Die-free spinning: A method for producing high performance polyethylene fibres and tapes

Malcolm R. Mackley and Samad Solbai
Department of Chemical Engineering, University of Cambridge, Cambridge, CB2 3RA, UK
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A new method of producing high performance polyethylenes employing the gel route is reported. In this method the use of a die or spinneret is unnecessary in order to spin the fibres or films.

(Keywords: gel spinning; high modulus; high performance fibres; polyethylene; tubeless siphon)

INTRODUCTION

High performance polyethylene fibres with a Young's modulus greater than 50 GPa and tensile strength greater than 1.0 GPa have been manufactured since the late 1970s by a number of processes derived from the pioneering work of Zwijnenburg and Pennings[1] and Smith and Lemstra[2]. In this paper we report a new technique of producing high performance polyethylene fibres and tapes using a method that does not require the process fluid to pass through a die or spinneret.

EXPERIMENTAL

A polyethylene gel is prepared by dissolving Hifax ultrahigh molecular weight polyethylene in dekalin. Typically a 0.5% w/v gel was prepared by adding the polymer powder to a preheated volume of solvent which was held at 90°C. Whilst continuously stirring, the mixture was then heated to 130°C and maintained at that temperature for 30 min. At this stage the gel had the appearance of a transparent, homogeneous viscoelastic fluid. However, we have experimental evidence which suggests that the gel retains some memory of its original solid form and this will be reported separately in a later publication. The final rheological characteristics of the gel varied depending on the precise thermal and mechanical history of the fluid but we found that the ability to die-free spin fibres from the gel was not critically sensitive to this variation.

The schematic arrangement of the die-free spinning process is shown in *Figure 1*. The gel is maintained under quiescent conditions in an open topped beaker at the bulk temperature recorded within the fluid in the range $T = 120°C–130°C$. Spinning is initiated by inserting a small metal rod of about 1.0 mm diameter into the solution and gently withdrawing the rod and attached gel fibre. The gel fibre was then threaded over a PTFE pulley and wound up on a motor driven spool. As the gel is withdrawn from the gel pool it forms a cylindrical parison (as shown photographically in *Figure 2*) which is stable and symmetric. Under typical drawing speeds of about 2 m/min the base of the parison had a diameter of about 5–10 mm with a final diameter of order 1.0 mm. The shape and dimensions of the parison surprisingly appeared to be relatively independent of the windup up speed of the fibre when operating under steady state conditions.

When the gel fibre emerges at the surface, cooling takes place between the gel and the surrounding air. Crystallization of the gel begins when the temperature falls below approximately 75°C and the final gel fibre produced is both compliant and contains solvent both within and on the surface of the fibre.

We have successfully spun gel fibres from 0.2%–1.0% w/v concentration solutions and at the present a maximum spinning speed for the 1 mm diameter precursor wet gel fibre of 15 m/min has been achieved. The system appears to be remarkably stable, giving a highly uniform fibre and in addition we have been able to spin several fibres simultaneously from the same pool of gel.

Partly to make subsequent handling easier we have chosen to harvest gel fibres in a tape form and this was

