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A DSC Study of Oriented Samples of a Blend of Linear and Branched Polyethylene

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Summary

Differential scanning calorimetry (DSC) of cold-drawn samples of a blend of linear (LPE) and branched polyethylene (BPE) shows that the melting point of the high temperature peak decreases monotonically with increasing draw ratio. This is in apparent contradiction to the data obtained for pure LPE, for which quite unanimously the melting point has been shown to increase with increasing draw ratio. An explanation of this deviation in behaviour between the blend of LPE and BPE and the pure LPE is proposed based on the idea that the transformation of the lamellar structure to a fibrillar structure involves several kinds of rearrangement including a mixing on a supermolecular level of the originally segregated LPE and BPE components. The crystal rearrangements occurring on heating (in the DSC) in oriented pure LPE that are responsible for the high melting point of this system are thereby hindered.

Introduction

It is wellknown that cold-drawing (PETERLIN 1965, MEINEL 1968, ILLERS 1970, SUMITA 1970, CLEMENTS 1979, GEDDE 1980) and solid-state extrusion (MEAD 1979) of isotropic linear polyethylene (LPE) results in the formation of a fibrous material with a higher melting point than the original material. In these studies the melting point (generally defined as the temperature of the melting peak as recorded by differential scanning calorimetry (DSC)) has been shown to increase monotonically with the draw ratio, particularly at draw ratios less than 10. GLENZ ET AL (1971) showed for drawn LPE that no relation exists between the melting point and the crystalline structure as studied by small angle X-ray scattering (SAXS) or wide angle X-ray scattering (WAXS). In fact, the fibrous LPE samples that had a higher melting point than the original isotropic samples were at the same time frequently composed of thinner crystals (GLENZ 1971). This seemed to contradict the Thomson-Gibbs equation. However, if the amorphous chains were crosslinked using γ radiation so that rearrangements of the crystals during the DSC scan were inhibited, an excellent correlation was obtained between the crystal thicknesses determined from these melting point data using the Thomson-Gibbs equation and those

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determined from SAXS and WAXS data (GLENZ 1971). These indications that rearrangements of the structure during heating are responsible for the increase in melting point observed was further substantiated by SAKURAI (1974): During the heating (at a rate of 18 K/min) of a LPE sample drawn 5x the SAXS long spacing was found to increase from 180 to 510 Å before the final melting occurred.

ILLERS (1970) showed that the orientation of the intercrystallite tie chains in the fibrous LPE increases the melting point. Samples that were prevented from shrinking exhibited a higher melting point than those that were allowed to shrink during melting. A possible explanation of this is that the melting point is increased as a result of the decrease in entropy of the oriented melted fraction which exists at a higher concentration in the samples that are prevented from shrinking.

In this paper, DSC data relating to cold-drawn samples of a blend of linear and branched polyethylene (LPE/BPE) are presented showing a decrease in melting point (defined as the melting point of the high temperature peak corresponding to the melting of the LPE component) with increasing draw ratio. This apparently contradicts the data obtained for pure LPE.

Experimental details and analysis of data

A sheet of a mechanical blend of 50 % (by weight) LPE (MI_2=0.7 and density=960 kg/m^3) and 50 % BPE(MI_2=0.7 and density=920 kg/m^3) was compression moulded at 455 K and cooled to room temperature at a rate of 0.5 K/min while still kept in the mould.The molecular weight of the blend was determined by gel permeation chromatography to be: M_n=12.4x10^3 and M_w=166x10^3. The density of the original nonoriented material (blend) is 944.3 kg/m^3. From the 3 mm sheet dumb-bell shaped specimens were machined and the faces were ground so that a 0.1-0.2 mm thick surface layer was removed from each surface.

Uniaxial drawing at an elongation rate of 5 mm/min (middle part of the specimens used were 60 mm) at 298 K were carried out in an Instron Tensile Testing Machine so that varying draw ratios ranging from 1 to 9 were obtained. The draw ratio is defined as the ratio between a length dimension parallel to the direction of drawing after drawing and the corresponding length before drawing. The draw ratios were determined by measuring the displacements a considerable time after unloading (>10 hours) of ink spots that were applied to the specimens before drawing.

