Polymer Bulletin 2, 775–783 (1980)

Polymer Bulletin

Influence of Spinning/Hot Drawing Conditions on the Tensile Strength of Porous High Molecular Weight Polyethylene

J. Smook, M. Flinterman and A. J. Pennings

Department of Polymer Chemistry, State University of Groningen, Groningen, The Netherlands

SUMMARY

Hot drawing in a temperature gradient has been applied to porous high molecular weight polyethylene fibers. The porous fibers were produced by spinning a 5% solution in paraffin oil and subsequently extracting the paraffin oil in n-hexane. Spinning/drawing under appropriate conditions resulted in a fiber with a tensile strength at break of 4.1 GPa. The porosity and tensile strength of a fiber were measured as a function of draw ratio. The influence of spinning/drawing conditions is discussed in relation to fiber texture and entanglement topology.

INTRODUCTION

The generation of ultra-high strength and ultra-high modulus polymers has been subject of extensive research for many years. So far, the most successful attempts to produce ultra-high strength structures of polyethylene have been methods starting from dilute high molecular weight polyethylene solutions, i.e. flow-induced crystallization in a Couette-apparatus, referred to as the 'surface growth' technique (ZWIJNENBURG, PENNINGS, 1976), hot drawing of solution spun fibers (SMITH, LEMSTRA, 1979, KALB, PENNINGS, 1979), how drawing 'surface growth' fibers (SMOOK et al., 1980). The high tensile strenghts at break of 3 GPa or higher achieved with these techniques must be due to the reduced number of defects in the crystal lattice of the fibers. Defects such as molecular entanglements, intertwinings, jogs, kinks, loops, chain ends, etc., hamper the complete alignment of the molecules and therefore reduce the tensile strength at break (PENNINGS, 1979). Decreasing the number of defects by using high molecular weight polyethylene and polyethylene solutions of low concentration accordingly leads to improved tensile properties.

In a recent note from this laboratory (KALB, PENNINGS, 1980) it was shown that fibers of extremely high tensile properties can also be obtained by hot drawing of porous high molecular weight polyethylene. The poor drawability of high molecular weight polyethylene was greatly improved by an increase in the free volume in the form of a high microporosity. The large free volume between the molecules and the crystallites lowers the energy

0170-0839/80/0002/0775/$01.80

barrier for transport of molecules and increases the molecular mobility necessary in order to get full extension of the chains. The porosity of the fibers was brought about by spinning a solution of polyethylene in paraffin oil through a conical die and by afterwards extracting the paraffin oil in n-hexane.

Further studies on this subject are reported in this letter. It will be shown that after spinning and extraction a loosely connected lamellar network has formed that can easily be drawn at elevated temperatures to high draw ratios (D.R.). After drawing has been completed a fiber with high tensile properties results (tensile strength at break of 4.1 GPa, Young's modulus of 106 GPa), revealing a highly extended fibrillar structure and a porosity of about 30% due to fibrillation. Furthermore attention will be paid to the deformation mechanism in relation to fiber texture during spinning and drawing.

EXPERIMENTAL

The linear polyethylene used in the present study was Hi-fax 1900 having a weight average molecular weight of about 4×10^6 kg/kmol. The polyethylene was dissolved in paraffin oil after addition of antioxidant at a concentration of 5% by weight under constant and slow stirring for 48 hours at a temperature of 150°C. Subsequently the solution was cooled down to room temperature and cut into little pieces. Spinning was performed in a Reifenhauser S013-25 extruder through different dies at 170°C. After spinning, the paraffin oil was extracted in n-hexane and the fibers were dried under vacuum.
The porosity of the fibers was determined from the volume, calculated from fiber weight and length, employing a density of 1000 kg/m^3 for polyethylene, and from the diameter as measured under the lightmicroscope.
Drawing experiments were carried out in a double walled glass cylinder of 1,5 m in length, through which hot silicon oil was pumped from a temperature regulated bath. A temperature gradient in the tube was established by means of a nitrogen stream creating a change in temperature of 80°C at the entrance to 148°C at the exit of the tube. The velocity of the fiber entering the tube was $4{,}4 \times 10^{-4}$ m/sec. Drawing was accomplished by means of different speed of the feed roll and the wind up drum.
Tensile tests were performed using a Zwick Z1.3B tensile tester at a cross-head speed of 2×10^{-4} m/sec and an original sample length of 25 mm at 20°C. Cross-sectional areas were calculated from fiber weight and length assuming a density of 1000 kg/m^3.