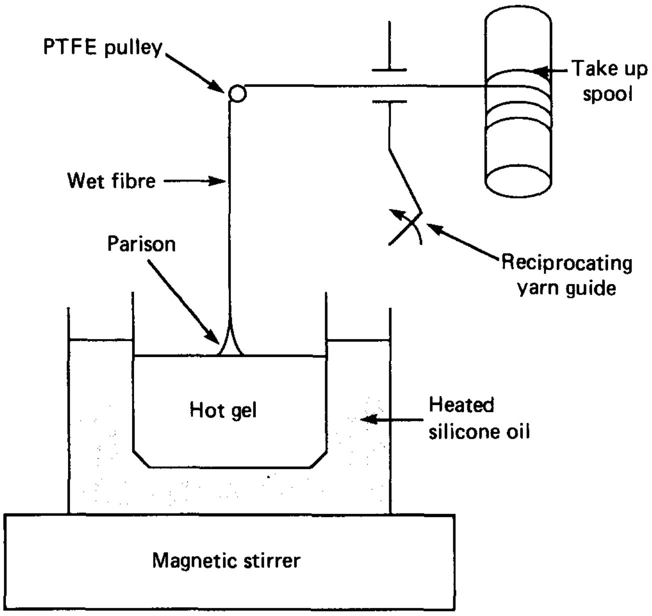

Figure 1 Schematic diagram of a die-free spinning process

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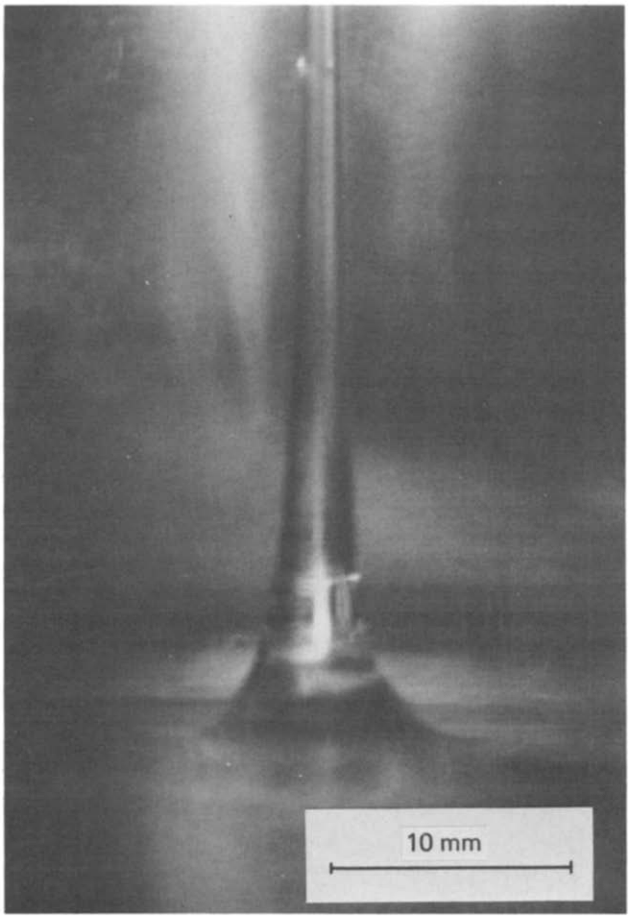

Figure 2 Photograph of a gel spinning process showing a wet gel fibre emerging from the fluid surface: polymer concentration = 0.5 w/v %; gel temperature = 130°C

achieved by winding the fibre onto a bobbin and simultaneously providing a slow horizontal traverse of the fibre along the length of the bobbin. In this way the fibres formed a coherent and nearly transparent film around the bobbin. The polyethylene film has characteristics similar to that of a sponge and a solvent can be removed either by applying mechanical pressure or by allowing evaporation to occur at elevated temperature but below the fibre melting point of about 138°C.

At this point the film has crystallinity with essentially no preferred molecular orientation. In order to achieve high chain anisotropy together with levels of high crystallinity the films were drawn at elevated temperature using a JJ tensile testing machine in the range between 80°C–120°C and at a crosshead speed of 100 mm/min. The cross sectional area of the specimens was determined by weighing known lengths of the samples and assuming a bulk density of 1000 kg m^{-3} for the polymer. It was found that draw ratios λ of between 1–50 could readily be achieved. The draw ratio being determined as the final increased length divided by the original length of grid spacings marked at 5 mm intervals on the surface of the film.

RESULTS

The composite tapes were found to exhibit good drawability and excellent final mechanical properties. A Young's modulus of 96 GPa was recorded for a composite tape drawn to 34 times its original length at 84°C as shown in *Figure 3*. These specimens were prepared from a 0.5% w/v solution spun at the rate of 2.0 metres/min. The corresponding tensile strength was approximately 1.74 GPa for a specimen length of 150 mm (*Figure 4*).

