Rheological Aspects of Fiber Spinning from Cellulose Solutions in *N*-Methylmorpholine-*N*-oxide

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ABSTRACT: Based on rheological experiments with a cellulose solution in *N*-methylmorpholine-*N*-oxide (NMMO), it was found that the shearing stress generated in the flowing viscoelastic fluid decreases with an l/d ratio in a rheometer capillary. This reduces the elastic response and the outflow of the fluid becomes more uniform. At constant temperature, the elongational viscosity of the solidified stream of the cellulose solution in NMMO is reduced with increase of the deformation rate, which makes it possible to increase the fiber-formation velocity within the air zone. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1860–1868, 2001

Key words: cellulose; NMMO; rheological investigation; elongational viscosity

INTRODUCTION

Lyocell fibers spun from cellulose solutions in *N*-methylmorpholine-*N*-oxide (NMMO) are manufactured by the dry–wet process. The flow in the spinneret capillary may be treated as a shearing of indefinitely thin layers of a fluid with a parabolic velocity distribution. The orientation of the macromolecules due to the lateral velocity gradient brings about a decrease in the internal friction, which results in a decrease of the viscosity with an increase in the shearing rate to reach a certain constant value at the moment when further macromolecule movement is retarded by the intermolecular bonds being formed.

Stress relaxation in the viscoelastic cellulose solution in NMMO causes a situation where the spinning solution stream flowing out of the spinneret orifice is characterized by periodically variable thickened and narrowed sections with a lower (Shark skin) or higher amplitude (melt fracture). This is a disadvantageous phenomenon from the point of view of fiber properties since the forces acting on the stream with variable diameters bring about a fluctuation of tensile stresses and nonuniform mechanical properties. According to Larson,[1] these disturbances depend on the properties of the extruded fluid and to a lesser extent on the orifice diameter, while a significant effect is exerted by the spinneret orifice length-to-diameter (l/d) ratio since an appropriately long-stream flow time in the capillary allows stress relaxation. In increasing the orifice length, however, one should take into account the growing flow resistance and pressure increase during the fluid extrusion. The outflowing stream after leaving the spinneret is drawn in air space. Under the influence of the force exerted by the fiber take-up system, the stream diameter decreases, followed by an increase in the linear velocity as the product of the velocity and the stream surface is a constant value.

Thus, the spinning solution stream flow in air space is a single-axis deformation caused by the longitudinal velocity gradient. The stream-drawing length depends on the spinneret orifice diameter, take-up rate, and stream temperature drop rate, while the susceptibility to deformation decreases along the path between the spinneret and the bath in which cellulose is solidified.

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Model studies on the Lyocell fiber formation process presented by Mortimer and Peguy[2–4] concerned, first of all, physical phenomena taking place within the air zone during monofilament drawing. Basic changes in the stream take place over the length of up to 50 mm below the spinneret. Within this space, the temperature of the filament decreases to the ambient temperature and the filament diameter and velocity gradient are stabilized. The filament orientation results from its drawing within the air zone and cellulose solidification conditions in the spinning bath, with both processes having a more or less equal effect on the final orientation. The increase in the volume flow through the spinneret with a growing diameter and length of orifices (increase in the l/d ratio) makes it possible to increase the draw ratio and, thereby, to increase the spinning velocity, decrease the elementary filament thickness, and increase the fiber strength.[5,6]

The present article discusses the effect of the spinneret orifice length in relation to its diameter on the flow resistance and uniformity of the extruded stream. To describe the phenomena taking place during drawing the filament being formed within the air zone, the longitudinal viscosity measurements at ambient temperature were used, although in the air zone the stream is characterized by variable temperature.

EXPERIMENTAL

Cellulose solutions in NMMO were prepared from spruce pulp with a polymerization degree of $DP = 680$, α-cellulose content of 93.5%, and moisture content of 5.2%. The solutions with a cellulose concentration of 15% were prepared in a laboratory IKAVISK MKD 0.6 reactor at temperatures up to 125°C, under a vacuum, with a 0.5% addition (in relation to α-cellulose) of propyl ester of gallic acid as an antioxidant.

