Flow-induced crystallization of PP/PE copolymers

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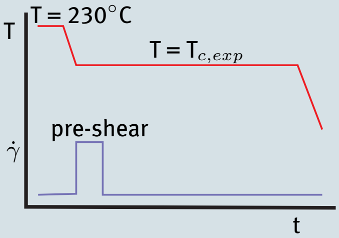
Introduction

The major disadvantages of PP are low temperature brittleness and opacity. A way to improve these properties is to use PP/PE random copolymers (RACO's) that also have the advantage of a decrease of the processing temperatures [1]. This study deals with the influence of ethylene content on crystallization behavior and the characterization of these materials for future modeling purposes.

Materials and methods

- A PP homopolymer and three PP/PE RACO's with different ethylene contents (Borealis, Linz).
- All grades have the same molar mass ($M_w \sim 310$ kg/mol) and polydispersity ($D \sim 3.4$) [2].
- Oscillatory experiments to determine the linear viscoelastic response.
- Short term shear experiments, see *Fig. 1*.



Melt material at 230°C
Cool to $T_{c,exp}$
Undercooling: $T_m - T_{c,exp}$=18°C
Apply pre-shear:
$\dot{\gamma} = 30s^{-1}, t_{flow} = 3s$
Follow crystallization process:
G' in time

Figure 1 *Short-term shear experiment.*

Results

The introduction of ethylene monomer in PP leads to:

- a decrease in crystallinity.
- a depression of the glass-transition (T_g), melt (T_m) and crystallization temperature (T_c, *Table 1*).

Table 1: Basic characteristics of the PP grades.

Type	Ethylene [mol%] 1)	T_g [°C] 2)	T_m [°C] 2)	T_c [°C] 2)	X_c [%] 2,3)
HD234CF	0	-2	163	112	45
RD204CF	3.4	-4	147	105	39
RD226CF	5.2	-5	143	101	37
RD208CF	7.3	-11	138	95	33

1) From [2], determined using NMR spectroscopy.
2) Determined using DSC, $\dot{T} = 10$°C/min
3) ΔH_m = 209 J/g for 100% crystalline PP, [2].

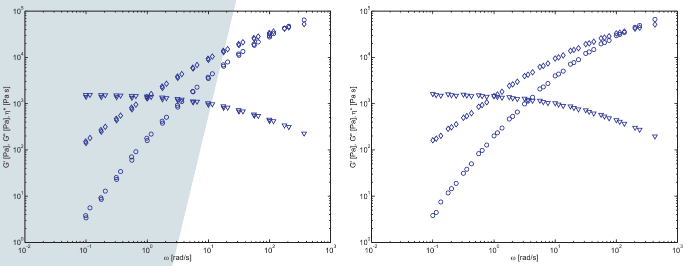


Figure 2 *Linear viscoelastic response of HD234CF (left) and RD208CF (right), measured at different temperatures and shifted to T_{ref} = 220°C. ○ = G', ◇ = G", △ = η^*.*

Although a clear influence of ethylene is seen on e.g. T_m, the linear viscoelastic behavior is not altered (*Fig. 2*).

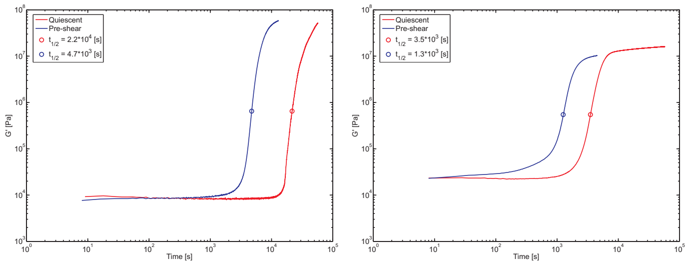


Figure 3 *Crystallization behavior for HD234CF (left) and RD208CF (right). Red = without flow, blue = with flow (pre-shear: $\dot{\gamma} = 30s^{-1}, t_{flow} = 3s$), ○: defines $t_{\frac{1}{2}}$.*

Conclusions

As known from earlier studies [3], the crystallization process is accelerated when shear is applied, *Fig. 3* (left). Crystallization of PP is also greatly influenced by the addition of ethylene when compared at the same undercooling, i.e. the half-time of crystallization ($t_{\frac{1}{2}}$) is decreased with almost 1 order of magnitude, *Fig. 3*.

Future work

A rheological classification of flow induced crystallization is proposed, which identifies different flow regimes [4]. The characteristics can be summarized in a plot (t_{flow}, $t_{\frac{1}{2}}$), see *Fig. 4* [5]. How this graph is influenced by the addition of ethylene will be the subject of future research.

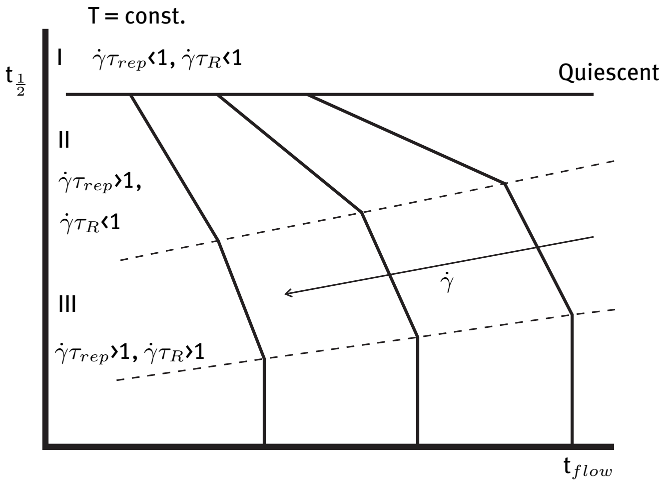


Figure 4 *Rheological classification of flow induced crystallization.*

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