JOURNAL OF MATERIALS SCIENCE 15 (1980) 2229–2235

Some observations on the production of polyethylene fibres by the surface growth method

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We present the results of a systematic study of the parameters affecting polyethylene fibre production by the surface growth method of Zwijnenburg and Pennings [1–4]. We show that the mass growth is a useful parameter for monitoring the efficiency of fibre production. A method of increasing the production rates several fold is descibed. The mechanical properties of the fibres are reported and are in broad agreement with those previously described by Zwijnenburg and Pennings [1, 2].

1. Introduction

In a recent series of publications [1–4] Zwijnenburg and Pennings have described a novel method for the production of polyethylene fibres from solution; this has become known as the surface growth technique. The macroscopic fibres produced by this method consist of bundles of small fibrils which show the characteristic shish-kebab morphology. The method employs a modified Couette apparatus into which a seed fibre is introduced through a side tube; when the seed fibre touches the rotor surface growth is initiated and a continuous fibre may be wound up. The most interesting characteristics of the process reported by Zwijnenburg and Pennings are: first the linear growth rates achieved by this method exceed by an order of magnitude or more those which can be obtained for shish-kebab fibres grown by other methods, and secondly the very high growth temperatures that may be achieved. Fibres grown at these very high temperatures (~ 120° C) have very favourable mechanical properties; indeed they are probably the stiffest and strongest polyethylene fibres as-yet produced [1, 2, 5].

The present experiments represent an extension of the work of Zwijnenburg and Pennings aimed at exploring in a systematic manner the various parameters (e.g. solution concentration, rotor size, fibre wind-up speed, etc.) which influence fibre formation; to our knowledge no such wide-ranging systematic studies have been previously reported. In addition to providing further documentation of the surface growth method, this work was carried out with the following two-fold purpose. First, the careful mapping of the parameters involved in the surface growth process should be of service for the understanding of the fundamental processes involved, and second, the knowledge of how the various parameters influence the fibre formation process should help to provide guidelines towards efficient fibre production. With these intentions in mind we shall do no more here than to present the results of our study and make some general comments about them; we shall not make any attempt towards a detailed analysis of what is observed.

2. Experimental details

2.1. The apparatus and materials for fibre growth

A sketch of the equipment used in this work is shown in Fig. 1. We used rotors of three different sizes (diameters 7.5, 8.2 and 8.9 cm) in the main vessel whose internal diameter was 9.4 cm. Two sets of rotors were used, one set made of brass the other of PTFE. As far as possible all rotors in each set had the same surface finish. They were all turned on the same lathe using the same conditions and the same tool (a different tool was used for brass and PTFE). In the growth experiments the apparatus was immersed in a silicone oil bath whose temperature was controlled to better than ± 0.05° C over the period of each experiment.

Solutions were made from Hostalen GUR high molecular weight linear polyethylene ($\bar{M}_n \sim 2 \times 10^5$, $\bar{M}_w \gtrsim 1.5 \times 10^6$) in laboratory grade xylene (supplied by BDH Chemicals Ltd). The solution

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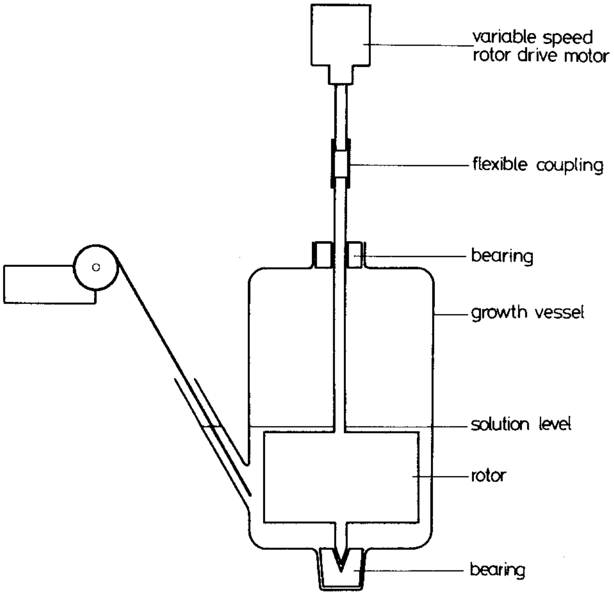

Figure 1 A sketch of the apparatus used for fibre growth.

concentrations quoted in this work were measured by evaporating the solvent from a known volume of the solution and weighing the polymer residue.

