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Further studies on the high-speed gel-spinning of ultra-high molecular weight polyethylene

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Summary

The high-speed spinning technique has been applied to very elastic solutions of ultra-high molecular weight polyethylene in paraffin oil in an attempt to produce a strong fiber in a one-step process. At a winding speed of 4000 m/min a fiber was produced with a tensile strength of 2.3 GPa, a Young's modulus of 46 GPa and a elongation at break of 6.5%. This fiber could not be hot drawn anymore. At a winding speed of only 1 m/min the same solution yielded after spinning and hot drawing a fiber with a tensile strength of 7.2 GPa.

Introduction

High-speed fiber spinning (1) has interested scientists for some two decades, a period in which considerable advances in our understanding and technological development have taken place. The basic objective is to increase the fiber productivity and simplify the spinning process by applying high-speed winders, which stretch the polymer melt to such an extent that a fully oriented and crystalline fiber is formed in one step. Winding speeds of over 10.000 m/min have been utilised in the case of polyethylene terephthalate with rather low viscosity (1) and one may wonder what sort of fiber structures are formed by subjecting highly viscoelastic solutions of ultra-high molecular weight polyethylene (UHMWPE) in paraffin oil in a spinning process to these high take-up velocities. As a result of using extremely long chain molecules, a prerequisite for generating strong fibers, their solutions are highly elastic, which easily gives rise to flow instabilities (2)(3) such as secondary flow vortices (4), elastic turbulence, pulsing flow and draw resonance. Also adsorption at the wall of the spinneret (5), rupturing of the entanglement network and formation of tight knots (6) seem to be involved in the fiber formation process. The mechanisms of these processes have still remained obscure and stretching of viscoelastic solutions beyond a critical value of the deformation rate may readily lead to brittle fracture of the spinline as a result of storage of part of the deformation energy (1). Nevertheless in our attempt to explore high-speed spinning of polyethylene solutions we were able to stretch the spinline by winding at a speed of 4000 m/min, thereby producing an as-spun polyethylene fiber with a tensile strength at break of 2.3 GPa, a Young's modulus of 46 GPa and an elongation at a break of 6.5%.

Experimental

Ultra-high molecular weight polyethylene (UHMWPE) used throughout this study was Hifax 1900 with $Mw=5.5x10^6$ and $Mn=2.5x\ 10^6$. $[\eta]=33$ dl/g measured in decalin at 135°C was determined by Viscotek Corp. (Porter, U.S.A.). 1.5 wt % UHMWPE was dissolved in paraffin oil in a manner described previously (7). All solutions were stabilised with 0.5 wt% of the anti-oxidant 2,6-di-t-butyl 4 methylcresol in order to prevent oxidative degradation in the course of the experiments. The as-spun fibers were extracted with n-hexane and subsequently dried in vacuo at 50°C. The spinning apparatus equipped with a conical die (5), having a exit diameter of 0.5 mm, is schematically represented in fig.1. The cylindrical oven around the spinline was 3.8 cm in diameter and 20.5 cm in length. The spinline length was approximately 50 cm and the winder was 50 cm in diameter.

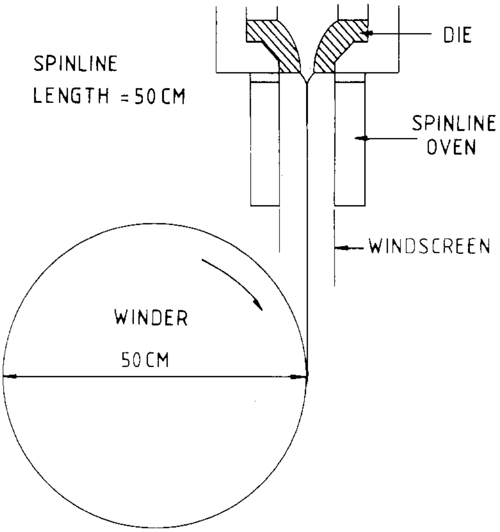

Figure 1: A schematic representation of the high-speed spinning set-up for UHMWPE solutions.

Tensile tests were carried out using an Instron 4301 tensile tester at a crosshead speed of 12 mm/min and a gauge length of 2.5 cm at roomtemperature. Differential Scanning Calorimetry (DSC) measurements were performed using a Perkin

Elmer DSC-7 at a scanning speed of 10°C/min. For constrained melting studies the fibers were wound around a small aluminium frame with dimensions of 4x4 mm. The scanning electron micrograph (SEM) of the fiber was taken with an ISI-DS 130 microscope. The fiber was covered with a thin gold layer to ensure sufficient electrical conductivity.

Results and discussions

Figure 2 presents the tensile strengths, ranging from 0.3 GPa to 7.2 GPa, as a function of the winding speed for fibers produced by extruding 1.5 wt % solutions of ultra-high molecular weight polyethylene (UHMWPE) in paraffin oil through a conical die at a temperature of 220°C.

