Journal of Thermal Analysis, Vol. 33 (1988) 1171–1176

DSC INVESTIGATION OF HIGH-STRENGTH AND HIGH-MODULUS POLYETHYLENE FIBERS

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Fibers were produced from two commercial grade linear polyethylenes (PE) of different molecular weight by flow-induced crystallization. DSC measurements were carried out with an annealing and melting program. Four melting peaks were found. The first peak, at the lowest temperature, can be identified with the melting of lamellar crystallized PE. Peak 2 corresponds to the melting of the main crystalline fraction of the fiber, and peaks 3 and 4 to the melting of constrained crystalline regions. The melting temperature depends on the molecular weight of the fiber material and on the drawing state.

In the past ten years, the possibility of achieving extremely high strength and stiffness values for fibers from flexible long-chain polymers has been demonstrated [1–3]. High values of both tensile strength ($\delta = 4.75$ GPa) and modulus ($E = 120$ GPa) have been obtained for high-molecular weight polyethylenes (PE) through the hot-drawing of "surface grown" fibers [4, 5].

Experimental

The linear PE used was Hostalen GUR with weight average molecular $M_w = 1.5\times10^6$ and number average molecular mass $M_n = 10^5$, in comparison with Scolefin A61 with $M_w = 1.4\times10^5$ and $M_n = 1.4\times10^4$. The method of crystal growth from flowing solutions in a Couette-type apparatus developed by Pennings et al. [1] was used to spin fibers from 0.5 wt.% solutions of these polymers in *p*-xylene at the crystallization temperatures $T_{cr} = 373$ K (A61) and $T_{cr} = 381$ K (GUR). Zone-drawing was performed in a multi-step process by moving a heated narrow metal strip along the fiber axis with the temperature and load successively increasing. The temperature was varied stepwise from 403 K to 418 K. The drawing technique corresponds to that used by Marichin et al. [5], and is quite similar to the method of Kunugi et al. [6]. Melting endotherms and heats of fusion were determined with a Perkin-Elmer DSC 1B. The temperatures at the maxima of the endo-

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therms were taken as the melting points of the samples. Indium was used for temperature and heat of fusion calibrations. DSC measurements were carried out at a constant heating rate (8 deg min^{-1}) to take the complete melting peak, or according to the following temperature program: heating from 320 K to temperature T_a (first melting), holding at T_a for 10 min, cooling from T_a to 320 K (crystallization), and heating up to total melting of the sample (second melting). T_a was changed from 400 K to 425 K (melting region of the fiber).

The fibers were prepared in the DSC sample pan in two different ways: (i) Free shrinking samples were allowed to shrink during the measurement procedure. (ii) Fixed samples were wound around a small piece of aluminium before being placed in the sample pan. In this way we measured the melting behavior of constrained fibrillar crystals.

Results

Figure 1 shows three DSC curves of complete melting for the PE fibers produced from GUR and A61. All diagrams exhibit three melting endotherms. These three partial peaks with rising temperature are named peaks 2, 3 and 4. Peak 1 is the melting peak of the initial polymer and cannot be observed on the first melting of the fibers. The shapes of the three partial peaks are very similar for all types of fibers. The material with higher molecular mass melts at higher temperature, and the melting region of the drawn

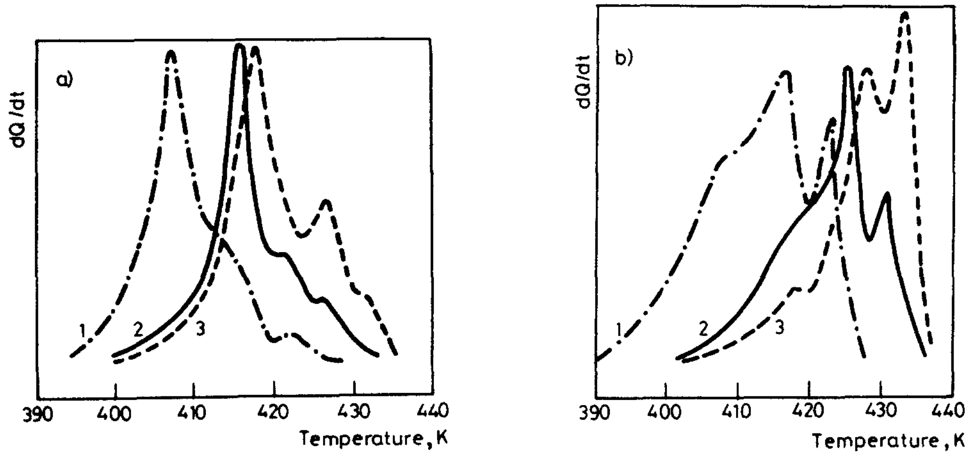

Fig. 1 DSC curves (schematic representation) of solution grown PE-fibers. a – free shrinking samples, b – fixed samples; 1 – A61, 2 – GUR, 3 – GUR, drawn ($\lambda = 2.5$)

sample is shifted to higher temperatures too. For shrinking samples, the partial peak area decreases with increasing temperature. For fixed samples, the melting temperature is shifted to higher valued as compared with shrinking samples, and peak 3 is increased.