From the drawn specimens, 5±0.5 mg samples with dimensions 4x4x 0.25 mm were cut and enclosed in Perkin-Elmer DSC aluminium pans according to standard procedures. The oriented samples enclosed were found to shrink during the heating. Melting endotherms were recorded in a Perkin-Elmer DSC-2 at three different rates: 1.25, 10 and 80 K/min scanning from 250 to 450 K. The DSC instrument was calibrated at 10 K/min by recording the melting of indium and tin. The calibration points of the temperature scale were obtained by extrapolation of the low temperature part of the melting endotherm down to the base line. For the other scan rates the temperature scale was adjusted according to a formula given in the Perkin-Elmer manual.

The definitions of the melting temperatures (T_{lp} and T_{hp}) and the procedure for crystallinity determination are shown in Fig.1.

The linearity of the base line is established on specific heat data by WUNDERLICH (1970).

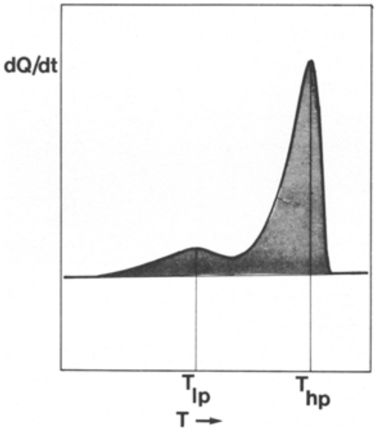

Fig.1. Melting endotherm of a typical LPE/BPE sample. Definition of temperatures of low temperature peak (T_{lp}) and high temperature peak (T_{hp}). Crystallinity is determined on the basis of the shaded area.

Results and discussion

The melting endotherms obtained at 10 K/min are shown in Fig.2.

With increasing draw ratio,the following effects are observed:

- T_{hp} decreases. This is observed at all the scan rates used, see Fig.3.
- T_{lp} increases. This is also evident at 1.25 K/min (scan rate) whereas T_{lp} is almost independent of draw ratio at 80 K/min, see Fig.4.
- The valley between the peaks becomes less deep. This is further shown in Fig.5 and can be attributed to a broadening of the high temperature peak towards lower temperatures.
- The low temperature part of the low temperature peak ($T<T_{lp}$) seems to be independent of draw ratio.

The increase in T_{hp} with scan rate is higher for higher values of T_{hp}. This is consistent with the behaviour of crystals showing so called superheating. The change in T_{lp} with scan rate decreases with increasing T_{lp}. The higher values of T_{lp} observed at 80 K/min are partly due to the fact that the samples were not in thermal equilibrium at this scan rate, mainly due to the poor contact between the sample and the sample pan. This is further substantiated by the fact that the T_{lp} data show a large amount of scatter at 80 K/min. Thermal non-equilibrium within the polymer sample is of minor importance. The data of WUNDERLICH (1971) indicates that the temperature variation within the particular sample used is less than 0.5 K at 80 K/min (scan rate). A comparison of the melting endotherms recorded shows that the melted fraction at T_{lp} is significantly higher at 80 K/min than at the other scan rates used, possibly due to a dominance of a broadening towards lower temperatures of the high temperature peak at 80 K/min scan rate. Without

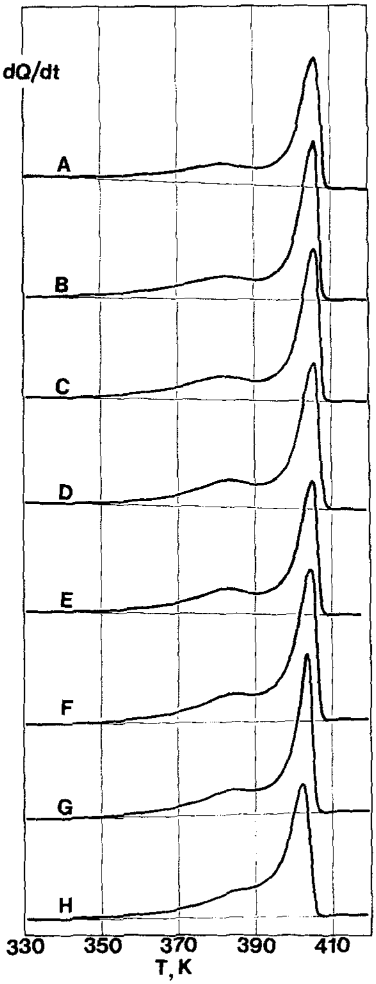

Fig.2. Melting endotherms of LPE/BPE samples of different draw ratios (λ). The scan rate is 10 K/min. A:λ=1,B:λ=1.2,C:λ=2,D:λ=2.8,E:λ=3.6,F:λ=5.6,G:λ=6.8,H:λ=8.6

