The Wet Spinning of Secondary Cellulose Acetate: Solution Rheology and Filament Spinnability

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The flow behaviour of a series of solutions of secondary cellulose acetate were examined in detail using a Weissenberg rheogoniometer. The solutions were then wet spun into solid filaments and their tensile properties examined. Filament spinnability was found to go through a maximum at a concentration of about 12·5 to 15 per cent of cellulose acetate in the spinning solution. It appeared that the rheological properties of the spinning solution did not exert any direct effect on filament spinnability, and that the flow behaviour of the liquid filament in the process of coagulating might be critical.

THIS PAPER deals with the rheological characteristics of solutions of secondary cellulose acetate which were spun into filaments. The physical properties of these filaments have been determined. Filament spinnability has been discussed in the light of the solution flow data in an attempt to answer the question; to what extent do filament properties depend on the rheology of the spinning solution?

Elsaesser[1] and Pupke[2] are among those who have published work on particular wet spinning systems. A general mechanical analysis of the fibre forming process has however been produced in a series of papers by Ziabicki[3-6]. The general considerations and conclusions in this work are valid for every process (wet, dry and melt) of fibre formation and this work is of great general interest.

The spinnability of fluids (i.e. their ability to form a stable liquid filament) has been the subject of some interest for a considerable time[7,8]. This is understandable in view of the technological importance of the spinning process in the manufacture of man-made fibres. Lodge[9] has fairly recently discussed the problem of spinnability in terms of the elongational viscosity of liquid filaments. Perhaps some of the more interesting experimental work in this field has been carried out by Ziabicki and coworkers[10,11]. These workers investigated the formation and breakage of liquid threads and concluded that the rheological behaviour of liquids affects the filament break process in a complicated way, the effects being different in various conditions. Moreover, they also concluded that under suitable conditions any 'rheological fluid' may be regarded as spinnable. This would suggest that the consideration of the spinning process in terms of the liquid filament alone is an unprofitable exercise. During spinning the filament is in a state of continual change as it alters from a fluid to a solid polymer. The problem of liquid filament formation only exists in the time interval between the emergence of the fluid from the spinneret and coagulation (this particular aspect will be dealt with in a later paper).

With the above points in mind it would seem more useful to extend the concept of spinnability to include the ability of a fluid to form, on spinning, a useful polymer filament. Mark[12] in a recent review of quantitative aspects of the spinning and drawing of fibres has quoted the definition of 'spinnability range' as being 'the highest extrusion velocity at which production of a homogeneous fibre of good proportions can still be maintained'. This agrees with the concept of spinnability stated above and it is this (i.e. spinnability related to the solid filament) which will be used in this paper.

EXPERIMENTAL

Materials

Secondary cellulose acetate obtained from British Drug Houses Ltd, was dried *in vacuo* over phosphorus pentoxide. The intrinsic viscosity of the polymer was determined using a modified Ubbelohde viscometer at 25°C, with acetone as solvent, by means of the equation[13]

$$\eta_r^{1/8} = 1 + \tfrac{1}{8}\eta C$$

where η_r denotes relative viscosity.

The degree of polymerization (DP) was calculated from the equation[14] $\eta = 0{\cdot}0244\ (\mathrm{DP})^{0{\cdot}76}$ and was found to be 209. C is the concentration in g/100 ml solution.

No change in DP was found as a result of wet spinning. Acetyl content was measured by standard techniques and was found to be 37·9 (%CH_3CO) both before and after spinning.

Spinning solutions were prepared by dissolving the dried secondary cellulose acetate in a solvent consisting of 95·5 per cent of glacial acetic acid: water by volume. The solutions were filtered and air bubbles removed before spinning.

Solution flow behaviour

The flow behaviour of the secondary cellulose acetate solutions used in wet spinning was examined using a Weissenberg rheogoniometer type R.16. This is essentially a cone and plate viscometer which can measure normal stresses and shear elasticity as well as viscosity at various rates of shear. The instrument has been described in full elsewhere[15].

All solutions were examined at 20°C. The diameter of both the cone and plate was 7·5 cm and the cone angle 1°36″.

Standard equations[15] were used to calculate apparent viscosity, recoverable shear strain and relaxation time from rotational experiments, and modulus of elasticity from oscillation experiments.

Shear rate (γ) in the spinneret was calculated on the assumption of laminar flow using the equation $\gamma = 4Q/\pi r^3$ where Q denotes volume rate of flow and r is the spinneret radius. The use of this equation is probably justified in spite of the short spinneret length since the design of the reservoir was such that the entrance to the spinneret was streamlined.