2.2. Growth of the fibres

Fibre growth was initiated with a seed fibre made in a previous experiment (the original seed was a piece of cotton). The seed was allowed to touch the stationary rotor which was then started. After a short induction time (up to a minute or two) there is a sudden increase in tension on the seed fibre as growth begins. At this moment the wind-up motor is started and the fibre is wound up; we found it advantageous to start the wind-up motor at a fairly high speed to prevent growth right round the rotor, the speed being steadily reduced so as to establish a steady-state growth. When we needed to grow fibres at temperatures above 118° C, growth was usually initiated at a lower temperature (115 to 118° C) and then the equipment was heated over a period of up to 1 h to the required growth temperature; during this heating, appropriate reduction of the wind-up speed was made to maintain the fibre cross-sectional area approximately constant.

During wind up the fibres carry with them some of the solution which crystallizes on them as they emerge from the growth vessel. This material is easily removed by washing in an excess of pure xylene at the growth temperature. We found, from experiments monitoring the weight loss, that washing in this way for 1 h was just sufficient to remove all this excess material. We therefore washed all specimens for 2 h at the growth temperature.

3. Results

3.1. Growth rates

It is a simple matter to vary the linear growth rate during an experiment: it is only necessary to change the speed of the wind-up motor. We found that in most cases we could vary the linear growth rate over about one order of magnitude; at the lowest rates the fibre started to grow around the rotor and eventually either broke of jammed the rotor due to its frictional force, while at the highest speeds the fibre became so thin that it broke under the wind-up tension.

In a series of experiments we measured the mass growth rate as well as the linear growth rate. The mass growth rate was calculated from the weight of a known length of fibre and the linear growth rate. A typical set of results is shown in Fig. 2 where the mass growth rate is plotted against the linear growth rate for a series of different solution concentrations. The curve in Fig. 2 were obtained using a brass rotor. When a PTFE rotor is used higher mass and linear growth rates are achieved (approximately 2 to 3 times those observed for brass rotors), but the shapes of the curves are quite similar.

We see from Fig. 2 that the mass growth rate is independent of the linear growth, and hence is unaffected by wind-up speed, up to some critical

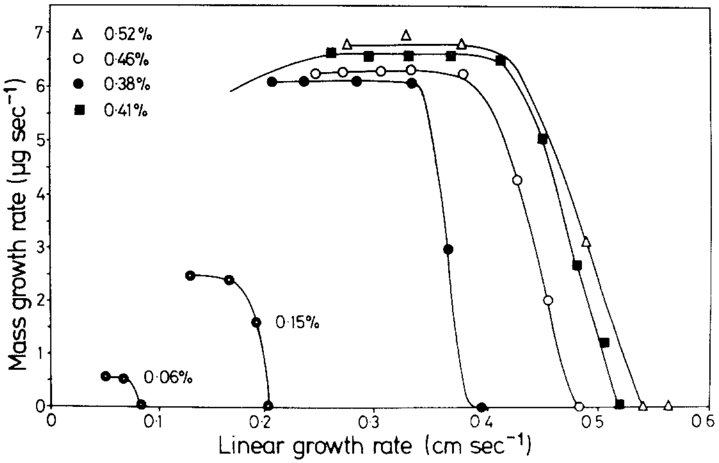

Figure 2 A series of curves showing how the mass growth rate varies when the wind-up speed (linear growth rate) is changed for a series of different solution concentrations. For this series of experiments the brass rotor of 8.9 cm diameter was used at a speed of 62 rpm and a temperature of 107.8° C.

speed, beyond which it falls rapidly to zero. The existence of this constant "plateau" region facilitates comparisons between other variables, a line which we shall pursue in what follows. It is also apparent from Fig. 2 that in this plateau region, the solution concentration has a marked effect on the mass growth rate, particularly at low concentrations, but beyond some critical concentation (ca. 0.4% wt/wt), the mass growth rate becomes independent of concentration. We found this conclusion, which is again illustrated, this time for a PTFE rotor, in Fig. 3 to be valid for all rotor temperatures and rotor speeds we investigated.

