Polymer Bulletin 16, 167–174 (1986)

Polymer Bulletin

Polyethylene

High-speed gel-spinning of ultra-high molecular weight polyethylene

A.J. Pennings*, R.J. van der Hooft, A.R. Postema, W. Hoogsteen, and G. ten Brinke

Department of Polymer Chemistry, University of Groningen, Nijenborgh 16, NL-9747 AG Groningen, The Netherlands

Summary

This communication is concerned with the gel-spinning of ultra-high molecular weight polyethylene (UHMWPE) at speeds up to 1500 m/min. It was found that 5 wt% solutions of UHMWPE in paraffin oil could be extruded through a conical die at a rate of 100 m/min. without the appearance of filament irregularities due to elastic solution fracture. These elastic turbulences occur at extrusion speeds of about 5 m/min. Without the addition of 1 wt% of Aluminium-stearate the spinline could be stretched at most to 60 m/min at 170°C but at 210°C it did not break at a speed of 1500 m/min.
These high-speed gel-spinning experiments at temperatures around 200°C yielded polyethylene fibers with a tensile strength of 3.5 GPa. It was observed that drying of the as-spun fiber containing n-hexane at constant length led to excessive crazing.

Introduction

In recent years there has been a steadily increasing research activity in the field of producing super-strong fibers of ultra-high molecular weight polyethylene (UHMWPE) by applying the gel-spinning and other techniques. Developments so far have led to the formation of fibers with the highest tensile strength values of around 8 GPa (1-2) and Young's moduli as high as 222 GPa have been reported (3). This elastic modulus was measured on fibers which were obtained by solid-state coextrusion of mats of single crystals (3-4) supposedly free from entanglements. The super-strong fibers were generated by spinning of semi-dilute solutions of UHMWPE in paraffin oil and subsequently extraction of the oil from the gel-filament with n-hexane and hot-drawing of the remaining porous fiber to the maximum draw ratio. The general consideration here is that defects in the fiber arising from the polymer chain ends can be reduced by utilizing extremely long molecules but this inevitably brings about that topological defects due to chain intertwinings are bound to be incorporated into the fiber structure. Attemps were made to minimize the number of these trapped entanglements in the fiber by starting from semi-dilute solutions and by applying elongational flow fields. However, the major problem affecting the mechanical properties arises from the flow of the transient entanglement network in the orifice and the stretching of the spinline. These highly elastic solutions give easily rise to flow instabilities causing "solution fracture". This immediately leads to fibers with poor properties (7-8). The elastic turbulence phenomenon

* To whom offprint requests should be sent

is known to be associated with the entangling of very long chain molecules and occurs at a critical shear stress at the wall of the die (9). Stretching of the spinline may suppress this phenomenon to some extent (10) but it has the disadvantage that it also reduces the tensile strength of the fibers substantially and may give rise to draw resonance (10). This drawback could be eliminated to a large extent by adding 1% by weight of Aluminium-stearate to the polyethylene solution as was found by Smook (5). This finding stimulated us to look for other ways to suppress the elastic turbulences and increase the stretchability of the spinline, obviously with the aim to produce super-strong polyethylene fibers at considerably higher speeds (11-13). Indeed we have found that "elastic solution fracture" does not occur at extrusion rates of 100 m/min. and moreover increasing the spinning temperature to around 200°C made it possible to spin smooth filaments at speeds of 1500 m/min. yielding fibers with a tensile strength of 3.5 GPa.

Experimental

The linear polyethylene sample (UHMWPE) used throughout this study was Hifax 1900 with $\bar{M}n = 2 \times 10^5$ and $\bar{M}w = 4 \times 10^6$. All solutions were stabilized with 0.5 wt% of the antioxidant 2,6-di-t-butyl 4 methylcresol in order to prevent oxidative degradation in the course of the experiments. For the gel-spinning runs, the UHMWPE was dissolved in paraffin oil at a concentration of 5% by weight. The dissolution temperature was 150°C and the solution was left at this temperature for 48 hours prior to cooling it slowly down to room temperature. The gel was cut using a cork-bore into cylinders which fitted rather accurately into the piston-cylinder apparatus. This