Wet spinning apparatus

Figure 1 shows a diagrammatic sketch of the wet spinning apparatus.

Nitrogen from a cylinder was fed to a constant pressure device A. This was based on a design by Cumberbirch and Harland[16] and enabled extrusion pressure to be varied between 0 and 50 cm of mercury (gauge). The nitrogen at predetermined pressure was fed via the two-way tap B to the extrusion vessel C. This vessel (volume about 50 ml) acted as a reservoir for the spinning solution, the solution being forced out of the bottom through the spinneret into the coagulating bath. The spinneret itself was made of Veridia glass tubing 0·2 mm long and 0·28 mm diameter. The coagulating filament passed through the coagulant via two guides F and then round two rollers G, which were driven at any required speed by an electric motor. Take-up speed was kept equal to the rate of extrusion. In order to ensure complete coagulation the filaments were left in a second bath before being washed, dried and conditioned.

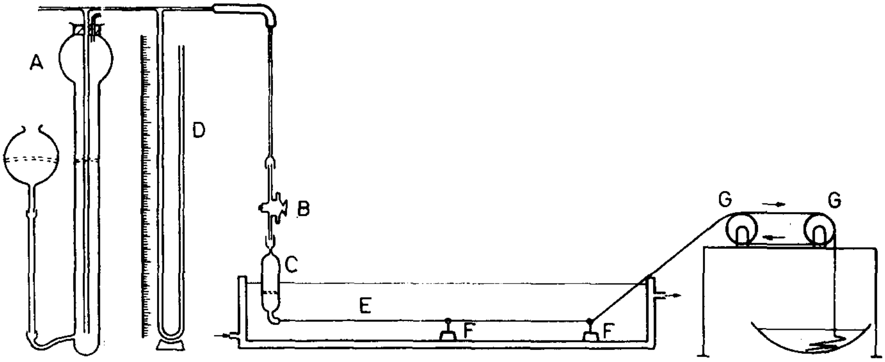

Figure 1—Wet spinning apparatus

The coagulating bath was of jacketted stainless steel construction. The coagulant temperature was controlled by passing water from a thermostatically controlled bath through the outer jacket. Direct heating of the coagulant itself was inadvisable because of its corrosive nature. The coagulant throughout these experiments was an aqueous solution containing 25 per cent analytical reagent grade ammonium acetate and ten per cent glacial acetic acid.

Tensile properties

Before testing the filaments were conditioned at 20° ± 1°C and 65 per cent ± 2 per cent relative humidity for 24 hours.

A table model Instron tensile tester was used to determine the load/extension curves of the filaments. A specimen length of 2 in. was extended at ten per cent per minute. From the load/extension curves, load and extension to break were measured and the mean values from five experiments were calculated. Yield point was located according to Coplan's construction[17]. Secant modulus at break was calculated as breaking stress per unit breaking strain.

Results and discussion

The flow behaviour of 7·5, 10, 12·5, 15 and 17·5 per cent solutions of secondary cellulose acetate in 95 : 5 glacial acetic acid : water solvent was examined under steady and oscillatory shear at 20°C. *Figure 2* shows the variation of log (apparent viscosity) with log (shear rate). Non-Newtonian behaviour was exhibited to a greater or lesser extent by all the solutions, with viscosity falling as shear rate increased. The maximum shear rate obtainable during steady shearing was controlled by the breakdown of laminar flow. Once this occurred the experiment was discontinued.

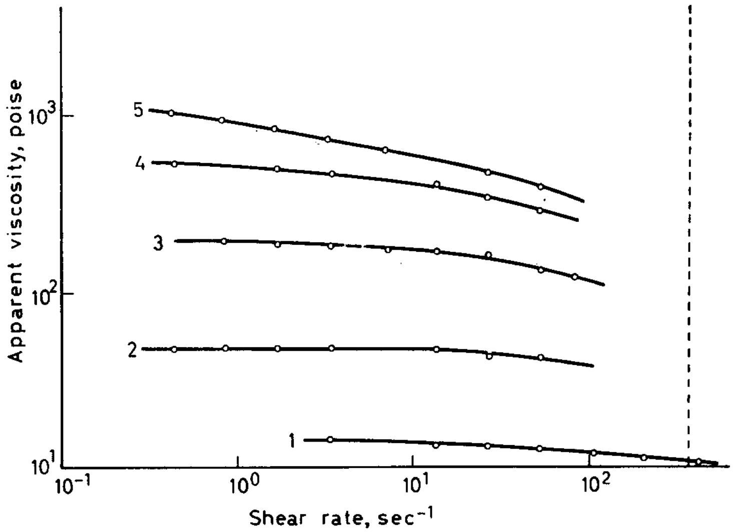

Figure 2—Shear dependence of viscosity for solutions of secondary cellulose acetate of various concentrations. 1, 7·5; 2, 10; 3, 12·5; 4, 15; 5, 17·5 per cent

