

## ENHANCEMENT IN CRYSTALLISATION BEHAVIOUR OF BRANCHED POLYETHYLENES

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In recent years the crystallisation behaviour of branched polyethylene (BPE) was studied using differential scanning calorimetry (DSC). On cooling from the melt, pure BPE develops an exotherm with a crystallization temperature peak ( $T_c$ ) that depends on the cooling rate and structural parameters, such as branching content and molecular weight. The  $T_c$  of BPE may also increase significantly by blending the BPE with a small amount of linear polyethylene (LPE)<sup>1,2</sup>. The thermograms on heating of commercial low LPE content blends that had previously been quenched from the melt show bimodal melting. Two lamellar populations are formed on fast cooling from the melt. LPE-rich crystals melt at higher temperatures and BPE-rich crystals are of lower melting temperatures. The increase in  $T_c$  is observed when a fresh quenched sample is heated to a temperature just below the high melting temperature peak of the LPE-rich crystals, and then cooled in a controlled manner inside the DSC. An early report showed that the increase in  $T_c$  was a function of blend composition, the maximum increase was found for a 3% LPE content blend<sup>1</sup>. Blends of similar LPE content isothermally held at a temperature above the highest crystallization temperature of the pure BPE, fail to show such large increase in  $T_c$ <sup>1</sup>. In addition, the observed shifts in  $T_c$  were independent of the cooling rate used to record the exotherm, although some improvement was found for blends that contained a more crystalline BPE<sup>2</sup>. Those early results pointed to the incorporation of some BPE segments within the LPE-rich crystals, as being responsible for the increase in  $T_c$  of the remaining BPE segments. This was reinforced by the fact that the melting temperature of the BPE on subsequent heating decreased with LPE content in the blend<sup>2</sup>.

Two LPE molecular weight fractions were purchased from NIST, 1483 ( $M_w = 32,100$  g/mol,  $M_w/M_n = 1.11$ ) and 1484a ( $M_w = 119,600$  g/mol,  $M_w/M_n = 1.19$ ). The BPE is a commercial low density type. LPE/BPE blends were prepared by precipitating the mixture from a homogeneous solution. DSC experiments were carried out using a Perkin Elmer Pyris 1. Quenching experiments were carried out from the melt by cooling into acetone at  $\sim -80$  °C. Heating traces were obtained at

10 °C/min, whereas cooling runs of fresh quenched samples from 118 °C were carried out at 5 °C/min after holding for 30 minutes.

Fig. 1 shows the crystallization temperature for pure BPE and for BPE in the blends recorded on cooling from 118°C at 5°C/min. The blends had been previously quenched from the melt. There is a large increase in  $T_c$  with the addition of a small amount of LPE in both types of blends. However, some variations in behaviour are observed between the blends when LPE of different molecular weight are used.

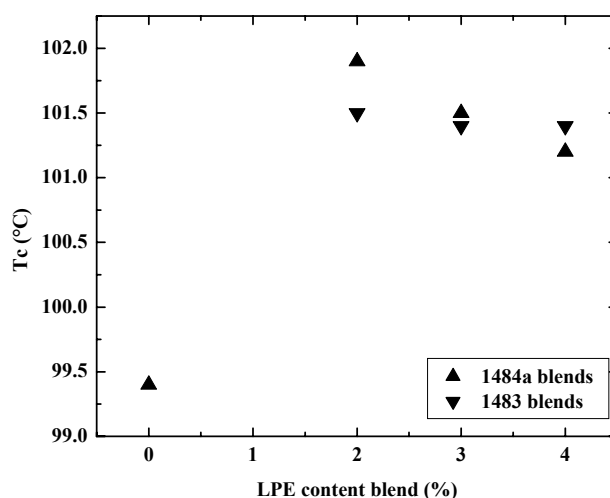


Fig. 1 Variation in crystallization temperature ( $T_c$ ) of BPE for blends that were previously quenched from the melt.

The crystallization temperatures recorded for blends containing a lower molecular weight LPE fraction are unchanged with blend composition. Blends of 1484a fraction, however, show strong blend composition dependence. We believe the closeness in crystallization rate between the BPE and the 1484a components plays a major role in the amount of BPE segments that are incorporated within the LPE-rich crystals. On subsequent heating, DSC traces reveal for the 1483 blends the appearance of a third melting peak located at even higher temperatures, which is presumed to be due to the crystallization of LPE segments that had earlier been incorporated into the BPE-rich crystals.

1) Puig CC, *Polym. Bull.*, **38** (1997) 715.

2) Puig CC, *Polymer*, **42** (2001) 6579.