Rheological classification of FIC P/E random copolymers

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Introduction
A recent evaluation of flow-induced crystallization (fic) experiments and theories [1] lead to the identification of three different flow regimes. Two characteristic times, the reptation time $\tau_d$ and the Rouse time $\tau_R$, define the transition between the regimes. For shear rates higher than $1/\tau_d$ but lower than $1/\tau_R$ only orientational effects on point nucleation take place. For shear rates higher than $1/\tau_R$ molecular stretching occurs leading to a fibrillar morphology. Figure 1 shows this effect. In this study the effect of ethylene addition within the iPP molecules on the flow-induced crystallization behavior is investigated.

Material and methods
Materials
A homopolymer (Borealis HD234CF) and a P/E random copolymer (RACO, Borealis RD204CF) with an ethylene content of 3.4% were used in this study. Both materials have the same molar mass ($M_w \sim 310$ kg/mol) and polydispersity ($D \sim 3.4$) [3]. The relaxation spectra determined from the basic linear viscoelastic properties $G'$ and $G''$ at $T_{ref} = 145^\circ$C are also similar: the longest relaxation time, $\tau_{long} \sim 10s$ and average relaxation time defined as $\tau_d = \sum_i g_i \tau_i^2 / \sum_i g_i \tau_i \sim 1s$.

Methods
A Rheometrics RDA III rheometer (Fig. 2, left) was used to perform short-term shear experiments at $T_c = 135^\circ$C. The procedure is shown in Fig. 2 (right). The material is molten at $230^\circ$C and subsequently cooled to the crystallization temperature. At $T_c$ a short shear step is applied (total shear $\dot{\gamma} = \dot{\gamma}_t = const.$) and the crystallization process is followed by monitoring $G'$.

Results
By the addition of ethylene the crystallization process is slowed down up to 1 decade in time (Fig. 3). Also the application of flow has less influence as in the case of pure iPP, which is shown in Fig. 4 (left) by the scaled half-time of crystallization $\theta$ (with $t_{1/2} = (t_i + t_e)/2$, fig. 3). This plot also shows that the flow is still not strong enough to stretch the molecules leading to fibrillar structures (regime III). However, $T_m$ of the RD204CF is 11$^\circ$C lower than of HD234CF. While undercooling ($\Delta T = T_m - T_c$) is the driving force for crystallization, results should be compared for different $T_c$.

Conclusions
The addition of a small amount of ethylene influences the crystallization behavior of iPP in 2 ways:

- At the same $T_c$ the crystallization process is slowed down up to 1 decade.
- Both at the same $T_c$ and at equal $\Delta T$ orientational effects on point nucleation are smaller.

References:

Figure 1 The effect of flow on structure formation of iPP [2]. Regime I (left), regime II (mid) and regime III (right).

Figure 3 Time build-up of $G'$ for HD234CF (left) and RD204CF (right).

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For the same $\Delta T$ the P/E RACO crystallizes faster than the iPP under quiescent conditions (Fig. 4, right), but the effect of flow is less pronounced.

Figure 4 Scaled crystallization half-time $\theta$ versus shearrate $\dot{\gamma}$ (left) and time build-up of $G'$ for RD204CF at $T_c = 124^\circ$C (right).

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