Ultrahigh-strength polyethylene filaments by solution spinning/drawing, 2. Influence of solvent on the drawability

Citation for published version (APA):

Smith, P., & Lemstra, P. J. (1979). Ultrahigh-strength polyethylene filaments by solution spinning/drawing, 2. Influence of solvent on the drawability. *Makromolekulare Chemie*, 180(12), 2983-2986.
<https://doi.org/10.1002/macp.1979.021801220>

DOI:

[10.1002/macp.1979.021801220](https://doi.org/10.1002/macp.1979.021801220)

Document status and date:

Published: 01/01/1979

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Short Communication

Ultrahigh-Strength Polyethylene Filaments by Solution Spinning/Drawing, 2^{a)}

Influence of Solvent on the Drawability

Paul Smith*, Piet J. Lemstra

Central Laboratory, DSM, Geleen, The Netherlands

(Date of receipt: September 12, 1979)

Introduction

High-modulus structures of linear polyethylene with Young's moduli of 70 GPa may be generated, for example, by drawing meltspun fibers to very high draw ratios¹⁾, solid-state extrusion (e.g., cf.²⁾) and by the solution-crystallization technique referred to as surface growth³⁾.

The tensile strength of the drawn and extruded materials is usually found below 1 GPa, whereas the longitudinal crystals of Zwijnenburg and Pennings may have a strength as high as 3 GPa. The superior strength of the latter filaments, which have comparable Young's moduli, is due to the high molecular weight of the polymer sample used^{4,5)}.

Previous attempts to draw or extrude polyethylene of similar molecular weight to high draw ratios only succeeded at relatively high temperatures, in fact above the melting point, where the effectiveness of the chain-extension process is known to be low (see⁶⁾). The structures thus produced, therefore, exhibited but moderately improved mechanical properties⁶⁾.

In a wide-ranging study on the processability of high molecular weight polymers it has been found that the effective drawability of these materials is drastically enhanced by spinning⁷⁾ or casting from dilute solutions. This effect will be illustrated in the present paper for polyethylene, and this improved drawability will be discussed in terms of a favourable intermolecular topology of the polymer.

Experimental Part

The polyethylene used in this study was high molecular weight Hostalen GUR ($\overline{M}_n = 2 \cdot 10^5$, $\overline{M}_w = 1,5 \cdot 10^6$). The solvent was decalin, a mixture of *cis*- and *trans*-decahydronaphthalene (from J. T. Baker Chemicals). Polyethylene solutions were stabilized by 0,5 wt.-% of the anti-oxidant di-*tert*-butyl-*p*-cresol.

Dilute solutions: Solutions of 2 wt.-% polyethylene in decalin were prepared at 150 °C. Subsequently, these highly viscous solutions were pumped at 130 °C through a capillary with a diameter of 0,5 mm and a length of 3 mm. The as-spun liquid filament was quenched to room temperature by passing through a bath filled with water. A gel filament that still contained about 98 wt.-% of the solvent was thus generated.

^{a)} Part 1: cf. ⁷⁾.

One group of these gel fibers, designated I, was drawn in a hot-air oven to various draw ratios. The drawing temperature was 120°C and the strain rate was about 1 s⁻¹.

A second set of gel fibers was extracted with methanol at room temperature for three days, and subsequently dried. No residual solvent was left within detectable limits. These dried fibers (set II), too, were drawn at 120°C, as described above.

Concentrated solutions: Hostalen GUR powder was mixed with various amounts of decalin ranging from 10 to 50 wt.-%. The blended polymer/solvent mixtures were extruded at 190°C, and the filaments obtained were subsequently drawn at 120°C.

The tensile properties of all drawn fibers 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 using a crystal density of 1000 kg/m³. The moduli quoted in this paper invariably refer to the initial moduli.

Results and Discussion

Dilute solutions

In the first set of experiments the wet gel fibers (I) were drawn to various draw ratios at a temperature of 120°C. During this drawing stage a complex process occurs of redissolution of the polyethylene crystallites that constituted the originally formed polymer gel, extension, alignment, and crystallization of macromolecules, and simultaneous evaporation of the solvent. In Fig. 1 typical stress-strain curves are presented of the polyethylene filaments with draw ratios 3, 15, and 32. The draw ratio refers to the reduction in cross-sectional area of the drawn fi-

Fig. 1. Stress-strain curves of solution spun/drawn polyethylene monofilaments. Draw ratios (A): 3, (B): 15, (C): 32

bers in respect to the dried undrawn ones. This Fig. shows that the drawing process drastically improved the mechanical properties of the monofilaments, which, in fact, is well known for polymeric materials.

The Young's modulus, tensile strength and strain at break that were calculated from these curves are listed in Tab. 1. The modulus and, in particular, the strength of the fiber with draw ratio 32 (90 GPa and 3,0 GPa, resp.) rank among the highest values reported for polyethylene filaments produced by the surface-growth technique of Zwijnenburg and Pennings³⁾ and exceed those of other drawn or extruded fibers^{6,8)}.