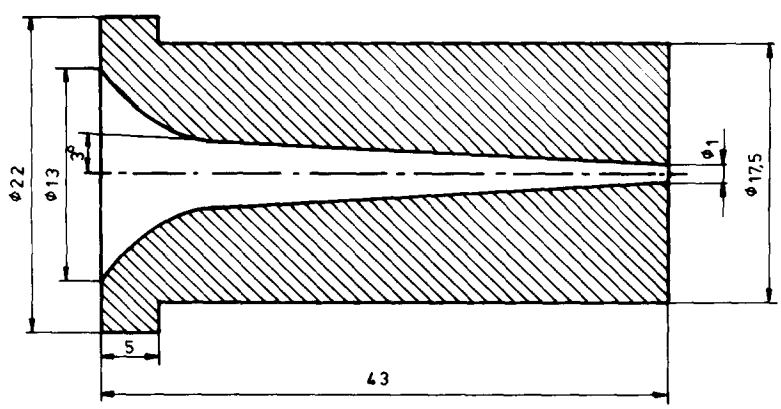

Fig. 1 A schematic representation of the conical die (length 43 mm, exit diameter, 1.0 mm).

instrument could contain 15 ml of polyethylene gel. It was equipped with a conical die (length 4.3 mm, exit diameter 1.0 mm) shown schematically in fig. 1. A winder, 250 mm in diameter was placed at a distance of 1 m from the exit of the die.
In the spinning experiments the extrudate was quenched in ambient air, resulting in the formation of a gel-filament. The paraffin oil was extracted from the gel with n-hexane and this as-spun fiber was dried in vacuum at 50°C. Hot-drawing was carried out at 148°C in a nitrogen atmosphere always to the maximum draw ratio.

Stress-strain measurements were performed on specimens which were 25 mm long. The Instron tensile tester was operated at a cross-head spead of 12 mm/min. The cross-sectional areas of the fibers were determined from the weight and length of the fiber.

Results and discussion

In previous studies on the gel-spinning of ultra-high molecular weight polyethylene (UHMWPE) we had been using a small extruder equipped with a long conical die (145 mm in length) and an entrance angle of only 6°. The disadvantage of this set-up is the large

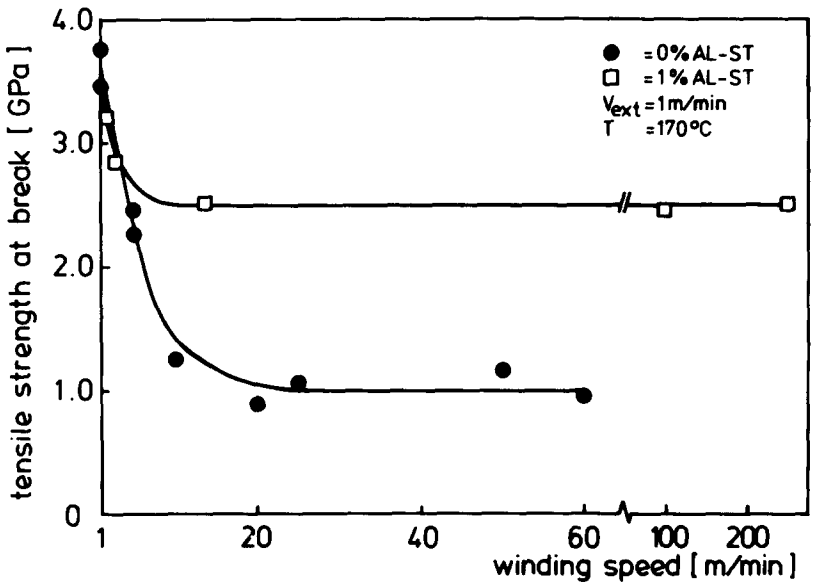

Fig. 2 Tensile strength at break of polyethylene fibers as a function of the winding speed during the spinning of 5 wt% solutions of UHMWPE in paraffin oil. Extrusion rate was 1 m/min. □, solutions containing 1 wt% of Aluminium stearate; ●, without Al-stearate.