Figure 2 shows absolute values of the enthalpies of fusion for the melting and recrystallization processes. The straight lines 1 and 5 show the values of the enthalpies of fusion of the fiber and the initial polymer, respectively.

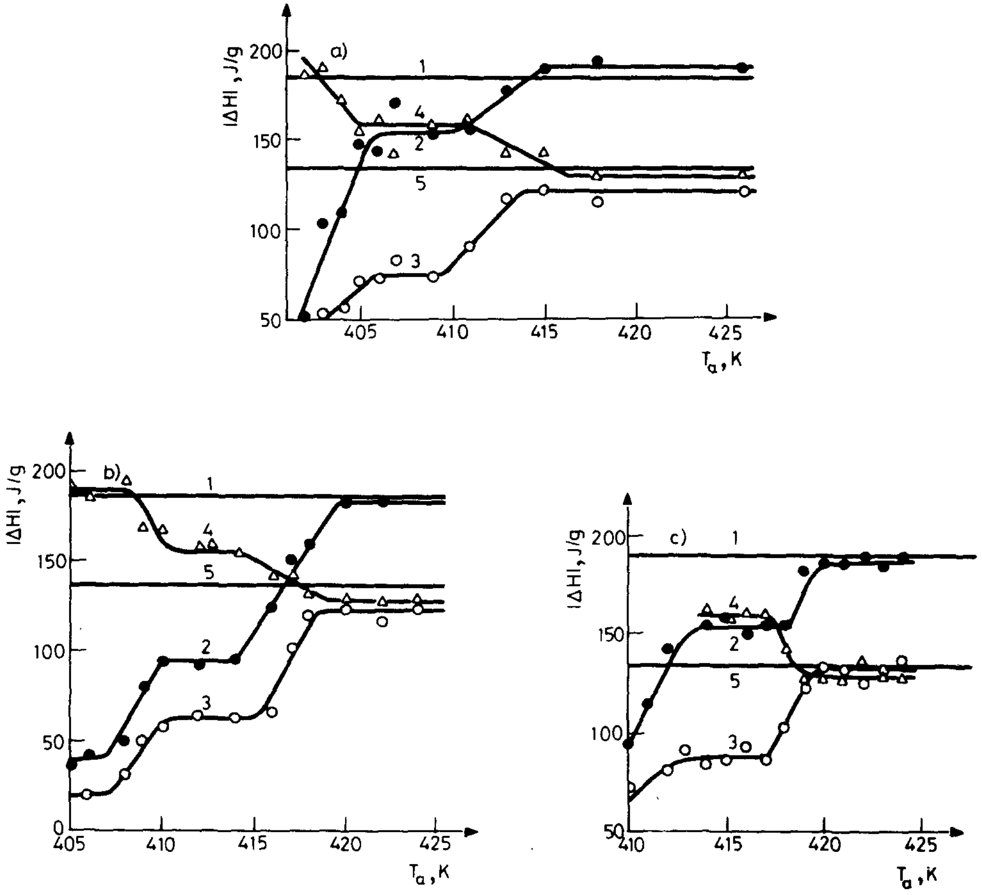

Fig. 2 Enthalpy of melting and recrystallization. a – A61 shrinking, b – A61 fixed, c – GUR shrinking,
1 – enthalpy of complete melting of the fiber
2 – enthalpy of melting up to T_a (first melting)
3 – crystallization enthalpy
4 – enthalpy of the final complete melting (second melting)
5 – enthalpy of the initial polymer