The resistance of the spinning solution flow through the spinneret orifice was measured using an Instron capillary rheometer. Four different capillaries were used with variable lengths, $l = 0.16$, 0.32, 0.64, and 0.80 mm, and with the same diameter $d = 0.16$ mm. Thus, the ratio l/d varied from 1 : 1 to 1 : 5. Rheological measurements were carried out at a temperature of 115°C at which the fiber-spinning trials were then performed.

RESULTS AND DISCUSSION

The pressure-drop gradient, dP/dL, is higher within the inlet area than that within the stabilized flow. This gradient increases with increasing the distance from the capillary inlet, reaching

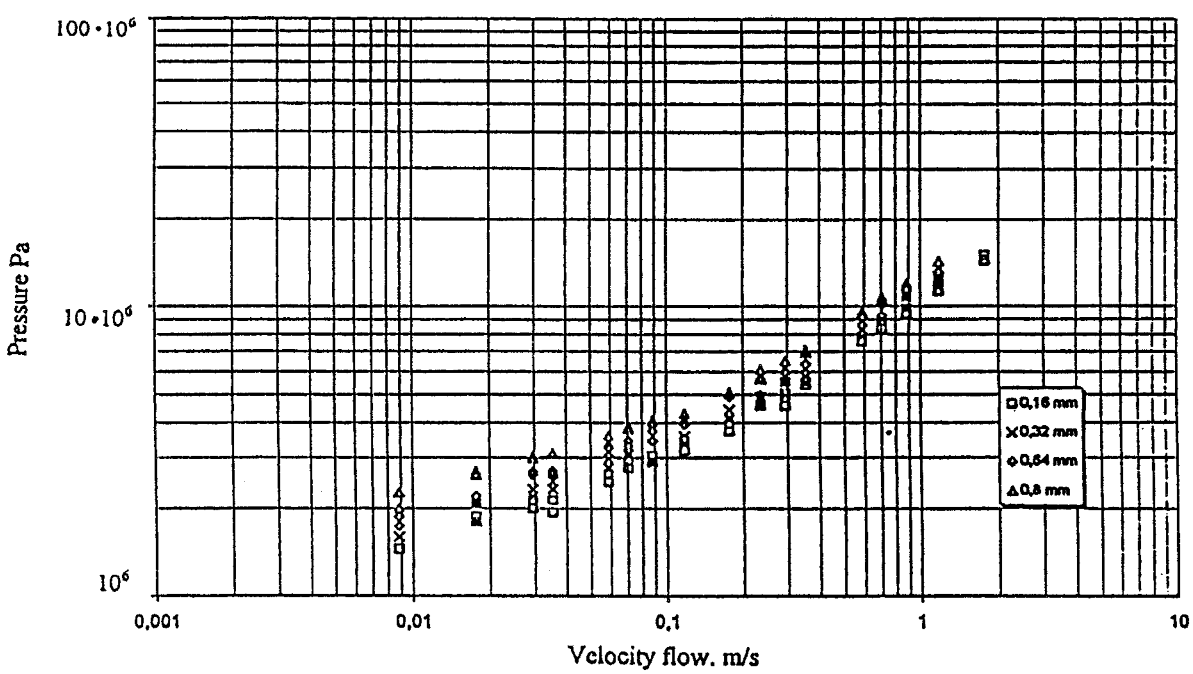

Figure 1 Pressure drop during flow through capillary: 15% cellulose + 0.5% Tenox.