internal surface area of the screw and the wall of the die onto which many of the very long chain molecules could get adsorbed. Another drawback is that at higher screw resolutions, necessary to attain higher extrusion rates, backflow of paraffin oil occurs. These difficulties could be overcome, at least in the part, by using a small piston-cylinder instrument. At first we spun with this arrangement the usual 5 wt% solutions of UHMWPE in paraffin oil at 170°C and an extrusion rate of 1 m/min. in order to find out whether there might be any difference with the extruder technique. After spinning, the gel-fibers were extracted with n-hexane and subsequently dried and hot-drawn at 148°C to the maximum draw ratio. A plot of the tensile strength at break as a function of the winding speed for the fibers so obtained in fig. 2 shows again that the strength decreases from approximately 4 GPa at a wind-up speed of 1m/min. to about 1 GPa at 20 m/min. The maximum take-up speed just before the spinline broke, turned out to be 60 m/min. The only difference with the extruder technique is that the lower strength level in the present set-up is 1 GPa, whereas previously only 0.2 GPa values were obtained. This difference might be attributed to the fact that the present die has a

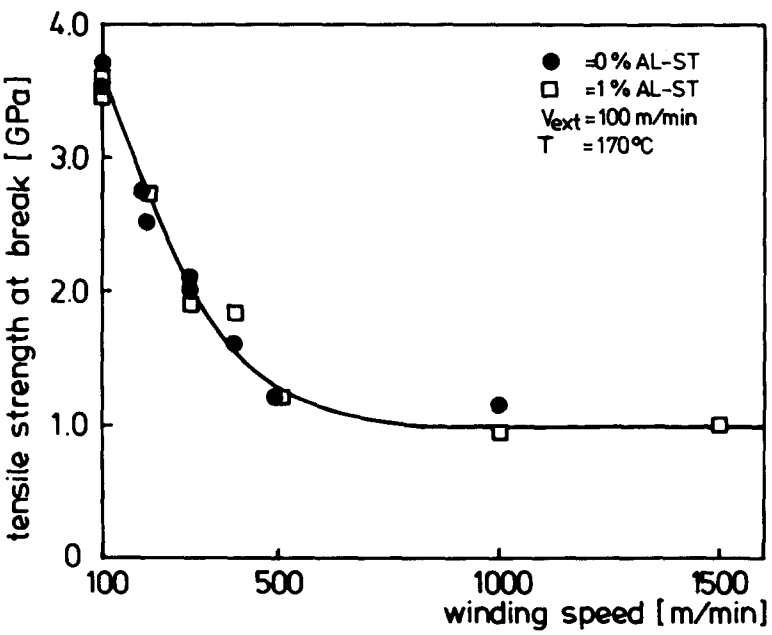

Fig. 3 Tensile strength at break of polyethylene fibers versus the winding speed. The fibers were spun at 100 m/min. ●, 5 wt% UHMWPE in paraffin oil; □, solutions containing 1 wt% of Aluminium-stearate.

considerably smaller internal surface area so that the effect of adsorption of the long polyethylene molecules is not so severe. Further reduction of the adsorption by doping the polyethylene solutions with 1 wt% of Aluminium-stearate leads in the present case to a rapid lowering of the strength to only 2.5 GPa. But this strength level could further be maintained up to winding speeds of approximately 300 m/min. at which the spinline broke. Threadline failure and concomitantly a decrease in tensile strength may result from rupturing of the entanglement network. This is likely to occur earlier in case the network is stretched on one end while the other end is anchored by the adsorbed layer on the wall of the die. This is basically our working-hypothesis for the lowering of the tensile strength in stretch-spinning. It might be verified by several experiments. For instance one could increase the extrusion rate in such a way that the residence time of the network in the spinneret is small compared to the time required for adsorption. Under these conditions the differences in the tensile strength-winding speed plot for the solution of UHMWPE in pure paraffin oil and the one doped with Al-stearate should vanish. The results presented in fig. 3 for both solutions extruded at a rate of 100 m/min. show that this is indeed the case. Wind-up speeds of 1500 m/min. could be achieved without fracturing of the threadline. The absence of elastic turbulences under