The values of the tensile strength are relatively low compared to the values reported for single strand fibres prepared by the gel extrusion process[3] and another technique that we have developed[4]. This is attributed to the susceptibility of the composite tapes to fibrillate and fail at the grips. A draw ratio of up to 60 has been obtained for single strand fibres prepared under the above conditions but we have not yet been able to measure the mechanical properties of these single fibres.

Figure 5a is a scanning electron micrograph of an undrawn filament showing the apparent lamellar structure and the porous nature of the gel spun fibre. This appearance is consistent with the structure reported by other workers[5] for gel spun polymers. A micrograph of a fibre drawn to about 10× is shown in *Figure 5b* showing the absence of the original porosity and its highly smooth appearance.

Figures 6a, *6b* and *6c* are microbeam X-ray diffraction patterns of a single fibre before and after being drawn to different draw ratios. *Figure 6b* shows a single fibre drawn to five times its original length and we note that the two

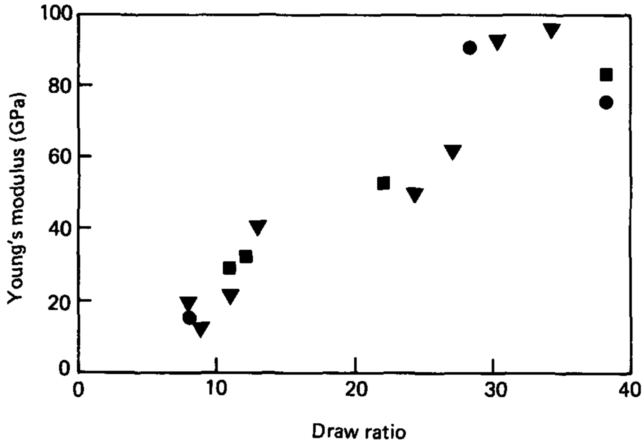

Figure 3 Young's modulus *versus* draw ratio for gel spun composite tapes: precursor fibres = 0.5 w/v% Hifax in dekalin; gel temperature = 130°C; wind up speed = 2.5 metres/min; drawing temperatures = (▼) 84°C, (■) 103°C, (●) 120°C

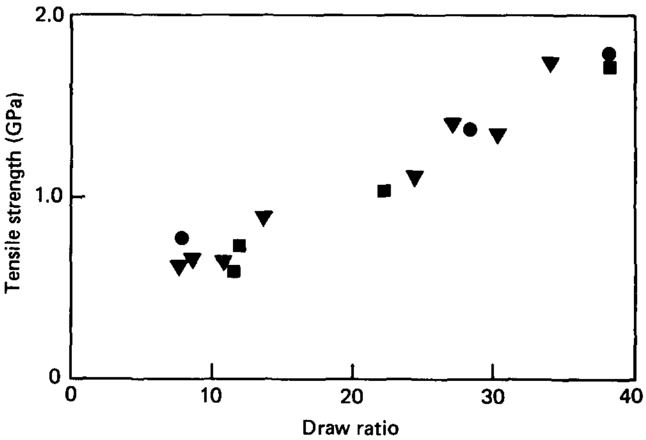

Figure 4 Tensile strength *versus* draw ratio for gel spun composite tapes (specimen lengths 150 to 200 mm). Details as per *Figure 3*

