Rheological classification of FIC : P/E random copolymers

TU/e technische universiteit eindhoven

Rheological classification of FIC P/E random copolymers

J.W. Housmans, G.W.M. Peters, H.E.H. Meijer
Eindhoven University of Technology, Department of Mechanical Engineering

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 τ_d and the Rouse time τ_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.

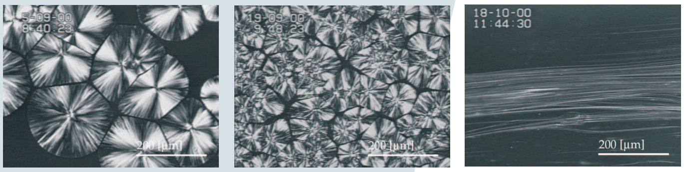

Figure 1 *The effect of flow on structure formation of iPP [2]. Regime I (left), regime II (mid) and regime III (right).*

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

Methods

A Rheometrics RDA III rheometer (*Fig. 2*, left) was used to perform short-term shear experiments at $T_c = 135°$C. The procedure is shown in *Fig. 2* (right). The material is molten at 230°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'.

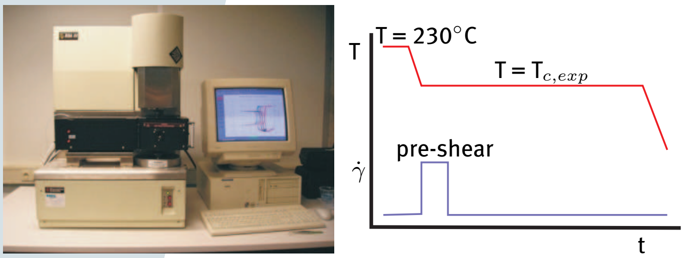

Figure 1 *Rheometrics RDA III (left), experimental procedure (right).*

Results

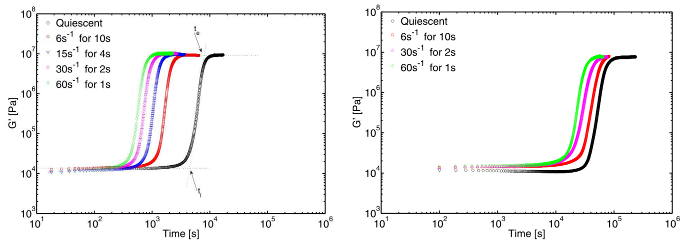

Figure 3 *Time build-up of G' for HD234CF (left) and RD204CF (right).*

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 θ (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°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.

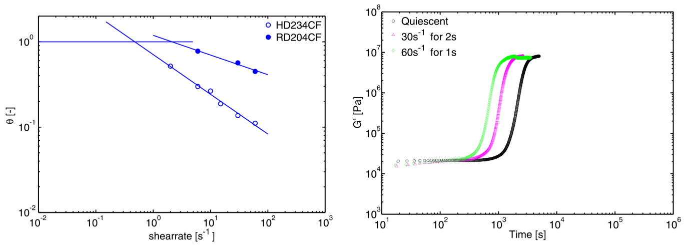

Figure 4 *Scaled crystallization half-time θ versus shearrate $\dot{\gamma}$ (left) and time build-up of G' for RD204CF at $T_c = 124°$C (right).*

For the same ΔT 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 ΔT 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

PO Box 513, 5600 MB Eindhoven, the Netherlands