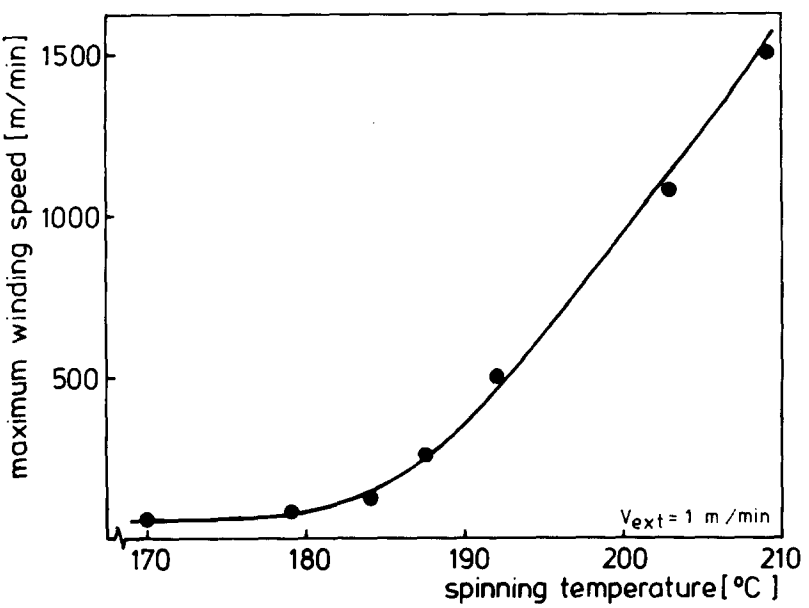

Fig. 4 The maximum winding speed at which the spinline breaks for 5 wt% solutions of UHMWPE in paraffin oil versus the spinning temperature. The extrusion rate was 1 m/min.

these circumstances does not mean that this phenomenon should only be attributed to adsorption. The stretching of the transient network may also be accompanied by syneresis which provides pure solvent that may act as a lubricant between the network and the die surface. This would then transform the flow that involves the release of entangelements by shear into a sort of plug-flow. These considerations indicate that the flow of entanglement networks may be very complicated just as the mechanism underlying the formation of elastic turbulences.
Nevertheless, adsorption seems to play a basic role and if this is the case one could for instance expect that the temperature might have a rather strong effect. For this reason experiments were carried out at different temperatures. The influence of temperature on the maximum wind-up speed for 5 wt% solutions of UHMWPE in paraffin oil extruded at a rate of 1 m/min. is shown in fig. 4. At 170°C the spinline fractures at 60 m/min. whereas at 210°C it did not break at the highest possible speed of 1500 m/min.
The remarkable enhancement in stretchability of the polyethylene solution with temperature also stems from the increase in chain flexibility which reduces the tendency of the polymer molecules to being adsorbed and allows a more rapid adjustment to the elongational flow field.

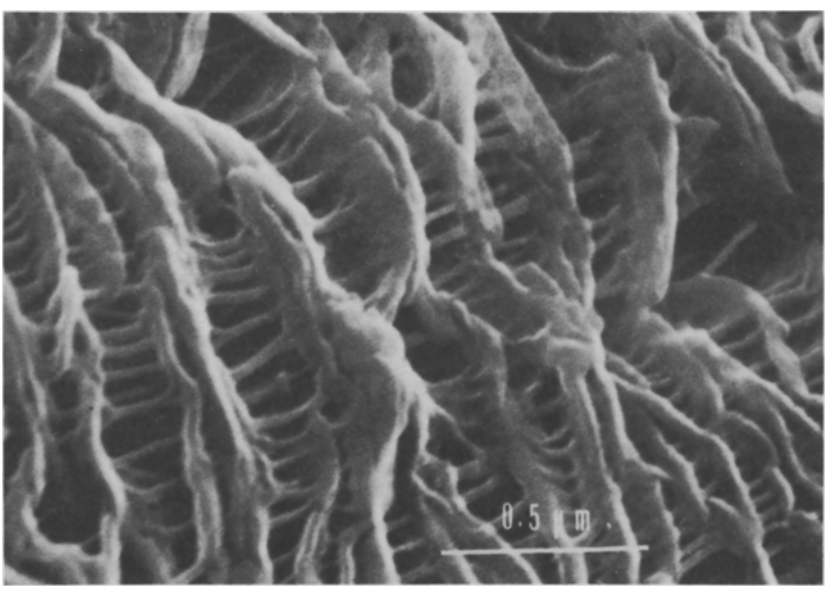

Fig. 5 SEM-micrograph of an extracted as-spun polyethylene filament exhibiting crazes.

Another way to diminish adsorption is to modify the inner surface of the die chemically. We had some succes by treating the aluminium

die with stearoylchloride which reacts with the hydroxyl groups at the surface making it completely hydrophobic.

