation density of the sheared samples. This information is directly applicable to polymer engineering applications where the formation of crystalline domains during processing often occurs at rapid-cooling conditions. Analysis of the structure at the micrometer-length scale of sheared PA 66 by polarized-light optical microscopy (POM) revealed large shish-kebab structures.

Keywords: Polymer Crystallization, Fast Scanning Calorimetry, Polyamide 66
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INTRODUCTION

Flow-Induced crystallization (FIC) is a lynchpin phenomenon that stands as a gateway to future advances in polymer engineering. Despite many research gains in FIC over the past 30 years, practical ramifications of FIC research are not common and polymer manufacturing remains more of an "art" than an applied science. [1] [2] Recent developments in fast-scanning chip calorimetry (FSC) enabled strong advances in the understanding of polymer crystallization, even at high supercooling of the melt.[1] However, so far these studies have been limited to polymer melt that has not experienced previous flow or shear loading, often melted at temperatures above the equilibrium melting temperature, intentionally destroying all flow-induced effects.

The acceleration of crystallization due to flow has been extensively studied at low supercooling by making use of the close relationship between rheology and crystallization mechanisms in FIC processes. [3] As such, the acceleration of flow-induced crystallization kinetics, including nucleation and subsequent crystal growth, have been characterized via parallel plate rheological techniques for selected polymers. [4] The chain-extended shish formed during FIC are active in subsequent crystallization mechanisms, even after a quench/re-melting cycle, provided the temperature does not exceed the equilibrium melting temperature. For engineering considerations, the leap must be made to investigate FIC behaviors at high supercooling of the melt, such as those occurring in many processing operations.

In the past decade, a renaissance has taken place in the field of quiescent polymer crystallization as researchers have established crystallization behaviors for many polymers across temperatures spanning from the glass transition temperature at high supercooling to melting temperatures, and under high heating and cooling rates. [5] These advances are largely due to the introduction of fast scanning calorimetric (FSC) techniques that can induce fast thermal cycling while sensing thermal transitions in nanogram scale polymer samples, nearly eliminating the thermal lag that limits standard DSC.

The combined effects of shearing time (τ_s), shearing rate ($\dot{\gamma}$), and temperature of the melt (Tm) drive the magnitude of FIC observed in the crystallization process. Considering these factors, several studies have quantified the role of

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"specific work" (W) during flow as the determining factor that drives the FIC process. [6] [7] [8] [9] The equation for specific work (W) is shown in Eq. 1, where σ is the applied stress and η the shear viscosity at the applied shear rate ($\dot{\gamma}$), with t_s the shearing time.

$$W = \sigma\gamma = \eta\dot{\gamma}^2 t_s \qquad (1)$$

The critical amount of work (W_c) required to induce oriented structures is also dependent on polymer backbone architecture and the molecular weight distribution. [10] [11] For example, if a small amount of W is added to model linear hydrogenated polybutadiene, the resulting point-like nucleation density increases as a function of W, and the final microstructure remains spherulitic. However, upon exceeding the W_c, a sharp transition is observed and the final microstructure becomes oriented in the direction of flow, adopting the typical shish-kebab structure.

This work represents the first attempt to characterize the crystallization behavior of an intentionally sheared polymer using FSC. In this work, we employed polyamide 66 (PA 66) for investigation of the accelerated crystallization behavior due to flow-induced precursors at high supercooling. The quiescent crystallization of this polymer has been extensively characterized, hence making it a logical choice for further FIC studies. [12]

SUMMARY

Fabrication of Samples for Study

Four discs of PA 66 were fabricated for thermal characterization. Three were created with a different maximum specific work at the outer radius (9, 73, and 290 MPa), and one was created with zero shear for baseline measurements. Fabrication employed an ARES-G2 rheometer (TA instruments, USA) equipped with 25 mm stainless steel parallel plate fixtures. For each disc prepared, there is a distribution of the shear rate and specific work across the radius of the parallel plate disc. The shear rate depends on the velocity of the rotation and the distance between the plates, resulting in a linear increase in shear rate from the radius to the edge. Theoretically, the shear rate at the center of the disc is zero.

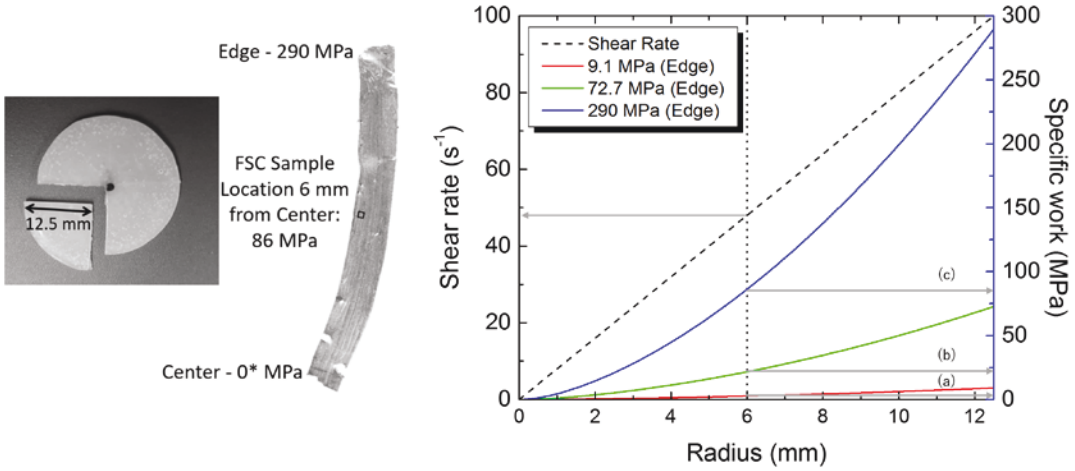

FIGURE 1. Left) Image of a PA 66 disc as prepared in rheometer. Middle) Sectioning of a 290-MPa PA 66 disc prepared via rotational rheological techniques. Right) Shear rate and specific work through the cross section of the three parallel plate discs. Identical sampling locations were chosen from each of the four discs, 6 mm distance from the center. Shown as an example, for the 200 MPa disc (c) at this location the applied shear rate was 30 1/s and the local specific work 86 MPa.