Figs. 4 and 5 show how the mass growth rate and the maximum linear growth both increase approximately linearly with the rotor speed. Fig. 6 shows how the maximum linear growth rate falls rapidly as the temperature is increased. Fig. 7 illustrates how the mass growth rate varies with the temperature for the different sized rotors. It is intriguing how the middle sized rotor permits far higher growth temperatures than either of the other two. This is also observed for the brass rotors but the maximum growth temperature for the 8.2 cm rotor is then only ~ 118.5° C.

3.2. The effect of changing the growth position

According to the growth mechanism of Pennings and Zwijnenburg depletion of material should occur near the growth front leading to a reduced growth rate. It would follow that if the growing tip were continuously displaced the growth rate should increase, an effect which would not only

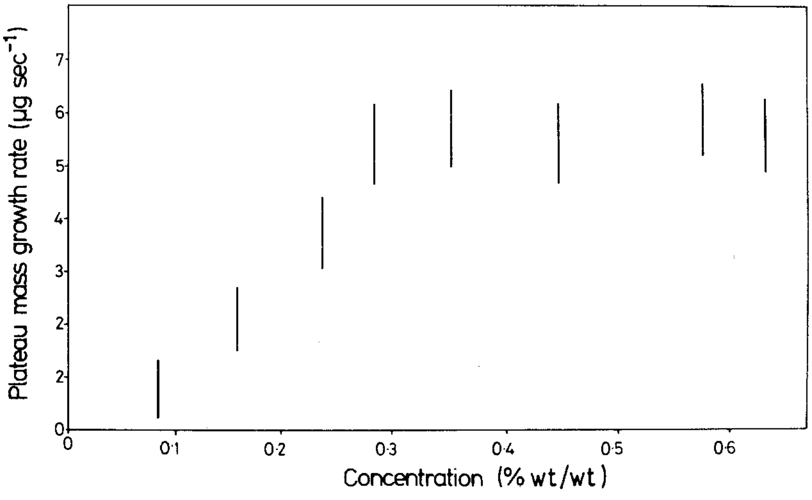

Figure 3 A typical graph showing how the plateau value of the mass growth rate varies with solution concentration. This figure is for the 8.2 cm diameter PTFE rotor at 60 rpm and 110° C.

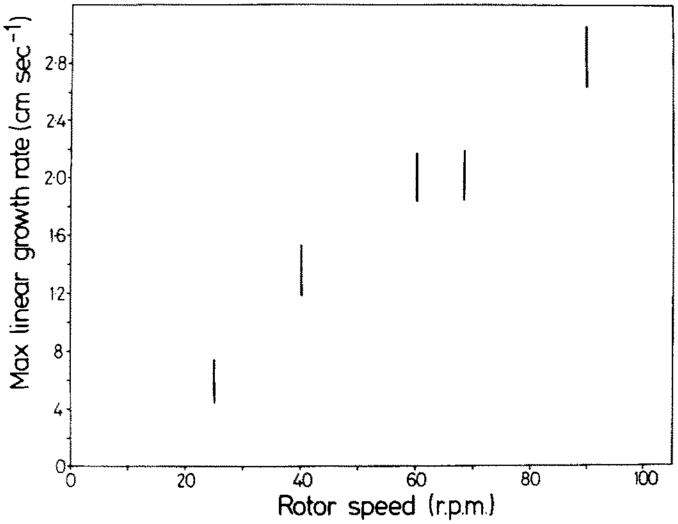

Figure 4 A typical graph showing the variation of the maximum achievable linear growth rate as a function of rotor speed. These data were obtained with the 8.2 cm PTFE rotor at 110° C with a solution concentration of 0.6% wt/wt.