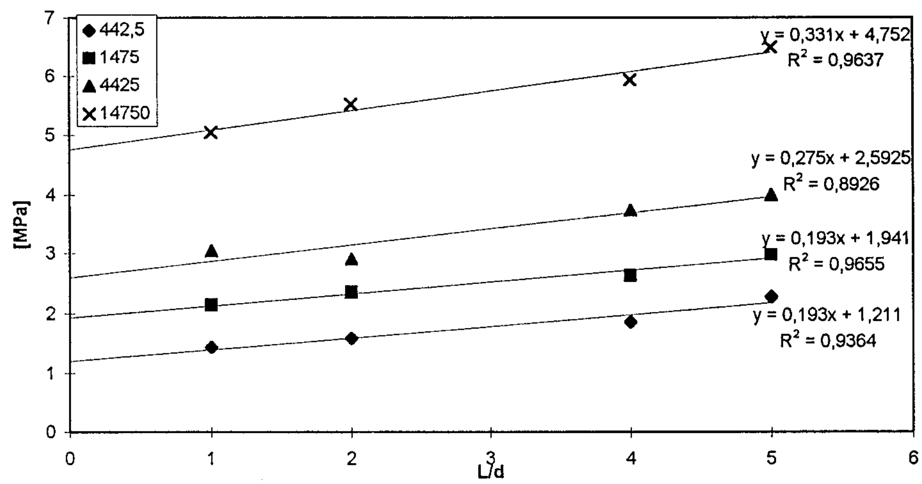

Figure 2 Extrusion pressure versus l/d ratio.

a constant value being characteristic of a stationary flow with which the lateral distribution of velocity is parabolic. According to Bagley,[7,8] the value of the dP/dL gradient can be determined when the actual capillary length L is replaced with an imaginary length L' ($L' = L + \Delta L$), which takes into account the pressure drop resulting from the increase in the fluid kinetic energy within the capillary inlet section.

The pressure drop versus flow velocity curves for capillaries with various lengths are shown in Figure 1. The effect of capillary length on the flow resistance is most noticeable with a low extrusion velocity. With increase in the extrusion velocity, the summary flow resistances grow faster than does the resistance resulting from the stationary flow with a constant velocity gradient in longer capillaries. For instance, the fivefold increase in the capillary length with an extrusion velocity of 0.009 m/s brings about an increase in pressure by about 50% (from 15.180 to 22.800 hPa), while with a velocity of 1.2 m/s, the pressure increase resulting from the elongated capillary is only 15% ($\approx$120,600 hPa at $l/d = 1$ and 138,000 hPa at $l/d = 5$). This indicates a considerable effect of the phenomena taking place at the capillary inlet on the total pressure drop (inlet effects).

These effects were quantitatively assessed using Bagley's method. Therefore, plots of the dependence of the extrusion pressure on the capillary length-to-diameter ratio were prepared for various shear rates (Fig. 2). This dependence is a linear function which was used to calculate pressure drops within the capillary inlet area versus the l/d ratio. Examples of the results obtained are shown in Table I.

For the capillary with $l/d = 1$, from 83.5 to 94.3% of the total pressure drop, depending on the shear rate, results from the resistance of fluid extrusion from the rheometer container to the capillary, while the contribution of inlet effects to the total pressure drop decreases with increasing the capillary length. On the basis of the described method, one can foresee how the increase in the l/d ratio in spinnerets will affect the pressure increase during fiber formation.

The flow curves of the cellulose solution in NMMO with various l/d ratios are shown in Figures 3 and 4. The stresses created in the capillary during shearing of the cellulose solution in NMMO with a high molecular aggregation supported by the mutual hydrogen bonding via solvent molecules have a character of almost reversible elastic deformations, bringing about pressure pulsation and periodical changes in the thickness of stream flowing out of the capillary. In addition to the stress relaxation, this is another cause of

Table I Pressure Drop Due to Inlet Effects ΔP_E in Relation to the Total Pressure Drop ΔP_T

	Shear Rate s^{-1}		
	442	885	1770
l/d	ΔP_E %/ΔP_T %		
1	83.5	90.7	94.3
2	76.3	82.7	86.0
3	65.0	74.0	80.0
4	53.2	65.4	73.2