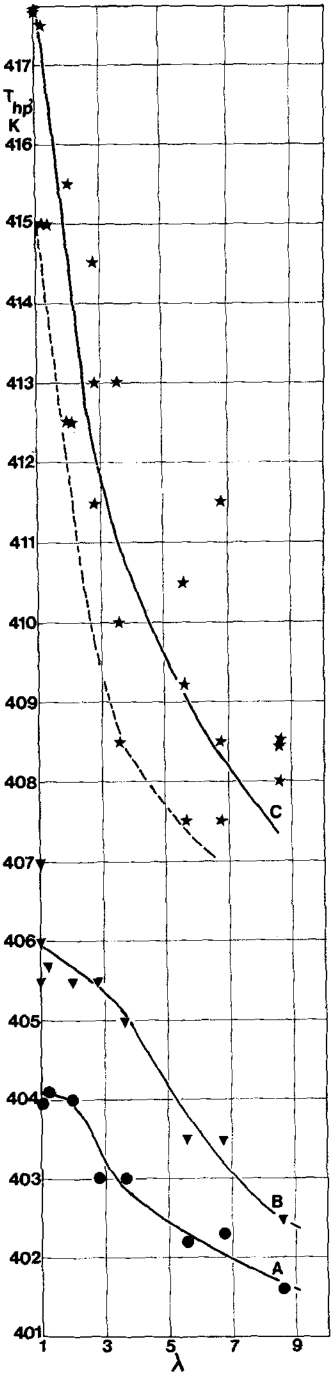

Fig.3. Temperature of high temperature peak (T_{hp}) as a function of draw ratio (λ). A: scan rate=1.25 K/min (●),B: scan rate=10 K/min (▼), C: scan rate=80 K/min (★). A minimum curve (broken) is shown for the data at 80 K/min (scan rate).

change of the melting characteristics of the crystals responsible for the low temperature peak (at 1.25 and 10 K/min), an increase of T_{lp} will be the result of the broadening of the high temperature peak. Thus, the crystals corresponding to T_{lp} (at 1.25 and 10 K/min) seem to show neither superheating nor crystal rearrangement.

The high temperature melting peak seems to be less affected than the low temperature peak by the thermal non-equilibrium at 80 K/min (scan rate), perhaps due to the fact that the contact between the sample and the sample pan is improved by the low temperature melting. Nevertheless, taking this non-equilibrium into consideration, a minimum curve of the data of 80 K/min scan rate (see Fig.3) seems to represent the real situation better than an average curve. The conclusions drawn based on the average curves that the crystals melting at T_{hp} show superheating is not altered by this.

The crystallinity increases only slightly on drawing, from about 50 % at draw ratio=1 to about 54 % at draw ratio=8.6. This is in principal agreement with earlier reported data on drawn LPE samples (e.g. MEINEL 1968).

The decrease in melting point of the LPE component of the LPE/BPE blend with increasing draw ratio indicates a reduced apparent crystal thickness in the oriented systems. This is in sharp contrast to the