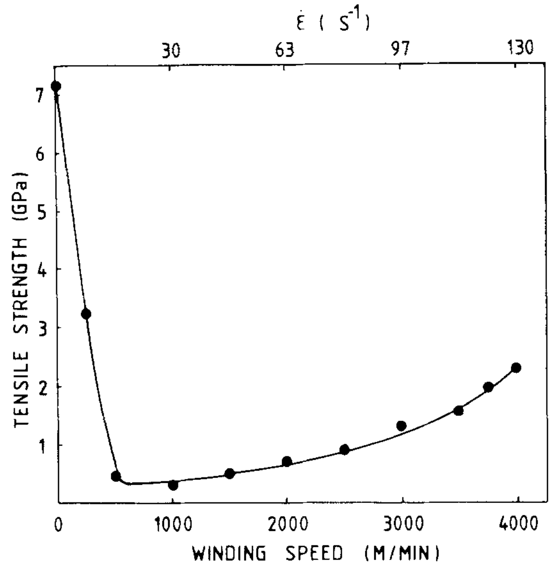

Figure 2:
The tensile strengths of polyethylene fibers as a function of the winding speed and the corresponding elongational flow rate, $\dot{\varepsilon}$, in the spinline.

The 7.2 GPa polyethylene fiber was produced by slow extrusion at 1 m/min and winding the threadline at the same speed. The as-spun fiber was stripped off its oil and the remaining lamellar texture was subsequently hot drawn at 148°C to a draw ratio of 200. By increasing the spinning speed to 100 m/min and raising the winding speed to 250 m/min the dry as-spun fiber could only be hot drawn to =40 while the tensile strength dropped to 3.2 GPa. A further dramatic reduction in strength to 0.3 GPa was observed upon increasing the winding speed to 500 m/min (8). This as-spun fiber could not be hot drawn anymore. This appears to be associated with the orientation-induced crystallization of the entanglement network in the spinline (8). The maximum winding speed could substantially be enhanced by using a heated shaft around the spinline in an attempt to suppress crystallization. For instance figure 3 shows the marked increase of the maximum winding speed as a result of raising the ambient temperature of the spinline.

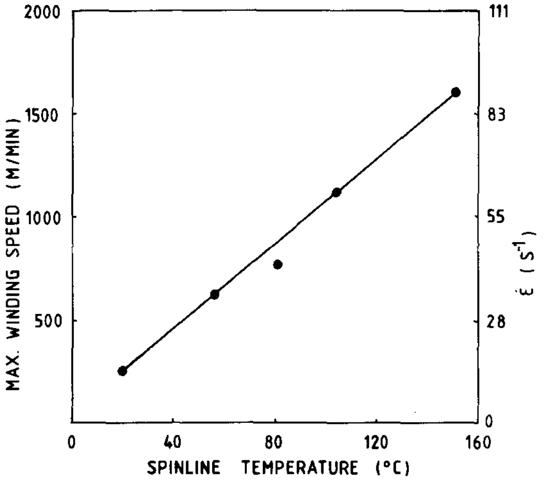

Figure 3: The maximum winding speed and the corresponding elongational flow rate, $\dot{\varepsilon}$, in the spinline as a function of the shaft temperature around the spinline for polyethylene solutions extruded at 1 m/min and 190°C.

At a shaft temperature of 160°C a take-up velocity of about 1600 m/min could be attained. The solution was then extruded at 1 m/min and 190°C. For 220°C and spinning at 100 m/min the maximum winding speed was 4000 m/min. All these high-speed spun fibers could not be hot drawn but we were rather surprised to find that the 4000 m/min fiber had a tensile strength of 2.3 GPa and a Young's modulus of 46 GPa and an elongation at break of 6.5%.

In the scanning electron microscope these fibers were found to be bundles of 6 µm thick fibers. The latter appear to consist of elementary fibrils. The lamellar component of the fiber could be determined by heating it at constant length in a DSC while being exposed to paraffin oil. The lamellar material in this constrained melting experiment will dissolve at a temperature of about 128°C and the fibrils exhibit first an endothermic peak resulting from the transition of the orthorhombic crystal structure into the hexagonal one at a temperature of 156°C.