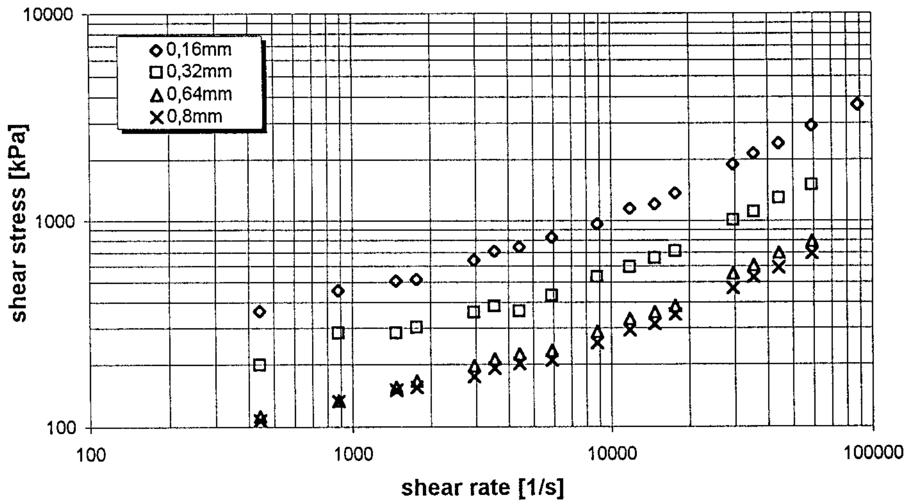

Figure 3 Shear stress versus shear rate: 15% cellulose + 0.5% Tenox.

disturbances in the cellulose solution in NMMO outflowing from the spinneret capillary. The shear stress and viscosity gradually decrease with increase of the capillary length. So, the capillary lengthening has a positive effect on the orientation of macromolecules in the capillary (spinneret orientation) and on reducing the outflow disturbances.

The irregularities of the outflow were measured using a melt flow indexer whose principle of operation consists of the flow of a polymer through a spinneret at a specified temperature under the pressure of a piston with various loads. Because the plastometer operation principle is similar to that of a capillary rheometer, the use of the former is a relatively simple and inexpensive procedure of assessing the rheological properties of fluids.

Similarly, as in the case of rheometer measurements, these measurements were carried out also at 115°C using spinneret orifices with the same diameter $d = 0.16$ mm and variable lengths: $l_1 = 0.27$ mm, $l_2 = 0.60$ mm, and $l_3 = 0.80$ mm, which made it possible to obtain various flow times of the solution with a cellulose concentration of 15% at the same plastometer piston load $F = 7.319$ kG.

From the photos of the extruded filaments (Fig. 5), it follows that the solution stream becomes more and more regular with increasing the time of flow through the spinneret. However, due to the above-mentioned pressure pulsation, it is im-

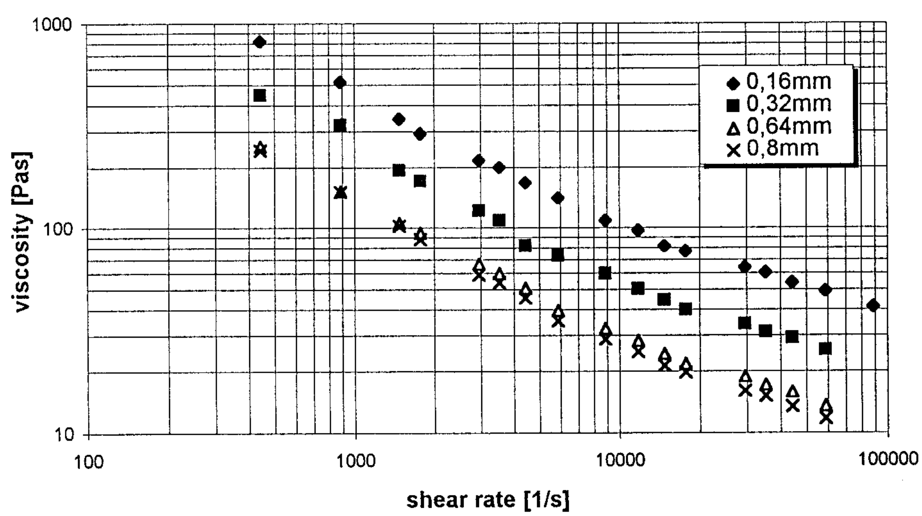

Figure 4 Viscosity versus shear: 15% cellulose + 0.5% Tenox.