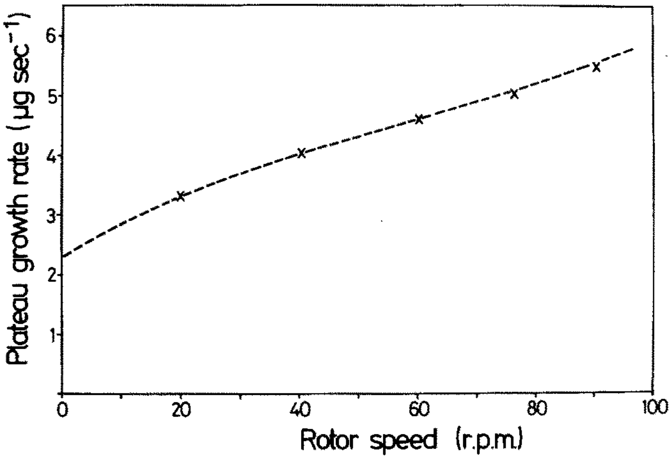

Figure 5 A typical graph showing how the plateau mass growth rate varies with the rotor speed. These results were obtained using the 7.5 cm brass rotor at 107.8° C and a solution concentration of 0.6% (wt/wt).

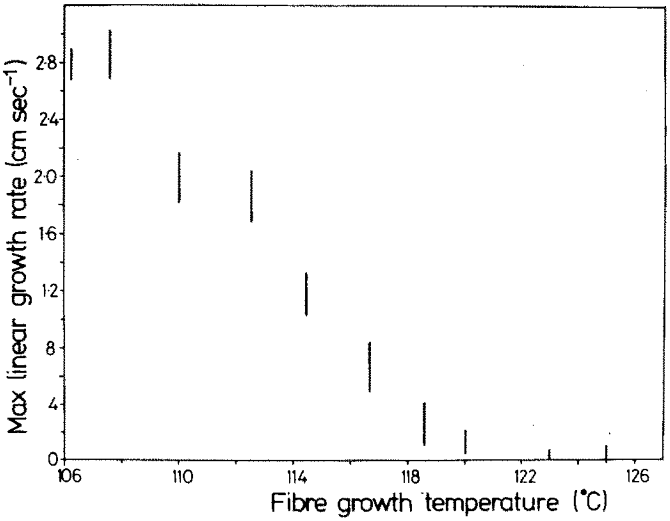

Figure 6 A typical graph showing the change in the maximum linear growth rate with the growth temperature. These results are for the 8.2 cm PTFE rotor at 60 rpm and a solution concentration of 0.55% (wt/wt).

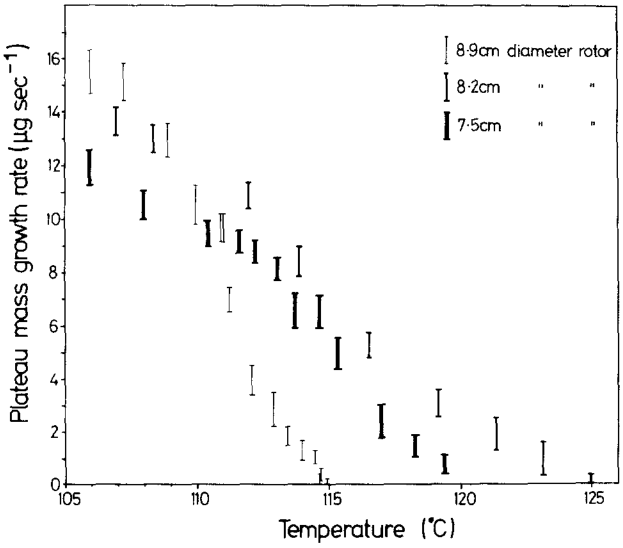

Figure 7 A series of curves showing how the plateau mass growth rate varies with the fibre growth temperature for all three PTFE rotors at 60 rpm and with solution concentration of 0.5 to 0.6% (wt/wt).

support the hypothesis in question but would also be of practical consequence for fibre production. This we set out to investigate.