Figures 3 and *4* show the change of log (normal stress) and log (recoverable shear strain) with log (shear rate) respectively. In both cases a more or less parallel series of lines were obtained over the range of shear rates examined. All the solutions had comparatively low recoverable shear strains.

The variations of relaxation time of the solutions with increase in shear rate are given in *Figure 5*. At all concentrations relaxation time appeared to decrease linearly with log (shear rate), the rate of decrease being greatest in the most concentrated solution.

Relaxation time is of particular interest in the wet spinning process. When the spinning solution emerges from the spinneret it immediately tends to relax since the shearing forces have been removed. At the same time the filament is normally being (a) extended in solution and (b) coagulated. The extension tends to reintroduce orientation in the molecules while the coagulating process precipitates them to form a solid filament. The rate at which the molecules relax may well therefore be critical. If the rate of coagulation is high compared with the relaxation time then the molecules

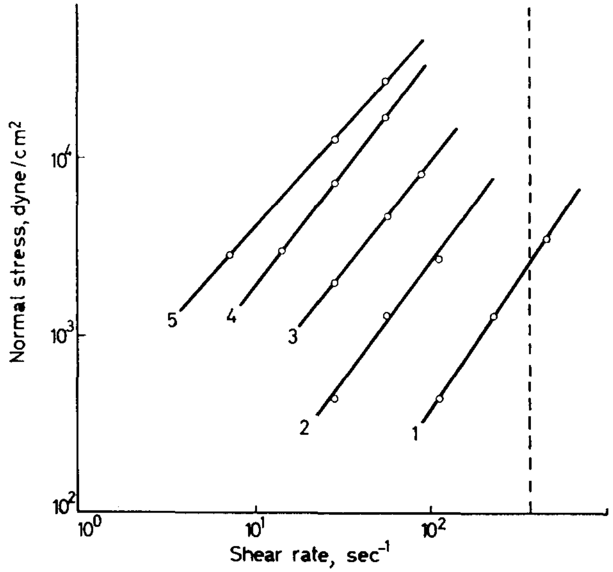

Figure 3—Shear dependence of normal stress for solutions of secondary cellulose acetate of various concentrations. 1, 7·5; 2, 10; 3, 12·5; 4, 15; 5, 17·5 per cent

will be coagulated in the filament in a more oriented form than they would be if relaxation was complete before coagulation. (In this work the take-off speed was equal to the extrusion speed, so that the extension in solution was negligible.)

The broken lines in *Figures 2* to *6* show the shear rate in the spinneret during spinning (370 sec^{-1}). *Figure 5* suggests that the relaxation time of the solution at this shear rate was about $5 \cdot 0 \times 10^{-3}$ sec. It would seem likely that in order for the liquid filament solution to be coagulated before complete relaxation had taken place the coagulation time would need to be less than this value. It is possible that this might be the case at that part of the filament immediately in contact with the coagulant. Complete relaxation would, however, almost certainly occur before the inner parts of the liquid filament had coagulated.

Polymer solutions have, of course, a spectrum of relaxation times. Where a polymer such as secondary cellulose acetate contains free hydroxyl groups there is a possibility of association between individual molecules (by hydrogen bonding). These statistically distributed secondary bonds between the chains are constantly dissociating and reforming and they are, as a result, short lived, i.e. they show very short relaxation times. At the other extreme are the relatively long relaxation times exhibited by polymer chain entanglements. The relaxation time measured by the rheogoniometer is an average value which is almost certainly more influenced by the long than by the short relaxation times.

Figure 6 shows that appreciable elastic forces were generated in the solutions as a result of shearing, particularly at the higher concentrations.