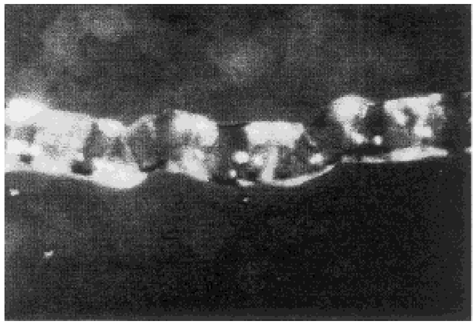

Photo no. 1
Load F = 7.319 [kG]
Flow time t = 1.8 [s.10^{-2}]

A 15% cellulose solution in NMMO
Spinneret orifice with dimensions: 0.16 mm x 0.27

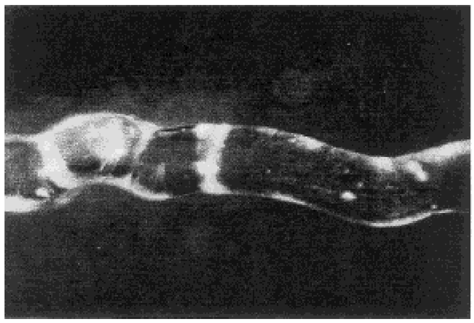

Photo no. 2
Load F = 7.319 [kG]
Flow time t = 3.9 [s.10^{-2}]

A 15% cellulose solution in NMMO
Spinneret orifice dimensions: 0.16 mm x 0.60 mm

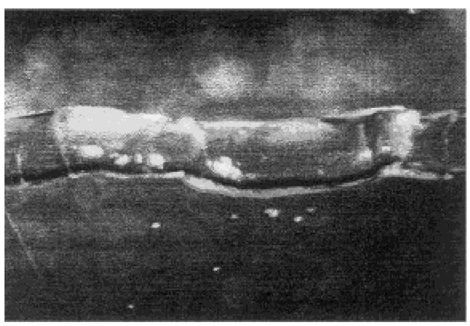

Photo no. 3
Load F = 7.319 [kG]
Flow time t = 4.6 [s.10^{-2}]

A 15% cellulose solution in NMMO
Spinneret orifice dimensions: 0.16 mm x 0.70 mm

Figure 5 Photos of filaments at various times of flow through the spinneret.

possible to avoid the periodical appearance of thickened sections of the stream.

Pictures were also taken of filaments at various flow velocities through the capillary with diameter $d = 0.4$ mm and length $l = 2.0$ mm (Fig. 6). Regular deformations of the outflowing stream appear at a linear velocity of about 0.03 m/min. Therefore, it is beneficial to spin fibers using spinneret orifices with higher diameters in which the volumetric flow increases and the linear velocity decreases.

The solution stream in the air zone undergoes longitudinal deformation due to the velocity gradient which is responsible for the orientation of macromolecules. The susceptibility to the longitudinal deformation is determined using the elongational viscosity known also as the extensional viscosity.