We threaded the seed fibre through a needle which was then moved up and down the rotor during growth so as to ensure that the growth position also swept the rotor surface. This motion was performed manually at a rate of approximately 1 cm sec^{-1}. We again measured mass growth rate as a function of linear growth rate (take up speed) and the results are shown in Fig. 8. It is immediately clear that much higher mass and linear growth rates can be achieved in this way.

3.3. Mechanical properties of the fibres

3.3.1. Tensile modulus

We measured the stiffness of the fibres at room temperature (20 to 22° C) using an Instron testing machine at an initial strain rate of 10^{-4} sec^{-1}; the fibres had an aspect ratio in excess of 250 which is sufficiently large that end effects may be ignored [6]. The secant modulus of a strain of 0.1% is quoted. We measured both the washed and unwashed fibres. In the unwashed fibres we found a very large scatter in our data with a general trend towards higher moduli at higher growth temperatures and higher linear growth rates. The range

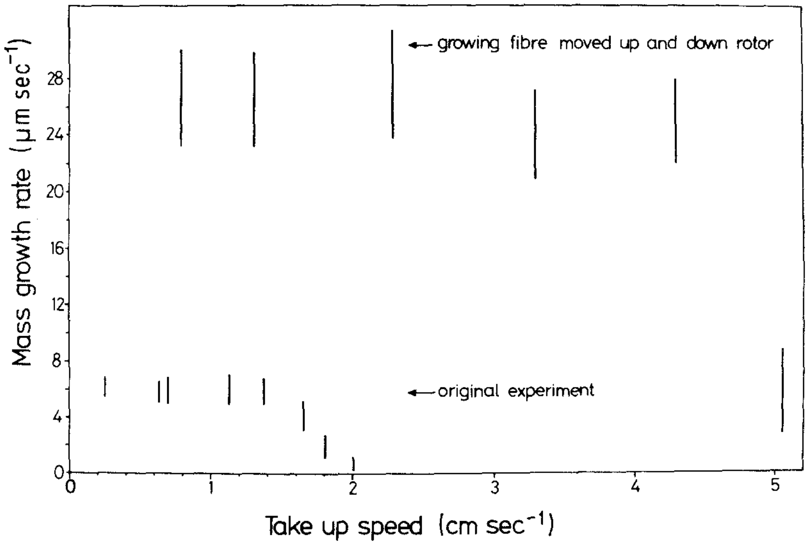

Figure 8 Two graphs of mass growth rate against linear growth rate illustrating the effect of a continuous displacement of the growth tip. Both curves are for the PTFE 8.2 cm diameter rotor at 60 rpm and 110° C.

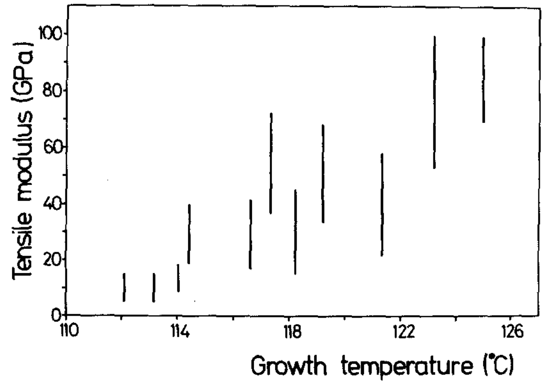

Figure 9 Graph showing the variation of the tensile modulus (0.1% strain, 10^{-4} sec^{-1} strain rate) with fibre growth temperature for the unwashed fibres.

of tensile moduli measured on unwashed fibres is shown as a function of growth temperature in Fig. 9. In the case of washed fibres we found little variation in modulus with the growth rate but a strong increase in modulus with increasing growth temperature as shown in Fig. 10.