RESULTS AND DISCUSSION

The cooled down 5% polyethylene solutions in paraffin oil were spun in an extruder at a temperature of 170°C. After spinning the paraffin oil was extracted in n-hexane and subsequently the porous fibers were dried under vacuum. Drawing experiments were carried out in a temperature gradient of 80-148°C. The use of a temperature gradient was found to be necessary in order to

avoid premature breakage of the fiber.

Some characteristic results are shown in table 1. Under appropriate conditions a tensile strength at break of 4,1 GPa and a Young's modulus of 106 GPa can be attained. Furthermore, table 1 shows that spinning conditions have a distinct influence on the ultimate tensile strength at break.
The variance in spinning conditions affects the amount of orientation produced in the gel fiber during spinning. Gel fibers which are slightly oriented after spinning (conical die) seem to be the optimal starting material for producing fibers of extremely high tensile strength. A lack of orientation in the spun fibers (cylindrical die) results in a noteworthy high porosity after spinning and a decrease in ultimate tensile strength can be noticed. On the other hand winding up the gel fiber with a high take up speed of 12,5 m/s during spinning reduces the ultimate tensile strength remarkably.

The influence of the spinning conditions must find a cause in the texture and the entanglement topology of the fiber after spinning and extraction. The poor drawability of melt processed high molecular weight polyethylene (CAPACCIO et al, 1976) is clearly due to the highly entangled network of which these materials consist. In solution the polymer molecules form a network by 'reptation' (de GENNES, 1971) with a considerable smaller amount of entanglements as compared with polymer melts (FERRY, 1970) The reduced number of entanglements which represent centres of friction during drawing, greatly enhances the molecular mobility and as a consequence the drawability. Obviously a minimum number of entanglements is necessary in order to constitute a network, that shows the ability to be drawn out into long thin dreads, the properly called 'spinnability' (LODGE, 1964). Therefore high molecular weight and a concentration high enough as to give coil overlap are necessary. After cooling the gel fibers to room temperature a large number of the entanglements becomes trapped between crystallites (KALB,PENNINGS in press). However, the nature of the crystallites is dependent on the orientation brought about during spinning. When already drawing during spinning the molecules will be oriented in the fiber direction before crystallization has taken place. As a consequence after crystallization more fibrous crystallites will have formed, which have a higher melting point than lamellar crystals and need higher drawing stresses during drawing. The applied load during drawing will mainly be carried by the fibrous crystallites which results in stress concentrations in the fiber. Furthermore it might be possible for entanglements, before crystallization has occured, to slip off, resulting in an increase of elastically not effective chains. Therefore it is more difficult to get complete alignment of the molecules and the ultimate tensile strength is reduced. The reason for the reduced tensile strength when almost no orientation is brought about may be due to the high porosity of the extracted fibers, which may cause the formation of macroscopic cracks. However, the influence of orientation before spinning will be investigated further in the near future.

TABLE 1.

No.	Porosity after extraction (%)	Drawing temperature (°C)	D.R. max.	T.S. max. (GPa)	Young's Modulus (GPa)	Elongation at break (%)	Cross Sectional Area ($10^{-9}m^2$)	Extrusion Characteristics
1.	25	80-148	70	4.1	106	6.0	0.21	Conical die, L = 100mm, D = 0.8mm
2.	41	80-148	60	3.5	81	6.0	1.10	Conical die, L = 100mm, D = 0.8mm
3.	65	80-148	55	2.3	82	4.8	11.6	Cylindrical die, L = 5mm, D = 2mm
4.	23	80-148	5.4	0.75	17	6.0	0.59	Conical die, L = 100mm, D = 0.8mm Take up speed= 12.5 m/s
5.	53	80-148	90	2.7	61	5.7	0.22	Conical die, L = 100mm, D = 0.8mm
6.		150	135	3.9	97	4.7	0.088	Conical die, L = 100mm, D = 0.8 mm Two-stage drawing

Some typical results of hot drawing porous polyethylene fibers.
By two-stage drawing is meant: First drawing in a temperature gradient (80-148) to a D.R. of about 40 and subsequent drawing maximally at a drawing temperature of 150°C.