Contrary to the widely described measurements of shear viscosity in the literature,[8] examination of the elongational viscosity has been reported to a lesser extent using various methods, while the hardly comparable results allow one to approximately foresee the polymer behavior during drawing.[9,10,11] One of the techniques which are experimentally close to the actual industrial

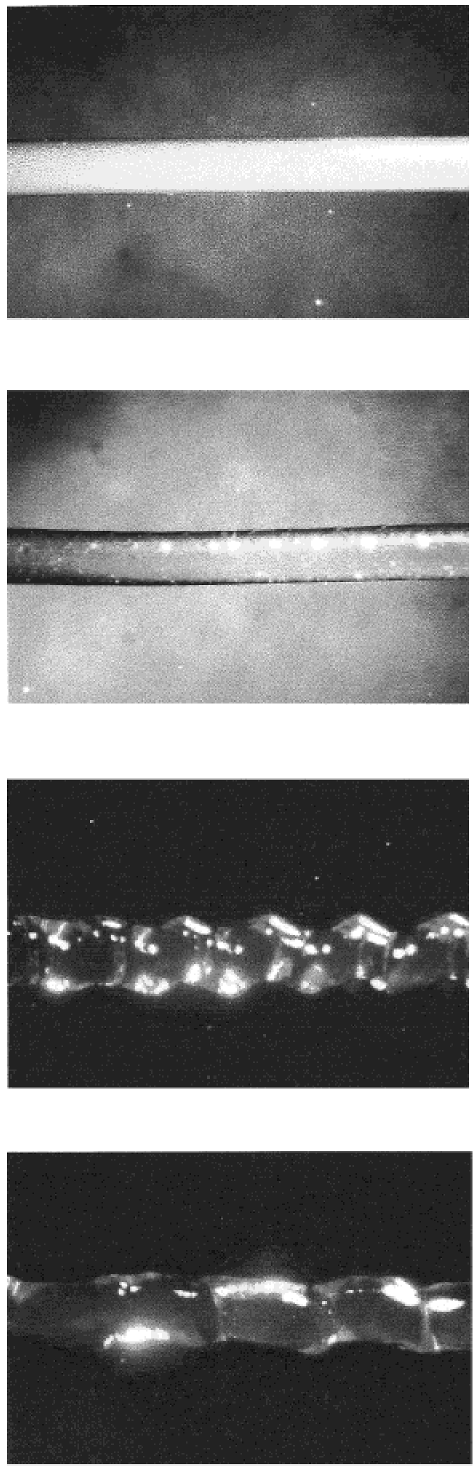

Figure 6 Photos of filaments at various flow velocity through the capillary.

processes is the drawing of a plastic filament extruded from a capillary rheometer on an Instron machine.

In this case, for a cylindrical sample clamped in the tensile testing machine and stretched with velocity V, the relative elongation (Henckey's deformation) is determined from the following relationship:

$$\varepsilon = l_n L/L_0 \quad (1)$$

where L_0 is the initial sample length, and L, the length after time t. The velocity of relative drawing for a single axis stretching is expressed by the formula

$$\varepsilon = \frac{1}{L}\frac{dL}{dt} = \frac{V}{L} \tag{2}$$

The tensile stress under the influence of force F is

$$\delta_E = \frac{4F}{\pi D^2} \tag{3}$$

where D is the sample diameter. With an assumption that the sample density is constant during drawing,

$$L_t A_t = L_0 A_0, \tag{4}$$

where A_0 is the initial sample cross section, and A_t, the sample cross section after drawing time t. By converting eq. (4), we obtain

$$L_t \frac{\pi D_t^2}{4} = L_0 \frac{\pi D_0^2}{4} \tag{5}$$

thus

$$D_t^2 = D_0^2 \frac{L_0}{L_t}$$

where D_0 and D_t are the initial sample diameter and after time t, respectively. Finally, the stress during drawing is

$$\delta_E = \frac{4F}{\pi}\frac{L_t}{D_0 L_0} \tag{6}$$

Thus, by measuring the drawing force of the sample causing its elongation versus time, the tensile stress and tensile viscosity η_E is calculated as expressed by the formula

$$\eta_E = \frac{\delta_E}{\varepsilon^\bullet} \tag{7}$$

The drawn sample was a filament with an initial length of 10 mm and diameter of 3 mm obtained by the extrusion of 15% cellulose solution in NMMO in a capillary rheometer.

