

## Rheological classification of FIC : P/E random copolymers

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# 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.

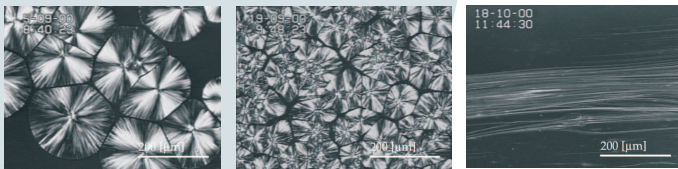


Figure 1 The effect of flow on structure formation of iPP [2]. Regime I (left), regime II (mid) and regime III (right).

## 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 ( $M_w \sim 310\text{kg/mol}$ ) and polydispersity ( $D \sim 3.4$ ) [3]. The relaxation spectra determined from the basic linear viscoelastic properties  $G'$  and  $G''$  at  $T_{ref} = 145^\circ\text{C}$  are also similar: the longest relaxation time,  $\tau_d^{long} \sim 10\text{s}$  and average relaxation time defined as  $\bar{\tau}_d = \sum_i g_i \tau_i^2 / \sum_i g_i \tau_i \sim 1\text{s}$ .

### Methods

A Rheometrics RDA III rheometer (Fig. 2, left) was used to perform short-term shear experiments at  $T_c = 135^\circ\text{C}$ . The procedure is shown in Fig. 2 (right). The material is molten at  $230^\circ\text{C}$  and subsequently cooled to the crystallization temperature. At  $T_c$  a short shear step is applied (total shear  $\gamma = \dot{\gamma}t = const.$ ) and the crystallization process is followed by monitoring  $G'$ .

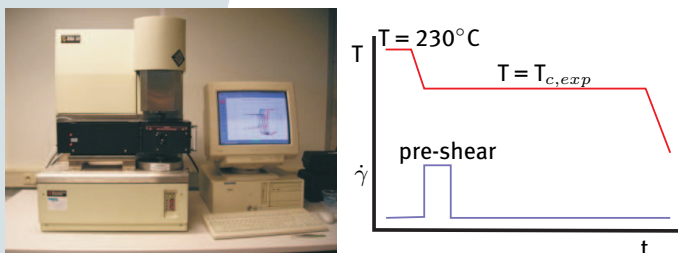


Figure 2 Rheometrics RDA III (left), experimental procedure (right).

## Results

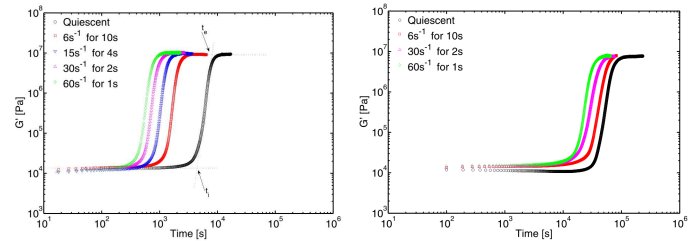


Figure 3 Time build-up of  $G'$  for HD234CF (left) and RD204CF (right).

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  $11^\circ\text{C}$  lower than of HD234CF. While undercooling ( $\Delta T = T_m - T_c$ ) is the driving force for crystallization, results should be compared for different  $T_c$ .

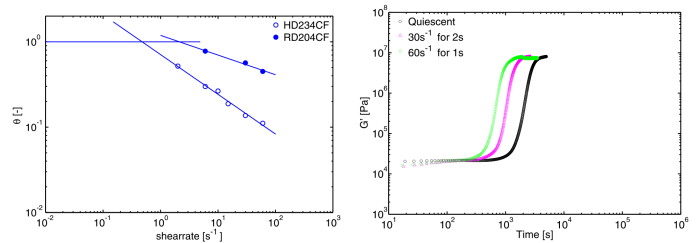


Figure 4 Scaled crystallization half-time  $\theta$  versus shearrate  $\dot{\gamma}$  (left) and time build-up of  $G'$  for RD204CF at  $T_c = 124^\circ\text{C}$  (right).

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.

## 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:

- [1] VAN MEERVELD, J. ET AL.: *Rheologica Acta* (2004) 44, 119
- [2] SWARTJES, F.: *PhD-thesis* (2001)
- [3] GAHLEITNER, M. ET AL.: *J. Appl. Pol. Sci.* (2005) 95, 1073