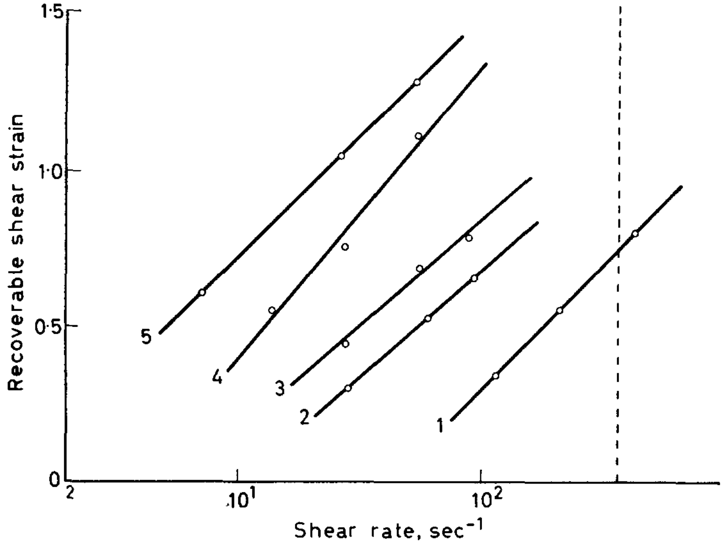

Figure 4—Shear dependence of recoverable shear strain for solutions of secondary cellulose acetate of various concentrations. 1, 7·5; 2, 10; 3, 12·5; 4, 15; 5, 17·5 per cent

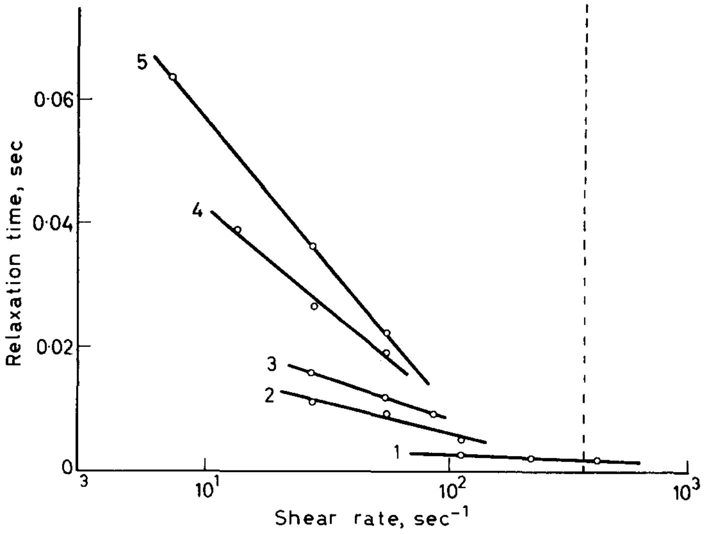

Figure 5—Shear dependence of relaxation time for solutions of secondary cellulose acetate of various concentrations. 1, 7·5; 2, 10; 3, 12·5; 4, 15; 5, 17·5 per cent

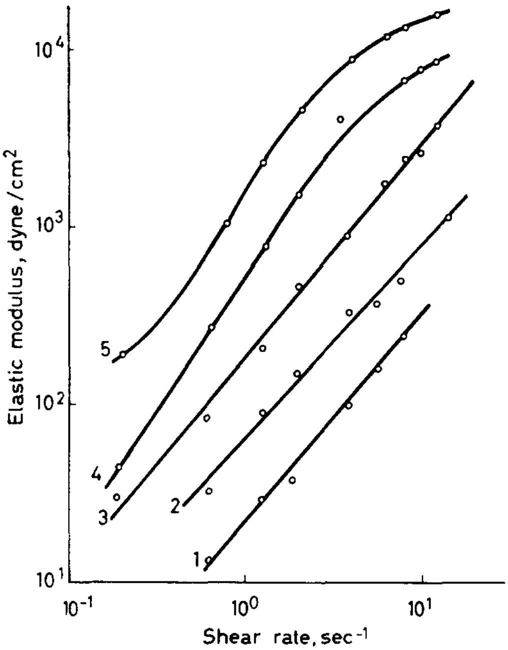

Figure 6—Shear dependence of modulus of elasticity during oscillation for solutions of secondary cellulose acetate of various concentrations. 1, 7·5; 2, 10; 3, 12·5; 4, 15; 5, 17·5 per cent

These forces are a function of the polymer entanglement density in the solution and would be very high if extrapolated to the shear rate actually used in wet spinning (370 sec^{-1}).