Since it is experimentally difficult to measure the elongational viscosity at variable temperature, the drawing was carried out at a constant temperature of 20°C and relative humidity of 65%. This is justified also by the fact that during

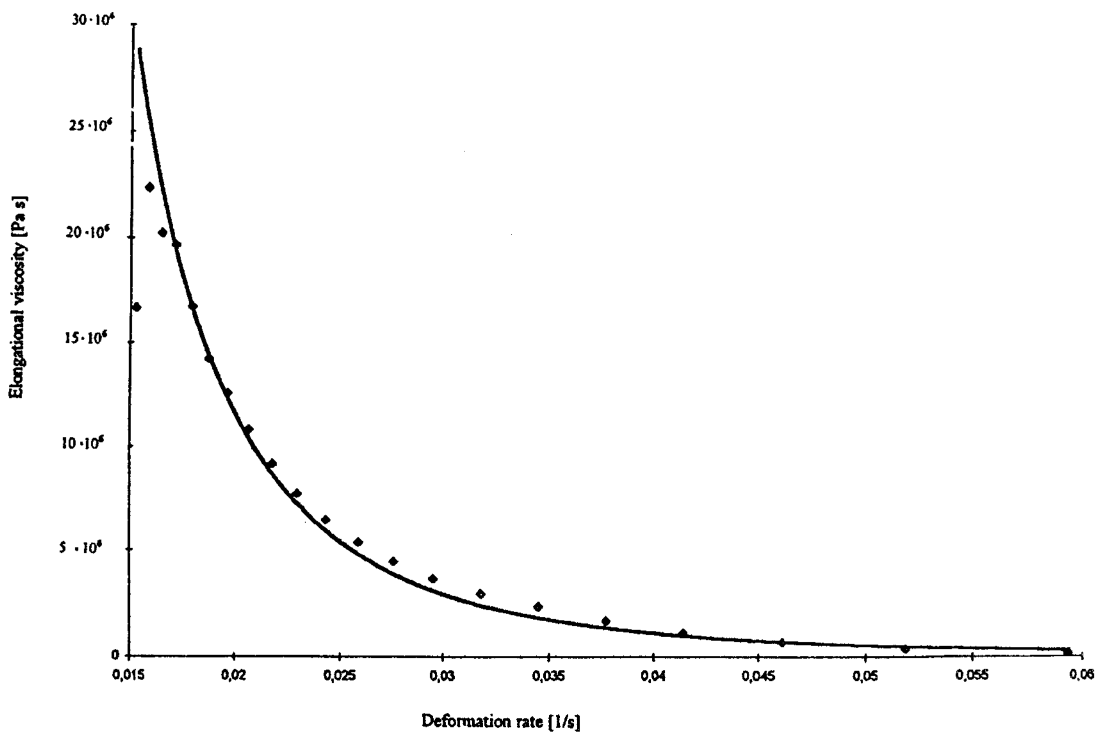

Figure 7 Elongational viscosity versus deformation rate.