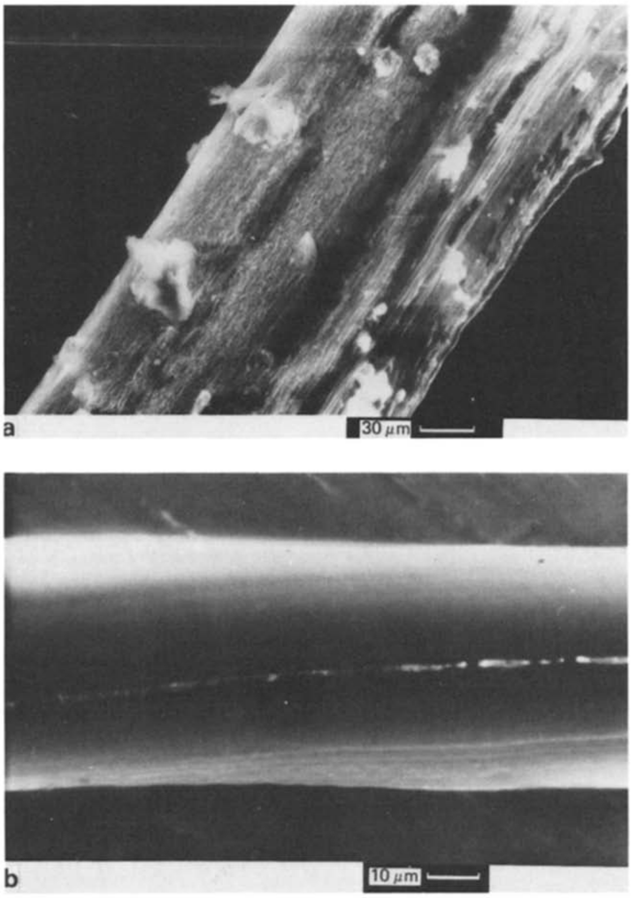

Figure 5 Scanning electron micrographs of: (a) an undrawn gel spun fibre; (b) a gel spun fibre drawn *ca.* 10×

first order circular rings which correspond to $2\theta = 21.3°$ and 24.0° are now compressed into arcs confined to the equatorial regions. These arcs are further reduced to form mere dots at much higher draw ratios as in *Figure 6c* which shows the diffraction pattern for a fibre drawn to 60×. The reflections correspond to $2\theta = 19.5°$, 22.1° and 24.1° respectively. These values at high draw ratios are consistent with the values quoted by Pennings *et al.*[6] and Turner-Jones[7] who suggested that they correspond to the (010), (100) and (110) reflections of the triclinic unit cell of polyethylene. The d.s.c. scans of the fibres drawn to 40× and carried out at a heating rate of 10 deg/min are shown in *Figure 7* which indicated the presence of transitions at 149°C and 159°C. These transitions are higher than the melting point of the unoriented polymer which is approximately 138°C.

DISCUSSION

Our general findings are consistent with those of Smith and Lemstra[3] in that high drawability of ultrahigh molecular weight polyethylene appears to be directly related to the low entanglement state produced by the processing from the gel state. Crystallization followed by elevated temperature drawing yields a high draw ratio and a very high level of chain anisotropy with associated enhanced properties.

The die-free spinning has similarities to the rheological tubeless syphon experiment which amongst others has been investigated by Macsporran[8]. In this context the die-free spinning experiment does represent a pure