Filament spinnability

Table 1 shows the tensile properties of filaments spun from solutions of different concentrations. Included in the tensile data are the coefficients of variance for the tenacity and breaking extension determinations.

Table 1. Variation of filament properties with polymer concentration in the spinning solution

Concentration of polymer %	*Tenacity*		*Breaking extension*		*Secant modulus at break g/tex per unit extension*	*Yield stress g/tex*
	g/tex	*CV** (%)	%	*CV* (%)		
7·5	3·8	0·0	3·4	23·5	113	3·8
10	5·0	1·65	18·7	10·0	27	4·3
12·5	6·3	3·65	28·1	4·1	24·3	4·7
15·0	7·7	1·95	32·4	3·3	23·4	5·1
17·5	7·8	2·0	37·0	11·4	20·7	5·0

*CV denotes coefficient of variation. Spinning conditions: temperature 20°C, solution flow rate $3{\cdot}4 \times 10^{-3}$ ml/min; take-up velocity 67·5 cm/min.

The breaking tenacity, breaking extension, and yield stress all increased as polymer concentration in the spinning solution increased. The coefficients of variance for the breaking tenacities were all extremely low. The coefficients of variance, however, for the breaking extensions showed a pronounced minimum with increase in polymer concentration in the spinning solution. If spinnability is regarded as the ability of a solution to be formed into a filament with uniform properties then these results indicate that spinnability goes through a maximum at a secondary cellulose acetate concentration of about 12·5 or 15 per cent under the spinning conditions used.

Figure 7 shows the variation of filament 'stiffness' with polymer concentration. Secant modulus at break was very high when the filament was spun from a 7·5 per cent polymer solution and fell rapidly from 113 to 27 g/tex per unit extension when the polymer concentration increased to ten per cent. Thereafter it decreased only slightly. The extremely high secant modulus at break shown below ten per cent polymer concentration in the spinning solution indicated that the filament was brittle and unsuitable for most textile purposes. Moreover, it was extremely difficult to spin the 7·5 per cent solution; breakages in the coagulating filament occurred continually.

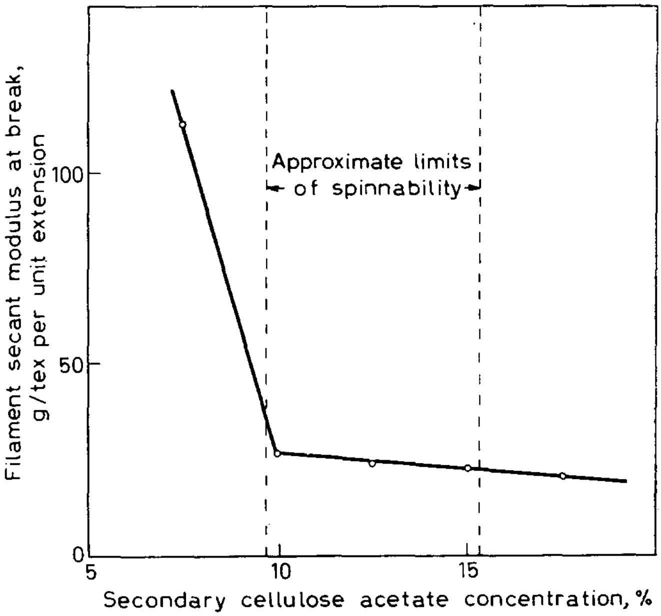

Figure 7—Influence of secondary cellulose acetate concentration in spinning solution on filament secant modulus at break

When the 17·5 per cent solution was spun, a large number of breaks occurred in the filament in the coagulating bath. Thus spinnability appeared to be very low for the 7·5 per cent solution because of the breakages and because of the high secant modulus at break of the resulting filament, and very low for the 17·5 per cent solution because of the breakages of the coagulating filament only. Between these two concentrations, spinning of the filament, under the conditions used, presented no problems, and the filaments seemed to have reasonable physical properties. As *Figure 7* indicates, then, these appear to represent the limiting concentrations for good spinnability. It should, however, be emphasized that the optimum concentrations of polymer would almost certainly be altered if coagulation conditions were altered.