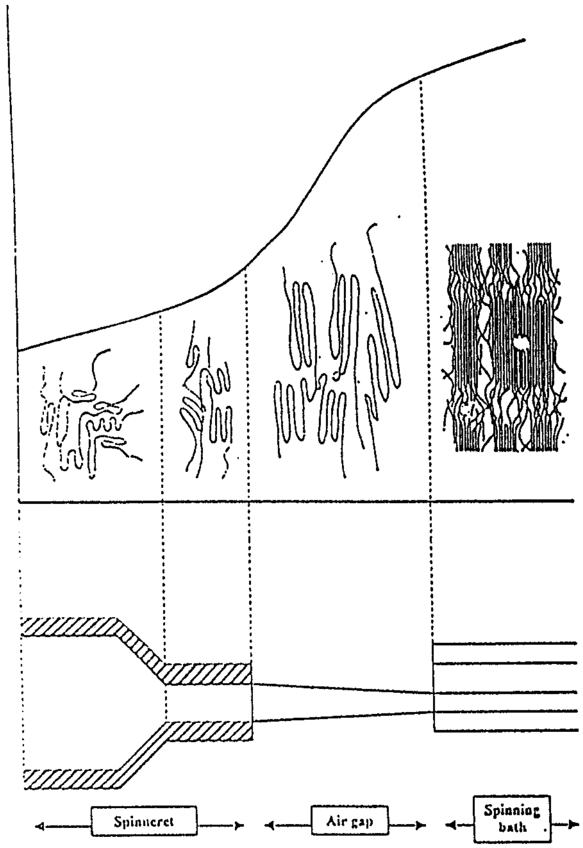

Figure 8 Schematic model of structural changes in fiber-spinning process by NMMO method.

fiber spinning from cellulose solutions in NMMO a rapid drop in temperature takes place over the length up to 50 mm from the spinneret surface.[2] Beyond this zone, physical transformations occur practically at ambient temperature. The elongational viscosity as a function of the deformation rate is shown in Figure 7.

The suggested schematic model of structural changes taking place during the deformation of the solution stream in the spinneret capillary within the air zone and in the coagulation bath is shown in Figure 8. In zones I and II, the cellulose solution in NMMO with a partial structural order resulting from intermolecular bondings, whose density increases with the cellulose concentration, undergoes orientation due to the lateral velocity gradient in the spinneret capillary.

When macromolecules have left the spinneret, only their partial disorientation occur. This is shown by the fact that the solutions formed with the use of spinnerets with longer capillaries, thereby being better oriented, are more susceptible to the elongation deformation.

The orientation in zone III consists of straightening the macromolecules due to the longitudinal velocity gradient within the narrowing solution stream. As at this stage cellulose is still in solution, the presence of a solvent makes it impossible to bind macromolecules with stronger hydrogen bonds. The structure which is characteristic of fibers, in which crystalline aggregates are divided by amorphous areas being oriented to a lesser extent, is developed during cellulose solidification in the spinning bath (zone IV).

CONCLUSIONS

The measurements carried out in a capillary rheometer have shown that the use of spinnerets with an increased capillary length-to-diameter (l/d) ratio has a positive effect on the spinneret orientation of spinning solutions and the reduction of outflow disturbances. The relationships characterizing the pressure drop as a function of the l/d ratio have a linear course. For a spinneret with $l/d = 1$, over 80% of the total pressure drop results from the resistance of forcing the fluid into the spinneret orifice, while the contribution of inlet effects to the total pressure drop decreases with increasing capillary length.

The shearing stresses generated in the flowing viscoelastic fluid decrease with increase of the l/d ratio. This brings about a reduced elastic response, and the fluid outflow from the spinneret becomes more uniform.

Regular deformations of the outflowing stream appear at a flow velocity of about 0.3 m/min. This indicates that the increases in the volumetric flow improves the uniformity of fiber formation, with the spinning velocity being increased at the same time. At constant temperature, the elongational viscosity of the solidified stream of the cellulose solution in NMMO decreases with increase of the deformation rate, causing a rupture of weak intermolecular bonds through the solvent and water molecules, which makes it possible the increase several times the formation velocity within the air zone.

The solidified filament subjected to drawing is a system containing cellulose, NMMO, and water. In this system, NMMO may be directly linked to the OH groups of cellulose with hydrogen bonds and indirectly through water molecules to adjacent cellulose macromolecules, causing the system to stiffen. The indirect bonds are weaker in energetic terms than are the direct bonds—their formation enthalpies are $DH = 4.26–4.76$ and 8.12–8.55 kcal/mol, respectively.[11] The indirect bonds are broken first under the influence of tensile stresses, the system rigidity decreases, macromolecules are straightened, and the viscosity rapidly decreases, already at a low rate of elongational deformation.

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