After disc fabrication, samples were removed from the parallel plate fixtures and sectioned for further analysis, as shown in Figure 1a. The disc section was then microtomed from center at a thickness of 12 micron. These thin sections were first analyzed with polarized light microscopy, as shown in Figure 2. In all samples that had been subject to shear before crystallization, shish kebab structures were identified. Spherulitic structures were identified in the zero-shear sample. Using a scalpel under polarized light, specific areas (approximately 100 microns by 100 microns) of the thin sample at a distance of 6 mm from the disc center were selected and obtained for further crystallization studies

on a Flash DSC1 (Mettler Toledo, Switzerland). At this location, the samples had been subject to 3 MPa (from the disc subject to the lowest maximum work level of 9 MPa), 22 MPa (from the disc subject to a maximum 72 MPa of work) and 86 MPa (from the disc subject to a maximum 290 MPa of shear work).

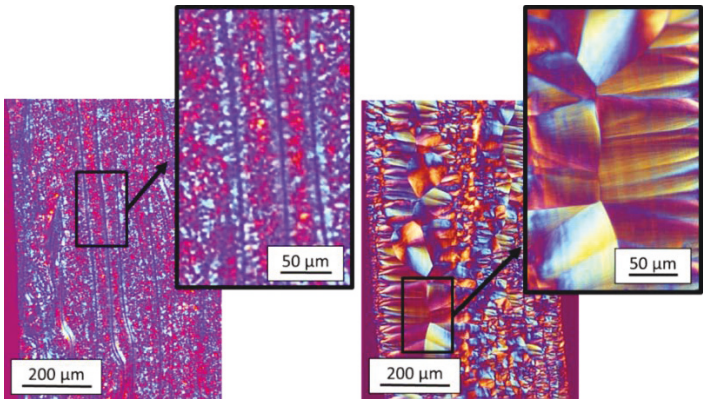

FIGURE 2. a) 72-MPa disc at 6 mm location (where W = 22 MPa, $\dot{\gamma}$= 45s^{-1}) box indicates obvious shish kebabs selected for FSC analysis b) zero-shear disc at 6 mm location, box indicates no shear orientation selected for FSC analysis. Flow direction is perpendicular to the surface shown.

Isothermal crystallization studies were used to investigate the influence of the visible flow-induced shish kebab structures on subesquent crystallization. Samples obtained from the thin strips shown in Figure 2 were placed onto the FSC chip and subject a temperature in the melt of 275 °C before being quenched to the target isothermal crystallization temperature. This temperature (275 °C) is lower than the equilibrium melting temperature, and so flow-induced structures (shish) are expected to survive, potentially acting as nucleation sites for subsequent crystallization. The halftime of crystallization at each isothermal temperature studied is shown in Figure 3. In summary, the high-temperature, heterogeneous nucleation-regime crystallization temperature is strongly influenced by the presence of flow-induced structures in the melt.

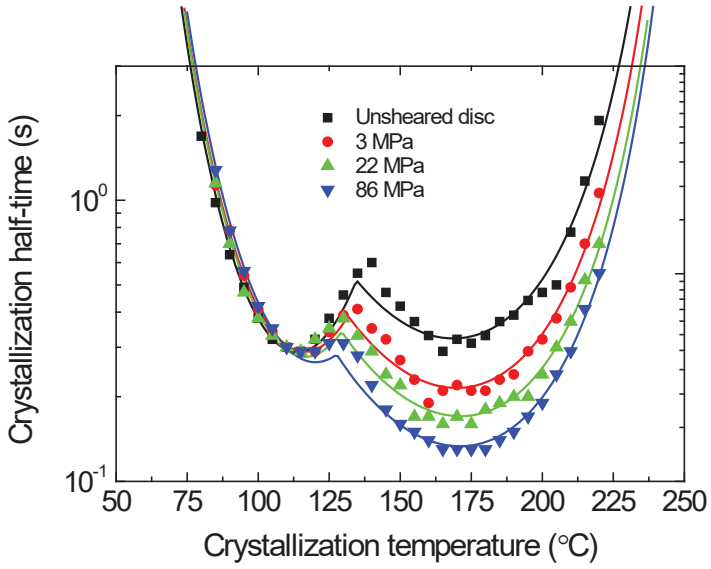

FIGURE 3. The halftime of crystallization for PA 66, subject to shear work levels indicated.

Increasing the amount of specific work that the polymer experienced prior to crystallization studies also resulted in an increased final crystallinity after cooling at rates less than 200 K/s.

TABLE 1. Crystallization Properties of Sheared PA 66

Amount of Shear Work Prior to Crystallization (MPa)	Halftime of crystallization at 170 °C (s)	Percent crystallinity after cooling at 1 °C/s
0	0.37	38
3	0.20	45
22	0.16	46
86	0.13	50

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Financial support from the National Science Foundation (NSF) (CMMI CAREER Award 1653629) and Deutsche Forschungsgemeinschaft (DFG) (Grant AN 212/20-2). is greatly appreciated. We also thank Dave Okonski of General Motors Research for Flash DSC support.

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