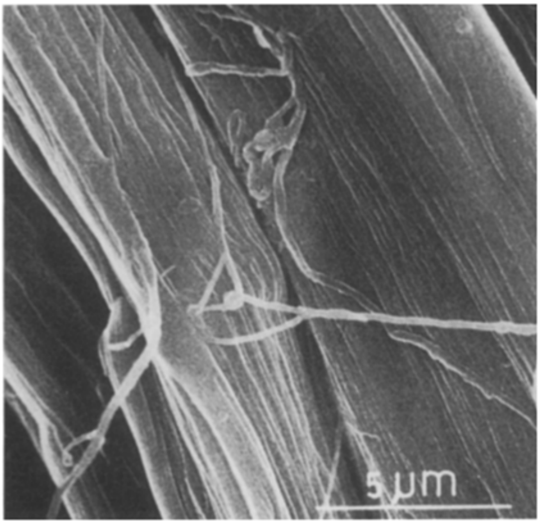

Figure 4:
SEM-micrograph of a bundle of extracted high-speed spun polyethylene fibers (2700 m/min).

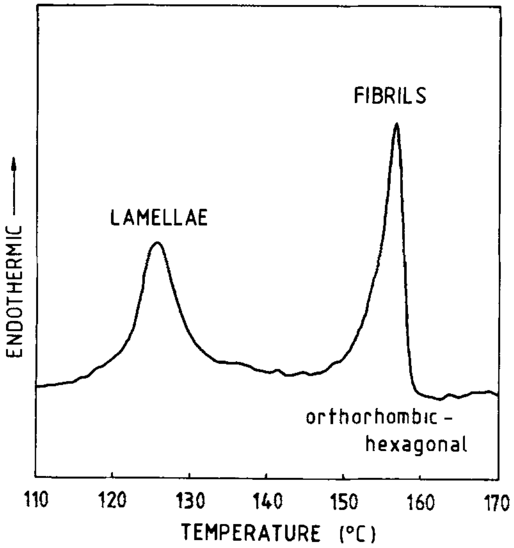

Figure 5:
Constrained melting thermogram of high-speed gel-spun UHMWPE fiber heated in the presence of paraffin oil.

The thermogram of figure 5 reveals that there is still a large portion of lamellar material left in the fiber. Apparently a large number of the entanglement-network strands have not been stretched in the high-speed experiment (9). This number also includes the rather large portion of loose chain ends, the concentration of which increases substantially upon dilution of the polymer. But the major part of the lamellar component originates from the network chains, whose end-to-end distance is oriented perpendicular to the stretch direction and cannot be pulled taut instantaneously. They first have to slip through the hooks formed by the adjacent entanglements. This requires another time scale than that needed for stretching the network strands between junction points parallel to the elongational flow direction. The deformation rate, $\dot{\varepsilon}$, times the relaxation time, τ, should be larger than a constant of the order of unity but especially the residence time of the network in the flow field should be long enough in order to achieve full extension of all the chains (10), (11), (12). If several stretched chains happen to crystallize in an early stage further transport of chains through entanglement loops may be inhibited. The fraction of fibrillar material should then correlate with the tensile strength. From the DSC thermograms the fraction of fibrillar material was assessed by dividing the 156°C peak area by that of the two peaks and plotted against the tensile strength in figure 6. It is evident that so far we have not found yet the optimum condition for complete oriented crystallization of the entanglement network in an elongational flow field. Furthermore, the present experimental study has also been blurred by flow instabilities due to the extreme elasticity of the polyethylene solutions. The extrusion rate was maintained at 100 m/min in order to avoid pulling the entanglement network out of the spinneret. Under these conditions the shear rate at the wall of the die is approximately 27×10^{3} s^{-1} It is concievable that this value

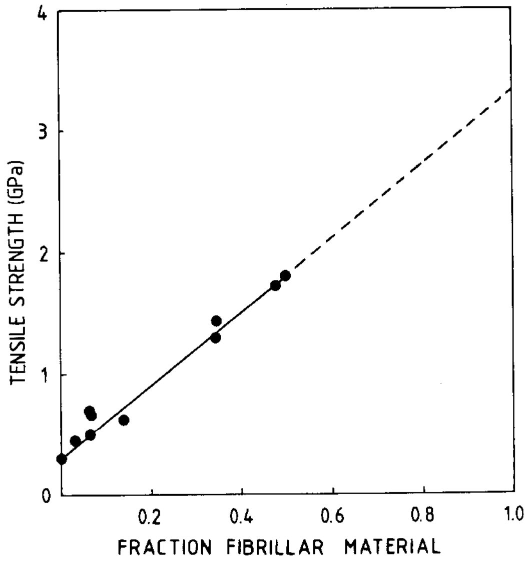

Figure 6:
The tensile strength of UHMWPE fibers versus the fraction of fibrillar material derived from DSC thermograms.

is already beyond the critical shear rate for the onset of oscillatory flow because after about 1 minute of extrusion, the spinline became rather irregular and the mechanical properties of these fibers were considerably poorer. This pulsing flow phenomenon appears to be associated with a slip effect at the wall of the spinneret which might be due to the strong tendency of these very long molecules to adsorb onto the wall. The time effects involved in adapting train tail loop configurations and the building up through these loops of an entangled layer may constitute this induction time.

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