3.3.2. *Fracture stresses*

Fracture stress and elongation to break were measured in the Instron using 10 cm lengths of fibre at an initial strain rate of 2×10^{-3}sec^{-1}. Only washed fibres were measured. The results are presented in Fig. 11 where the mean fracture stress (referred to the initial cross-section) and elongation to break are plotted as a function of temperature. In each case a total of 20 measurements were made.

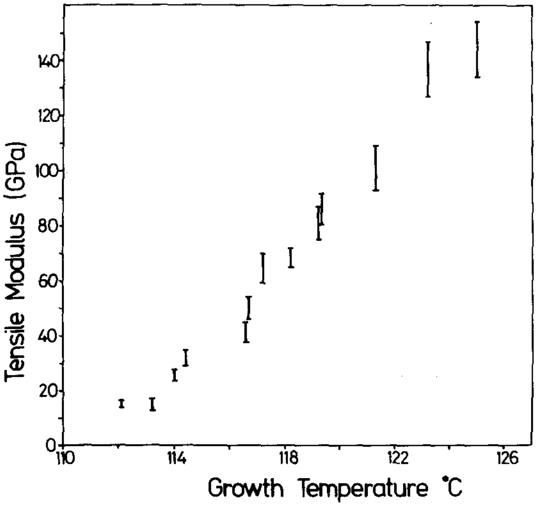

Figure 10 Graph showing the variation of the tensile modulus (0.1% strain 10^{-4} sec^{-1} strain rate) for the washed fibres, as a function of growth temperature.

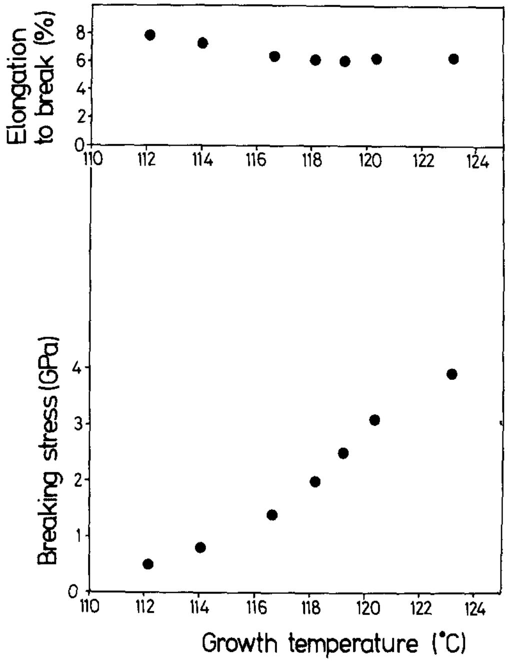

Figure 11 Graphs showing the variation of mean breaking stress and elongation to break of washed fibres as a function of their growth temperatures.

4. Discussion

The data on the modulus, strength and linear growth rates we have presented in this paper are in reasonably close agreement with those previously reported by Zwijnenburg and Pennings [1–4]. We have extended their work in two principal directions. First we expressed the yield of fibre in terms of the mass growth rates and we have been able to show that it is over a large range of conditions independent of the take up speed or linear growth rate. Secondly we have been able to use this constancy of the mass growth to explore the effect of other variables and to utilize knowledge thus gained to achieve remarkably high fibre growth temperatures (up to ca. 125° C) and also to improve the rates of production of such fibres which possess advantageous mechanical properties. The experiment where we showed how sweeping the fibre growth front across the rotor surface leads to much increased production rates should be compared with the work of Coombes and Keller [7] who used a tapered rotor and found that owing to the taper the growth front moved up the rotor in a continuous fashion thus forming a film. The growth rates they measured are quite high and are closer to those reported here when the fibre was moved up and down the rotor.

In addition to aiding the achievement of maximum fibre output, the above findings are also important pointers with regards to the understanding of the underlying mechanism. These results in conjunction with the near constancy of the mass growth rate suggest that in the normal process material is quickly depleted from the area of the growth front and that the growth rate is limited by the rate at which fresh material arrives at the growth front.

Acknowledgement

P. J. B. wishes to thank I. C. I. Ltd for financial support during this work.

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Received 4 January and accepted 29 January 1980.