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Ultrahigh-Strength Polyethylene Filaments by Solution Spinning and Hot Drawing

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INTRODUCTION

The past decade has seen a rapidly growing interest in high-modulus and high-strength polymeric fibers (see e.g. CIFERRI, WARD 1979). The methods to prepare these filaments are based on cold/hot drawing (CAPACCIO, WARD 1974), two-stage drawing (CLARK, SCOTT 1974), hydrostatic (GIBSON et al. 1974) and direct (SOUTHERN, PORTER 1970; TAKAYANAGI et al. 1966) extrusion, elongational flow (PENNINGS et al. 1972; ZWIJNENBURG, PENNINGS 1976) and on the intrinsic rigidity of particular macromolecules in solution (e.g. CIFERRI 1975). High-modulus polyethylene filaments with Young's moduli of about 70 GPa have been produced by CAPACCIO and WARD (1974) through drawing. PORTER et al. (1970) performed solid-state extrusion to obtain polyethylene structures with similar mechanical properties. The tensile strength of these materials is usually found below 1 GPa (CAPACCIO, WARD 1975; KOJIMA, PORTER 1978). Longitudinal crystals of polyethylene with a Young's modulus of 100-120 GPa and a tensile strength of 3-4 GPa have been obtained from solution by ZWIJNENBURG and PENNINGS (PENNINGS 1977) in a Couette-type apparatus employing a crystallization technique referred to as surface growth.

This short communication describes some preliminary results on alternative routes to produce high-strength and high-modulus polyethylene filaments with a uni-axial Young's modulus of 90 GPa and a tensile strength of 3 GPa. The method is based on a simple solution-spinning and drawing process that can be performed continuously.

EXPERIMENTAL

The polyethylene used in this study was the high molecular weight Hostalen GUR with $\bar{M}_n = 2. 10^5$ and $\bar{M}_w = 1.5 . 10^6$. The solvent in the present experiments was decalin from J.T. Baker Chemicals. Polyethylene solutions stabilized by 0.5 % w/w of the antioxidant di-t-butyl-p-cresol (DBPC) were prepared at 150 °C.

Polyethylene monofilaments were spun from a 2 % w/w solution of the polymer in decalin at a temperature of 130 °C. The highly viscous solution was pumped through a capillary with a diameter of 0.5 mm, and was subsequently quenched to room temperature. The fila-

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ments thus produced were drawn in a hot-air oven in a temperature range from 100-140 °C at a strain rate of 1 s^{-1}.

The tensile properties of the drawn filaments were determined at room temperature using an Instron tensile-tester (model 1195). The testing speed was 10 cm/min and the initial sample length was 15 cm. All stress values were related to the original cross-sectional area of the specimen. This area was calculated from the mass per unit length of the fiber employing a crystal density of 1000 kg/m^3. The moduli quoted in this paper refer to the initial Young's moduli.

Melting thermograms of the filaments were recorded with a differential scanning calorimeter (Perkin Elmer DSC-2) at a scan speed of 10 °C/min, according to standard procedures.

RESULTS AND DISCUSSION

The initial Young's modulus, the tensile strength and the strain at break of the filaments drawn at 120 °C to various draw ratios are given in Table 1. The draw ratio refers to the cross-sectional area reduction ratio of the drawn filaments and the dried undrawn fiber.

TABLE 1

Mechanical Properties of Solution Spun/Drawn Polyethylene Monofilaments

Draw ratio	Young's modulus, GPa	Tensile strength, GPa	Strain at break
3	5	0.3	0.108
15	41	1.7	0.068
32	90	3.0	0.060

The Young's modulus and, in particular, the tensile strength of the fiber with draw ratio 32 (90 GPa and 3.0 GPa, resp.) compare with the values of polyethylene filaments produced by the surface growth technique of ZWIJNENBURG and PENNINGS (1976) and exceed those of other drawn or extruded fibers (CAPACCIO, WARD 1975; KOJIMA, PORTER 1978).

In Fig. 1 DSC-thermograms are presented of the dried undrawn filament and of unconstrained fibers with draw ratios of 15 and 32. The undrawn monofilament had a peak melting temperature of 133.0 °C and the 15 times drawn fiber 141.0 °C. Curve C of the filament with a draw ratio of 32 exhibits one pronounced maximum at 145.5 °C, which is indicative of a high crystal perfection. A second, small, peak was observed in thermogram C at 152.0 °C. This endotherm may be due to a solid-solid transformation from the orthorhombic crystalline phase to the hexagonal one, as was found in melting longitudinal polyethylene crystals (PENNINGS, ZWIJNENBURG 1979).

It is of interest to note that removal of the solvent from the as-spun filaments, prior to drawing, gave similar results

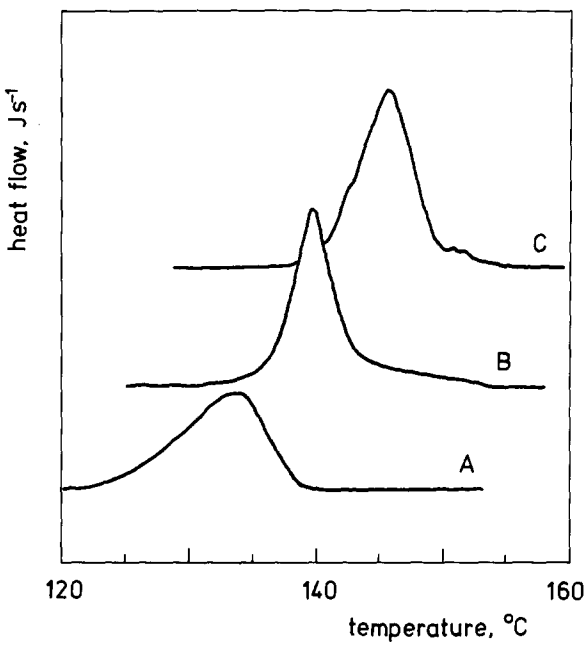

Fig. 1 - DSC-melting thermograms of polyethylene fibers produced by solution spinning/drawing. Scan speed: 10 °C/min. Draw ratios: A - 1; B - 15 and C - 32.

with respect to the mechanical properties of the polyethylene fibers.

Obviously, the described method to produce high-strength and high-modulus filaments is in an embryonic stage. Variables such as the draw ratio, strain rate, drawing temperature and stress, etc. need to be investigated in more detail to understand the mechanism of the fiber formation involved. These studies are in progress and will be published shortly.

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