Returning to an examination of the rheological characteristics of the solutions, *Figures 2* to *5* show that zero shear viscosity, normal stress, relaxation time, recoverable shear strain and elastic modulus all increased with secondary cellulose acetate concentration. If a solution concentration of 12·5 per cent polymer is taken as the optimum concentration for spinnability then this would suggest that the rheological characteristics giving this would be those shown by this particular solution under the particular spinning conditions used. One possible support for this is the fact that large numbers of breakages occurred in spinning both the low viscosity, 7·5 per cent solution and the relatively viscous 17·5 per cent solution. The explanation for this probably is that the former was of too low a viscosity to withstand the elongational forces to which it was subjected as it left the spinneret, even though coagulation would occur fairly quickly. The latter, on the other hand, would tend to have a much slower rate of coagulation because of the high filament viscosity. This would mean that it would be easily attenuated and consequently breakages would occur in the liquid fluid filament.

Influence of shear rate on filament properties

In view of the above conclusions it is of interest to examine the effect that shear rate in the spinneret, i.e. spinning rate, has on filament properties. Since the solutions are non-Newtonian at high shear rates, increasing shear rate decreases viscosity and relaxation time, but increases normal stress, recoverable shear strain and modulus of elasticity. Shear rate was increased by increasing the nitrogen pressure on the spinning solution and hence increasing the rate of flow through the spinneret.

In each experiment, take-up speed was adjusted to compensate for the increased rate of flow, keeping stretch in the bath negligible. As *Table 2* shows, shear rate was found to have little or no effect on filament properties over the range of shear rates investigated. There is a possibility that tensile strength goes through a maximum with increasing shear rate, but this is marginal.

These results are contradictory to those reported by Morbey[18] who claimed that the properties of a mixed acrylic and secondary cellulose acetate fibre altered with the shear rate in the spinneret. Since this worker achieved the different shear rates by altering the spinneret diameter while keeping solution flow rate and take-up speed constant, his results must be regarded as more an illustration of the effect of filament thickness on properties than of flow rate. Krause *et al.*[19], on the other hand, have found that shear rate in the spinneret has no effect on the tensile properties of filament.

It has been claimed by Ziabicki[5] that during spinning only the elongational (Trouton) viscosity should be considered in the region of flow after the liquid filament has left the spinneret and before solidification. In the results reported in *Tables 1* and *2* since no appreciable stretch was applied to the liquid filament, it was reasonable to use shear viscosity. In this situation there is a constant ratio of Trouton to shear viscosity, in Newtonian liquids at least, of 3 : 1. Trouton viscosity increases, however, with rate of elongation. It is possible therefore to examine qualitatively the influence of Trouton viscosity by increasing the rate of take-up relative to the rate of extrusion. It was found, *Table 3*, that as the ratio of take-up speed to extrusion rate (stretch ratio) increased from 0·8 : 1 to 1·92 : 1, secant modulus at break decreased slightly while tenacity, and yield stress increased slightly. Breaking extension remained unchanged. While these effects are not large they are significant. Elongation occurs only in the uncoagulated filament, not in the solid coagulated filament. The most probable mechanism is that suggested previously, namely, that the elongation induces orientation of the polymer molecules, prevents further relaxation of the polymer molecules already oriented by shearing forces in the spinneret, and hence influences physical properties. This would seem to confirm Ziabicki's conclusions that Trouton viscosity is an important factor in spinning.

Table 2. Variation of filament properties with shear rate in the spinneret

Shear rate sec^{-1}	*Tenacity g/tex*	*Breaking extension* %	*Secant modulus at break g/tex per unit extension*	*Yield stress g/tex*
255	6·8	23·9	27	5·2
462	7·3	24·5	30	5·3
706	7·7	26·8	28	5·3
845	6·8	23·5	30	5·2
980	7·0	25·7	28	5·3

Spinning conditions: temperature 20°C, polymer concentration 12·5 per cent.

Table 3. Variation of filament properties with stretch ratio during spinning

Stretch ratio	*Tenacity g/tex*	*Breaking extension* %	*Secant modulus at break g/tex per unit extension*	*Yield stress g/tex*
0·80	6·6	21·5	27	5·4
1·00	7·1	23·4	27	5·8
1·31	7·1	22·2	26	5·8
1·92	7·4	22·4	24	6·0

Temperature 20°C; solution flow rate $8{\cdot}2\times10^{-2}$ ml/min; take-up velocity 103 cm/min; polymer concentration=12·5 per cent.

In conclusion, it would appear that the rheology of the spinning solution as measured under laminar shear, does not in itself play a particularly important part in determining solid filament properties. This is not altogether surprising since the fluid filament is in the process of continual change from the moment it emerges from the spinneret until it finally solidifies. It would seem, therefore, that the rheology of the coagulating filament could be critical, and this will be considered in a later paper.

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