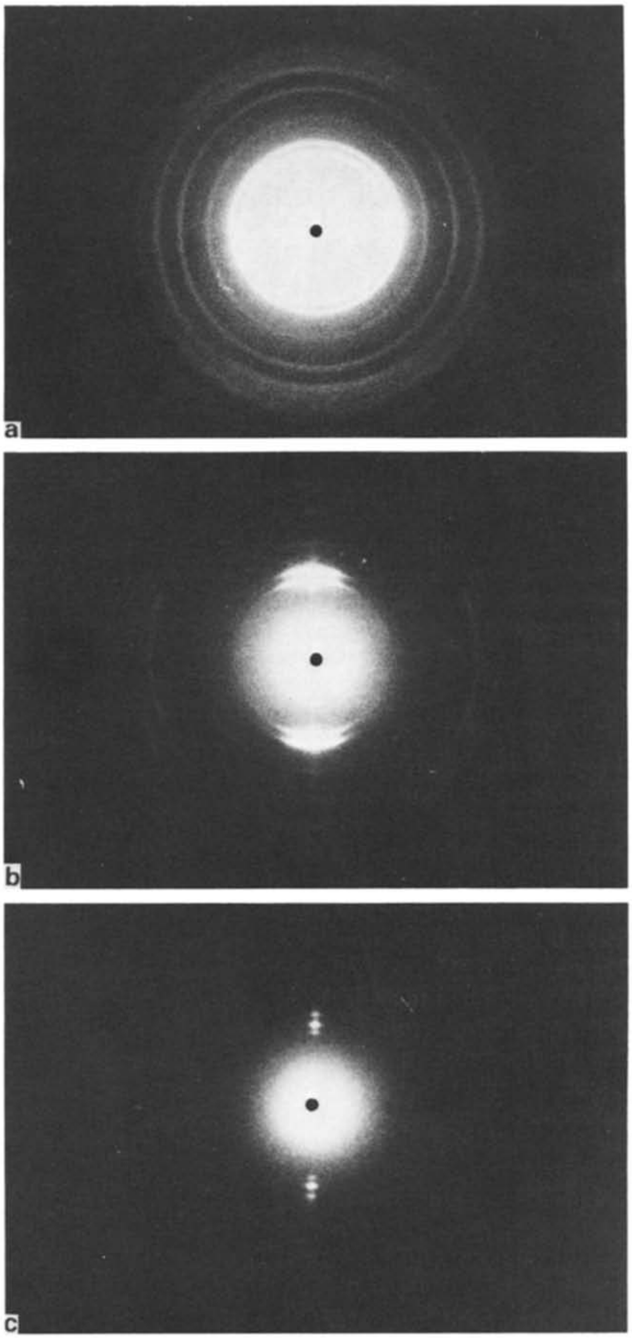

Figure 6 Microbeam X-ray diffraction (fibre axis – horizontal) of: (a) an undrawn fibre; (b) a gel spun fibre drawn 5×; (c) a gel spun fibre drawn 60×; (specimen prepared as in *Figure 3*)

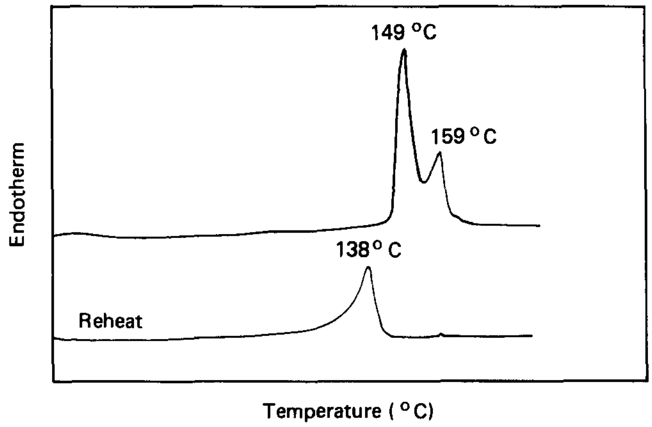

Figure 7 D.s.c. scans of a gel fibre drawn 43×. Details as per *Figure 3*; draw temperature = 120°C (scan rate = 10 deg/min)

extensional flow geometry which is worthy of detailed examination. It is somewhat surprising to note that we found the precursor fibre to have essentially no anisotropy although it has been subjected to prior solidification in a moderately high extensional flow. This contrasts with the experiments reported by Frenkel[9] where he used a spinning geometry similar to that of our own to produce orientation within the drawn parison for certain polymer solutions. The spinning geometry is also reminiscent of the 'Indian rope trick' method for the interfacial polymerization of polymers such as nylon[10], however in both of the above cases the objective is not to prepare a low entanglement solid precursor geometry which is then subjected to high draw ratios.

The die-free spinning process offers possible process advantages over the spinneret route[2] in that amongst other factors, problems associated with melt flow instabilities, die swell and spinneret blockage are overcome. In addition the method of die-free spinning may also be applicable to systems that contain strong acids such as lyotropic liquid crystal polyamide solutions where corrosion and wear of the spinneret is significant.

Finally we have found that by applying appropriate starting boundary conditions it is possible to harvest directly from the gel pool a tape rather than a fibre geometry. This leads to the possibility of using die-free spinning for the continuous production of both uniaxially and biaxially oriented films.

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