One final observation which seems to be very pertinent to the process of gel-spinning is the transformation of the lamellar structures present in the as-spun fiber into a fibrillar one upon hot-drawing and the ease with which the extracted fiber crazes upon evaporation of the hexane. Fig. 5 shows a scanning electron micrograph of a polyethylene fiber spun at 170°C, exhibiting many fibrils with 20 nm in diameter bridging the lens-shaped void. Crazing seems to occur when the wind-up speeds are low and the hexane extracted fibers are set to dry at constant length. At higher wind-up speeds shish-kebabs are formed as a result of oriented crystallization of the stretched network. The diameters of the fibrils in the crazes and the ones between the platelets of the shish-kebabs seem to be quite similar (14). They decrease with increasing wind-up speed and decreasing temperature analogous to the variation in fibril dimension as observed for glassy polymers like polycarbonate by Paredes and Fischer (15). Fibril formation in crazes originates from the instability of the interface acceleration around a void when the polymer system has been subjected to external stresses. This meniscus instability problem, first described by G.I. Taylor (16), may be generally applicable and therefore also responsible for the break-up of the stretched entanglement network in a state of supercooling. The entanglements and intertwinings seem to accumulate in regions which after further lowering of the temperature solidify into lamellar structures. In the hot-drawing step following the spinning the lamellae are converted into fibrillar material. It is to be expected that not all intertwinings and entanglements will be released in this process. We have shown that hot-drawing gives rise to fracturing of the chains and undoubtedly to the incorporation of trapped entanglements and tight knots (17). This type of scissioning of chains in the process is not the strength determining factor. For instance by spinning a solution without additive and high wind-up speeds we ended up with a tensile strength of 1.2 GPa. The intrinsic viscosity of this material was 15.5 dl/g while that of the starting polymer was 20.0 dl/g. The weak fiber was dissolved again in paraffin oil and spun under optimal conditions yielding a fiber with a tensile strength of 3 GPa. This clearly illustrated that the fiber strength does not exclusively originate from the chain length but rupturing of the entanglement network seems to be a more severe cause of flaws that governs the mechanical properties.

The main conclusion of the present investigation therefore is that gel-spinning of ultra-high molecular weight polyethylene at high-speed is possible, provided that conditions are chosen such as high extrusion rates and temperatures which avoid severe rupturing of the entanglement network.

References

1. D.C. Prevorsek, Proc. Symp. Fiber Sci. and Techn., Hakone, Japan, 18, (1985)
2. V.A. Marichin, L.P. Mjasnikova, D. Zenke, R. Hirte and P. Weigel, Pol. Bull., 12, 287 (1984)
3. T. Kanamoto, A. Tsuruta, K. Tanaka, M. Takeda and R.S. Porter, Polymer J., 15, 327 (1983)

4. K. Miyasaka, Proc. Symp. Fiber Sci. and Techn., Hakone, Japan, 27, (1985)
5. J. Smook, Ph.D. Thesis, Groningen (1984)
6. A.J. Pennings, J. Smook, J. de Boer, S. Gogolewski and P.F. van Hutten, Pure and Appl. Chem., 55, 777 (1983)
7. J. Smook and A.J. Pennings, J. Mater. Sci., 19, 31 (1984)
8. J.H. Southern and D.R. Paul, Polym. Eng. Sci., 14, 560 (1974)
9. J.H. Southern and R.L. Ballman, Tex. Res. J., 53, 230 (1983)
10. C.D. Han, "Rheology in Polymer Processing", Acad. Press (1979)
11. A. Ziabicki and L. Jarecki in High-speed fiber spinning: Science and Engineering aspects ed. A. Ziabicki and H. Kawai, Wiley and Sons Inc., (1985)
12. H.M. Heuvel and R. Huisman in "High-speed fiber spinning", Wiley and Sons Inc. (1985)
13. J. Shimizu, N. Okui and T. Kikutani in "High-speed fiber spinning", Wiley and Sons Inc. (1985)
14. A.J. Pennings, Proc. Symp. Fiber Sci. and Techn., Hakone, Japan, 20 (1985)
15. E. Paredes and E.W. Fischer, Makromol. Chem. 180, 2707 (1979)
16. G.I. Taylor, Proc. Roy. Soc. Lond., A210, 192 (1950)
17. P.G. de Gennes, Macromol., 17, 703 (1984)

Accepted July 16, 1986

C