Tab. 1. Mechanical properties of solution spun/drawn polyethylene filaments

Set	Draw ratio	Young's modulus in GPa	Tensile strength in GPa	Strain at break in %
I	3	5	0,3	10,8
I	15	41	1,7	6,8
I	32	90	3,0	6,0
II	3	6	0,4	10,1
II	15	38	1,7	7,0
II	22	55	2,2	6,2

It should be noted that the draw ratios achieved in the solution spinning/drawing process are substantially higher than the maximum draw ratio of about 5 which is attained in drawing melt-processed Hostalen GUR at the same temperature^{6,5)}. In view of the known fact that low molecular weight material, which is commonly present in heterodisperse polymers, may act as plasticizer in drawing or extrusion⁹⁻¹¹⁾, the initial presence of solvent in the gel fibers seemed to account for the high draw ratios reached in the present process. However, the plasticizing action of the solvent did not seem to explain the high efficiency of the drawing.

In order to eliminate the possible role of the solvent in the drawing stage, the set of extracted gel fibers (set II) was drawn at 120 °C. The Young's modulus, tensile strength and the strain at break of these drawn fibers are given in Tab. 1. This Tab. shows that removal of the decalin from the gel filaments, prior to drawing, reduced the attained draw ratio to some extent. Apparently, the solvent had a slight plasticizing effect, indeed. The efficiency of the drawing process did not appear to be affected by removal of the solvent. This can be concluded from the fact that the mechanical properties of the drawn filaments of both sets are identical at the same draw ratio.

Concentrated solutions

It was found that fibers obtained from the concentrated polyethylene/decalin solutions, which contained 10–50 wt.-% of solvent, could not be drawn to high draw ratios at 120 °C. A draw ratio of about 5 appeared to be the upper limit, which is similar to the maximum draw ratio attained in drawing melt-processed Hostalen GUR.

We thus face the interesting phenomenon that high molecular weight polyethylene fibers which are spun from dilute solutions exhibit a dramatically increased drawability compared with melt-spun filaments and fibers obtained from concentrated solutions. Having eliminated the plasticizing action of the solvent as the main cause (in set II), we must invoke structural dif-

ferences in the polymeric solids generated from the melt or concentrated solutions, on the one hand, and, on the other hand, from dilute solutions, in order to explain the present findings.

It is well known that high molecular weight polyethylene is difficult to process to form a homogeneous, continuous structure. This is primarily due to the high viscosity of the material. As a result, melt-processed filaments of high molecular weight polyethylene may contain numerous defects, notably remnants of grain boundaries, which cause fracture upon drawing. In a dilute solution of this polymer the macromolecules form a tenuous network with a substantially smaller number of entanglements in comparison with the undiluted melt. Naturally, a certain minimum quantity of entanglements is required to constitute a homogeneous macromolecular network, i.e., a sufficient high molecular weight of the dissolved polymer is needed in combination with a concentration that causes coil overlap. Such a tenuous network is likely to have a much more favourable intermolecular topology than the highly entangled, possibly discontinuous, melt-processed material for the generation of a structure of extended and aligned macromolecules.

Quenching the dilute polymer solution to room temperature gives rise to fixation of the network structure due to the formation of fringed-micelle type of crystallites acting as physical crosslinks. In subsequent hot drawing, very effective stretching occurs of the macromolecules that are temporarily anchored in these microcrystallites. The delay in the dissolution or melting of the crystallites prevents relaxation of the polymer molecules in the drawing process.

Removal of the solvent from the gel structure, prior to drawing (set II), did not seem to result in a major change in the overall intermolecular topology at the drawing temperature.

More detailed studies on the influence of the drawing temperature, molecular weight, etc. on the structure and properties of the polyethylene filaments produced by the solution-spinning/drawing technique will be published shortly.

The authors are indebted to Prof. *R. Koningsveld* for his continuous encouragement and stimulation, and to Dr. *H. C. Booij* for reading the manuscript and for his valuable comments.

- ¹⁾ G. Capaccio, I. M. Ward, *Polymer* **15**, 233 (1974)
- ²⁾ J. H. Southern, R. S. Porter, *J. Appl. Polym. Sci.* **14**, 2305 (1970)
- ³⁾ A. Zwijnenburg, A. J. Pennings, *J. Polym. Sci., Polym. Lett. Ed.* **14**, 339 (1976)
- ⁴⁾ P. J. Flory, *J. Am. Chem. Soc.* **67**, 2048 (1945)
- ⁵⁾ P. Smith, P. J. Lemstra, in preparation
- ⁶⁾ G. Capaccio, T. A. Crompton, I. M. Ward, *Polymer* **17**, 644 (1976)
- ⁷⁾ P. Smith, P. J. Lemstra, *J. Mater. Sci.*, in press
- ⁸⁾ S. Kojima, R. S. Porter, *J. Polym. Sci., Polym. Phys. Ed.* **16**, 1729 (1978)
- ⁹⁾ P. J. Barham, A. Keller, *J. Mater. Sci.* **11**, 27 (1976)
- ¹⁰⁾ G. Capaccio, T. A. Crompton, I. M. Ward, *J. Polym. Sci., Polym. Phys. Ed.* **14**, 1641 (1976)
- ¹¹⁾ S. B. Warner, *J. Polym. Sci., Polym. Phys. Ed.* **16**, 2139 (1978)