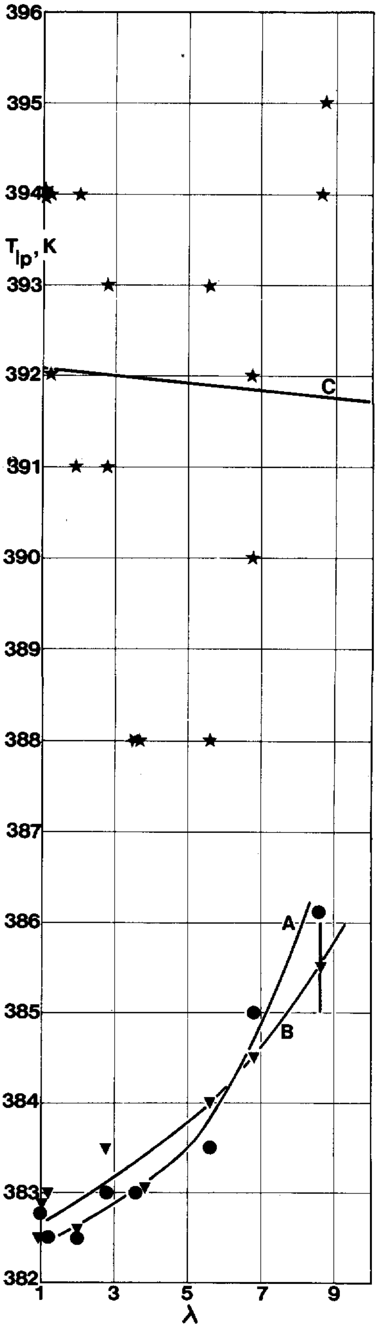

Fig.4. Temperature of low temperature melting peak (T_{lp}) as a function of draw ratio (λ). A: scan rate=1.25 K/min (●), B: scan rate=10 K/min (▼), C: scan rate=80 K/min (★).

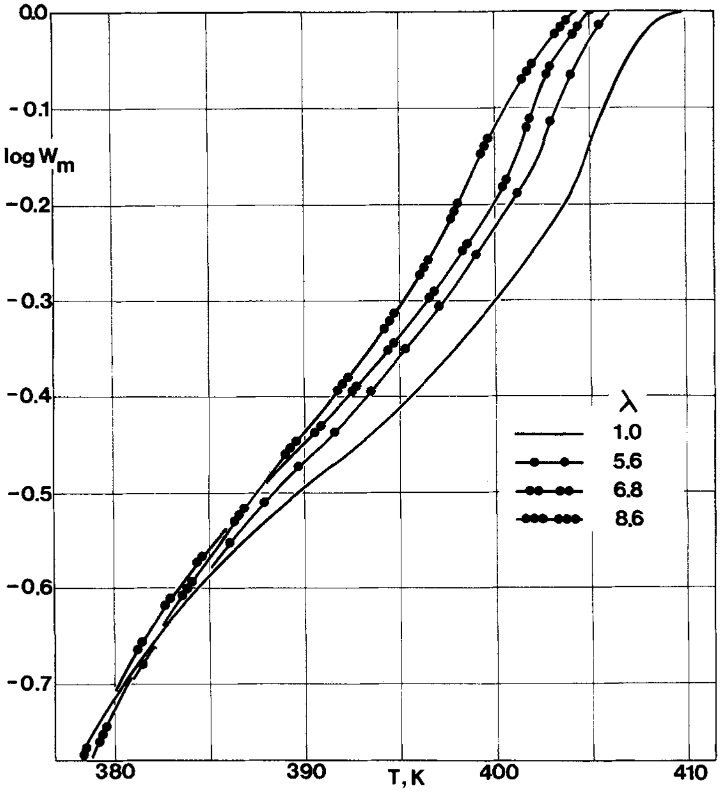

Fig.5. The logarithm of the fraction (originally crystalline) that is melted at temperature T (log W_m) as a function of temperature T of samples of different draw ratios (λ) as shown in the figure. The scan rate is 10 K/min.

melting behaviour of drawn pure LPE, in which a rapid rearrangement of the crystals occurring during the heating in the DSC is responsible for the increase in melting point on orientation (see the introduction). These rearrangements are in some way inhibited in the drawn LPE/BPE systems. If LPE existed as an isolated separate phase in the drawn systems, the behaviour of drawn pure LPE would be preserved in the LPE/BPE system. However, the fact that it is not indicates the presence and the influence of the BPE component on the drawn LPE phase. A possible explanation is that the transformation of the original lamellar structure to a fibrillar structure which occurs as a consequence of drawing involves large-scale rearrangements of the structure by several mechanisms including chain slip, crystallite disintegration. unfolding of coiled chains (PETERLIN 1971) and, particularly important in this case, a kind of mixing (on a supermolecular level) of the originally mostly segregated LPE and BPE components effectuated by the mechanisms mentioned. Thus, we suggest that two interpenetrating fine-scale networks,one of drawn LPE crystals and the other of drawn BPE crystals, are formed. The rearrangements responsible for the melting point increase in drawn LPE by the growth of the originally small oriented LPE crystals into larger crystals, which occurs during the DSC scan, is hindered by the presence of the penetrating BPE crystal network. The minor amount of mixed LPE/BPE crystals formed by initial cocrystallization may also be influencial.

Furthermore, the lowering of the melting point of the oriented LPE crystals in the blend is accountable for the broadening of the high temperature peak towards lower temperatures and thus the diminishing of the valley between T_{lp} and T_{hp} as the draw ratio is increased. Also the shift of the low temperature peak maximum can be attributed to this.

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