Fig. 1 shows a SEM-micrograph of a slightly oriented fiber after spinning and extraction. The morphology consists of a loosely connected lamellar network. From earlier work it is known that lamellar structures can be drawn quite easily. Lamellar crystal mats of branched ethylene-propylene copolymer could be drawn over 50 times at room temperature (HOLDSWORTH, KELLER, 1968). These lamellar structure possess a large internal surface and a high surface free energy and therefore the driving force for extension of the chains is large.

Thus the formation of a loosely connected lamellar network with a reduced number of trapped entanglements as in the slightly oriented extracted fibers reveals a much more favourable intermolecular topology for the drawing process as compared with the highly entangled, highly viscous melt processed materials.

In order to gain an insight into the drawing process, the porosity and tensile strength at break were measured as a function of draw ratio (Fig. 2). A high porosity of about 45% was found before drawing, indicating a large free volume between the molecules and the crystallites, which lowers the energy barrier for transport of molecules as follows from the equation for non-recoverable creep (WILDING, WARD, 1978). In the early stages of drawing, however, the porosity strongly decreases to 10% at a D.R. of 10. This decrease in porosity is related to the transformation of lamellar to fibrous crystallites involving unfolding of chains. The fibrous crystals in this stage still contain a lot of defects and are poorly oriented as appears from the small increase in tensile strength. Indeed the cooling of an extracted fiber in liquid N_2 and subsequent breaking already leads to the formation of fibrils in the fracture surface, as can be seen by SEM (Fig. 3). The fibril formation may come about by a mechanism as mentioned by PETERLIN and CLARK and SCOTT (PETERLIN, 1971; CLARK, SCOTT, 1974). Due to a domain structure (HOSEMANN et al., 1966) in lamellae, the lamellae do not deform uniformly, but break into blocks which then reform to fibrils. The originally laterally neighbouring domains in the lamellae have become longtudinally neighbouring blocks in the fibrils. Upon further drawing the tensile strength at break increases linearly with draw ratio to a D.R. of 40. In this drawing stage further orientation is accomplished by further unfolding of chains and removal of defects. Above 133°C the mobility of the chains is sufficient to move through crystallites (TORFS et al. in press). Migration of defects can occur and a great deal of defects are removed in this way.

However, above a D.R. of 40 no further increase of tensile strength at break occurs.
This may be caused by the fact that a certain amount of defects cannot be removed. In this drawing stage slippage of chains past each other occurs without further removal of defects. The resistance of some defects against migration is enormous, for instance a trapped entanglement, with two elastic effective chain ends of about equal length can only be removed when one of the chain ends is going to be pulled against the direction of the applied force field of the drawing stress (Fig. 4).

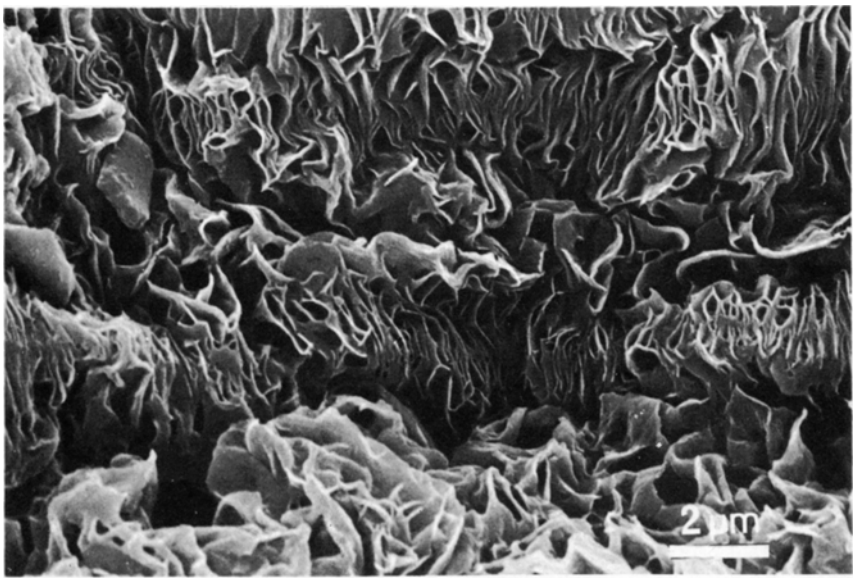

Fig.1. A SEM-micrograph of a slightly oriented fiber after spinning and extraction revealing a texture consisting of a loosely connected lamellar network.

