Title: **Memory of crystallization in the melt of commercial linear low density polyethylenes processed in an open twin-screw extruder**

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Images:

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Abstract:

Compared with a constant recrystallization rate of commercial linear low density polyethylenes (LLDPE) as a function of melt temperature, copolymers reprocessed in an open twin-screw extruder display the expected strong melt-memory features upon meltrecrystallization. Recrystallization from dilute solution had the same effect in commercial copolymers. In the twin-screw melt re-processing, besides further consumption of additives, a small content of long-chain branches and crosslinks are incorporated to the copolymer structure, thus uncovering self-nucleation features that speed up recrystallization and are related with the major copolymer microstructure. The observed difference in re-crystallization behaviour between metallocene type and Ziegler-Natta type copolymers, both with equivalent average comonomer content and molecular mass, is due to the inter-chain comonomer distribution. While below a critical melt temperature, for metallocene-made and low density polyethylenes the recrystallization rate increases continuously with decreasing melt temperature, in broadly distributed Ziegler-Natta (ZN) copolymers there is an inversion of the temperature gradient of the rate at the onset of liquid-liquid phase separation (LLPS). The mass fraction of highly branched molecules required to observe the onset of LLPS via recrystallization was evaluated from the TREF profiles, and the effect of self-nucleated melts at different levels on the overall spherulitic morphology is observed via polarized optical microscopy.

Keywords: Ethylene copolymers, Twin screw processing, Crystallization, Melt memory, Liquid-liquid phase separation, Long chain branching

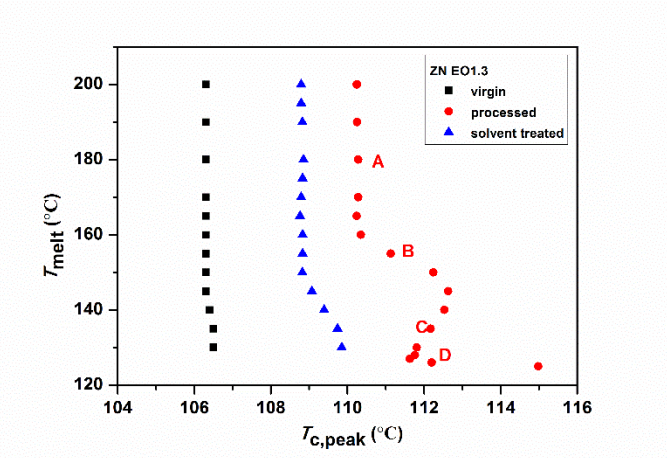

Fig. 1. Plot of the initial melt temperature (T_{melt}) versus the peak crystallization temperature ($T_{c,\ peak}$) observed on cooling at 10 K/min. Example shown is for ZN EO1.3.