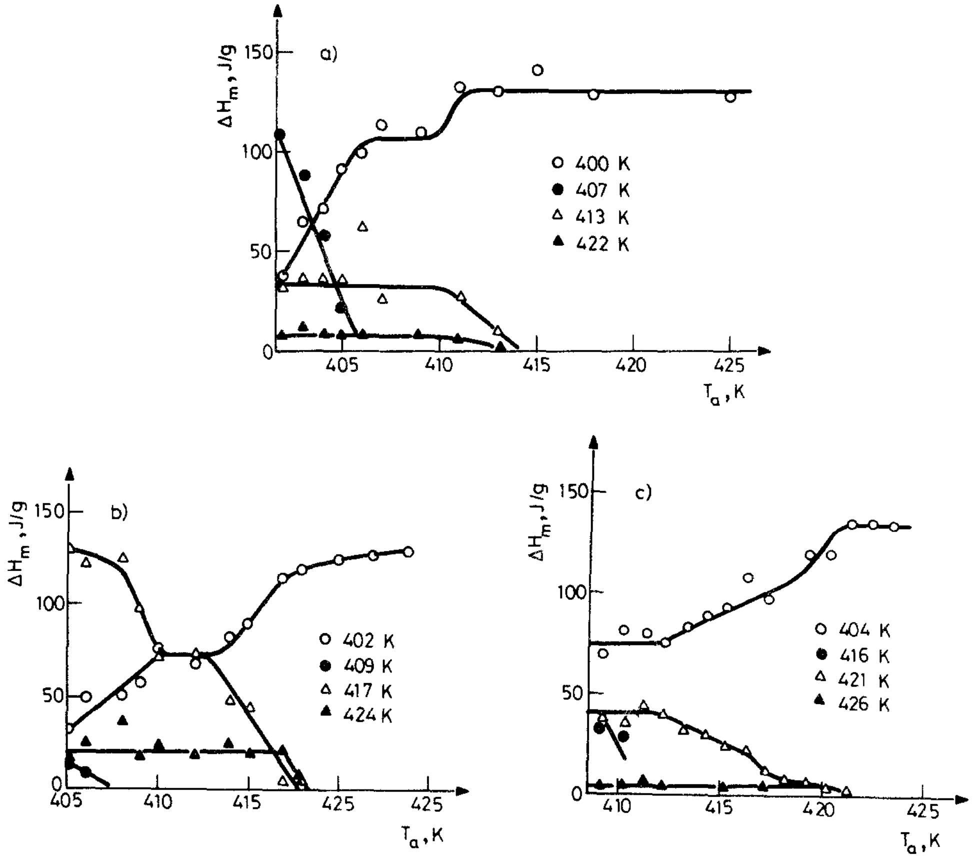

Fig. 3 Enthalpy of the partial peaks of second melting versus T_a. a – A61 shrinking, b – A61 fixed, c – GUR shrinking

Curve 2 reveals the enthalpy of fusion in the first melting (up to T_a). The enthalpy of fusion in the first melting (up to T_a). The enthalpy of the first melting increases in two steps. The first step can be identified with peak 2 (Fig. 1), and the second step is therefore equal to peaks 3 and 4, i.e. peak 2 can be separated from peaks 3 and 4 by the annealing procedure.

In Fig. 2, a difference may be observed between the melting enthalpies of the first (curve 2) and second (curve 4) melting processes. This means that there is a marked difference between the crystalline structures of the initial and the recrystallized fibers. The recrystallized fiber exhibits nearly the same behavior as the initial polymer, not only with respect to the enthalpy of fusion, but also with respect to the temperature of fusion. This is shown in Fig. 3. The increase of peak 1 (lowest temperature) in the second melting with increasing T_a can be explained as due to an increasing amount of crystalline material in the fiber, which was already melted in the first melting process. Consequently, the three melting endotherms of the fiber (peaks 2, 3 and 4) decrease in a stepwise manner with increasing T_a.

Conclusion

Four distinct melting peaks were found in the DSC measurements. The first peak (at the lowest temperature) can be identified with the melting of lamellar crystallized PE. The other three peaks are partial peaks of the fiber melting process. The temperature of the melting region depends on the molecular weight of the fiber material. Peak 2 can be separated from peaks 3 and 4, and corresponds to the main crystalline fraction if the fiber is allowed to shrink. Peaks 3 and 4 can be identified with the melting of constrained crystalline regions [7].

This corresponds to the fact that the melting of fixed samples gives melting endotherms with a reduced peak 2 and a large peak 3. The melting of free shrinking samples gives the inverse realtion. Drawing of the fibers increases the thermal stability of the fiber structure and the influence of constraint regions on the melting process.

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Zusammenfassung – Durch strömungsinduzierte Kristallisation wurden Fasern aus zwei kommerziellen linearen Polyethylenen (PE) unterschiedlichen Molekulargewichts dargestellt. DSC-Messungen mit einem Temper- und Schmelzprogramm zeigten 4 Schmelzpeaks. Der erste – bei der niedrigsten Temperatur – entspricht dem Schmelzen von lamellar kristallisiertem PE. Peak 2 zeigt das Schmelzen des kristallinen Hauptanteils der Fasern, Peak 3 und 4 das Schmelzen der erzwungenen kristallinen Bereiche. Die Schmelztemperaturen hängen vom Molekulargewicht des Fasermaterials und seinem Verstreckungsgrad ab.

РЕЗЮМЕ — Методом кристаллизации в струе получены волокна из двух продажно доступных сортов линейного полиэтилена с различным молекулярным весом. ДСК измерения были проведены в программе отжига и плавления. Установлено четыре пика плавления. Первый пик с наиболее низкой температурой идентифицирован как пик плавления кристаллического полиэтилена с ламеллярной структурой. Второй пик соответствует плавлению основной кристаллической фракции волокна, а третий и четвертый пики — плавлению кристаллически напряженных областей. Температуры плавления зависят от молекулярного веса полиэтиленового волокна и степени его вытянутости.