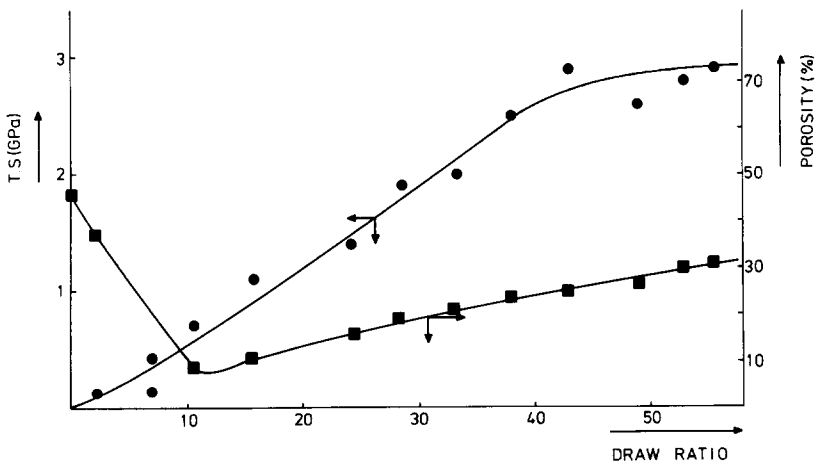

Fig.2. Plot of the tensile strength at break and the porosity of a fiber as a function of draw ratio. Drawing occurred in a temperature gradient of 80-148°C.

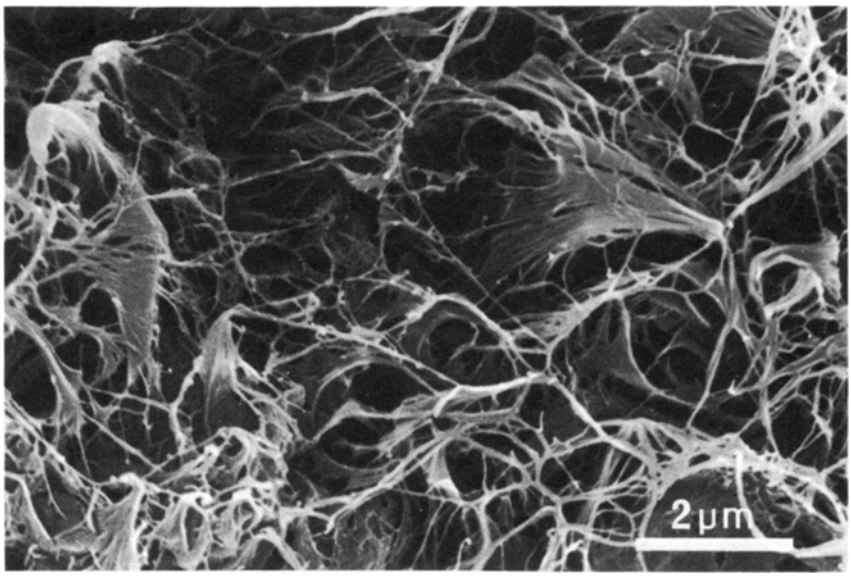

Fig.3. A SEM-micrograph of the fracture surface of a fiber cooled down in liquid N_2 and subsequently broken.

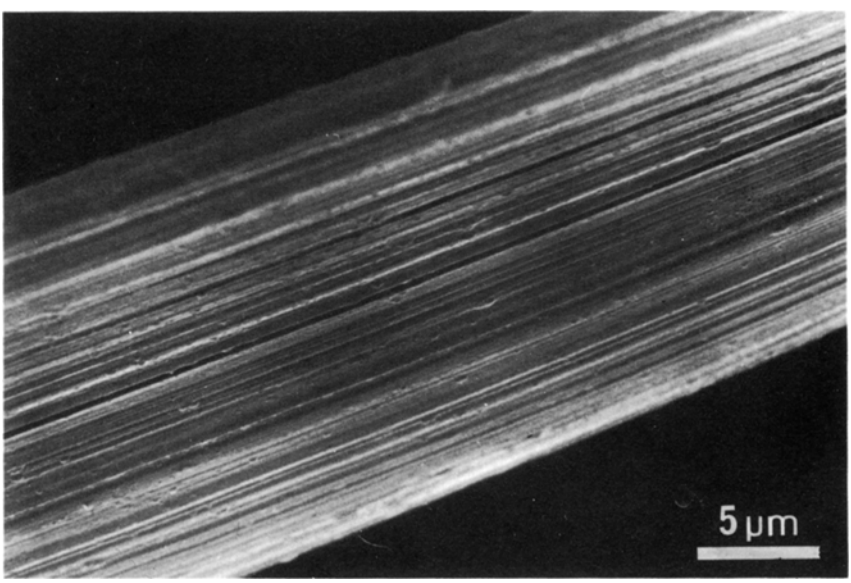

Fig.5. A SEM-micrograph of a fully oriented fiber revealing a highly extended fibrillar structure.

In a system with a viscosity of about 10^{11} Poise (SMOOK, PENNINGS, to be published) this seems highly improbable.

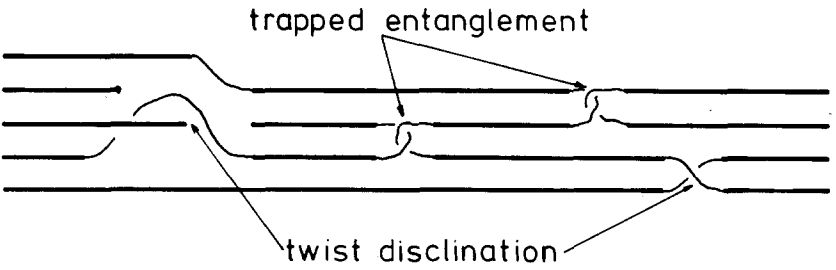

Fig.4. Examples of defects, which can not be removed by drawing.

The number of defects, which cannot be removed upon drawing, is influenced by the spinning conditions and determine the ultimate tensile strength at break that can be attained.

However, when drawing was accomplished in two drawing stages, i.e. drawing to D.R.=40 in a temperature gradient of 80-148°C and subsequently drawing until breakage occurs at a drawing temperature of 150°C, without a gradient, a remarkable increase in tensile strength at break was noticed. Certain defects, which could not be removed in the first drawing stage, might have vanished during the second drawing. Further investigations have to establish whether this was a lucky experiment or whether two-stage drawing leads to better results.

The decrease in porosity at small D.R.'s is followed by an increase in porosity above D.R. is 10. Ultimately a porosity of 30% is achieved at a D.R. of 55, due to the formation of internal longitudinal voids. (CAPPACCIO, WARD, 1976; JARECKI, MEIER, 1979) Fig. 5 shows a SEM-micrograph of maximally drawn fiber revealing this fibrillation.

CONCLUSIONS

From the results reported in this letter a number of conditions can be distilled, which have to be fulfilled in order to produce fibers of extremely high tensile properties by spinning/hot drawing.

i. Reduction of the number of defects, such as entanglements, chain ends, etc. is attained by using high molecular weight polyethylene and dilute solution of polyethylene.
ii. Spinning the polyethylene solution and subsequent extraction results in a loosely connected lamellar network, with a high drawability.
iii. Orientation induced during spinning before crystallization should be avoided, because this leads to the formation of

fibrous crystallites, which show a higher resistance against drawing than lamellar crystallites.

iv. After spinning and extraction the fibers show a high microporosity. The large free volume between the molecules and crystallites lowers the energy barrier for transport of molecules and therefore increases the drawability.

ACKNOWLEDGEMENT

The authors gratefully acknowledge B.A.Klazema for his assistance in the SEM-experiments and D.Zwittink for his assistance in the experimental work.

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Received June 9, 1980