Methods for Reducing the Tendency of Lyocell Fibers to Fibrillate

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SYNOPSIS

A study has been made of the influence of various process parameters on the fibrillation characteristics of Lyocell fibers, which are spun from a solution of cellulose in *N*-methylmorpholine-*N*-oxide (NMMO). The parameters were air gap length, temperature, and humidity; line speed; draw ratio; polymer solution cellulose and water contents; and coagulation bath concentration and temperature. Fibrillation was induced in the fibers by an ultrasonic treatment and compared by defining a fibrillation index from optical micrographs. By selecting combinations of the parameters described above, fibrillation can either be increased or decreased without significantly affecting the tensile properties of the fibers. A method for spinning nonfibrillable filaments on a laboratory scale is presented. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Fibers produced with the cellulose/NMMO/water system (Lyocell) are known to fibrillate under conditions of wet abrasion.[1-7] This is due not only to its high orientation, but also to its apparent lack of lateral cohesion[4] compared to other cellulosic fibers. This adversely affects the launderability of the product in textile end uses, but in other markets (such as nonwovens) it proves to be an advantage.

A similar characteristic was encountered with the development of Polynosic rayons, which fibrillated much more than the Viscose rayons from which they were derived.[8] This was attributed to the highly oriented, parallel fibrillar structure in the Polynosic, which contrasted with the thick, resilient fibrils in conventional Viscose and the helical structure in cotton fibers.[9,10] The problem was addressed with the use of additives in the spin bath, notably formaldehyde, which imparted a "pseudo helical" rather than a parallel structure to the fibrils, although an acceptable explanation of how this happens was never given.[9-11]

Such a modification is not possible in the case of fibers spun from NMMO, because there is little chemistry in the system. This stems from two facts: First, it is a direct dissolution process; the cellulose is not derivatized when it is in solution.[12] Second, all the orientation in the process occurs in the spinneret hole and the air gap between the spinneret and the coagulation bath. This inevitably gives the fiber a well-oriented and parallel fibrillar structure which is prone to delamination.[1,7]

There are several possible ways of modifying the structure and hence the fibrillation tendency of the fiber. These are (1) putting additives into the polymer solution, (2) changing the spinning parameters, (3) modifying the spinning bath, and (4) treating the finished fiber. Recently, two solutions were proposed related to (3) and (4) above.[5,6]

Our paper is related to modifying the structure and hence the tendency to fibrillate of Lyocell fiber through methods (2) and (3). Three earlier papers[7,13,14] describe how different parameters in the spinning process influence the formation and the final structure of the fiber. Here, we study the way these parameters affect the fiber's ability to fibrillate. In addition, further parameters have been examined

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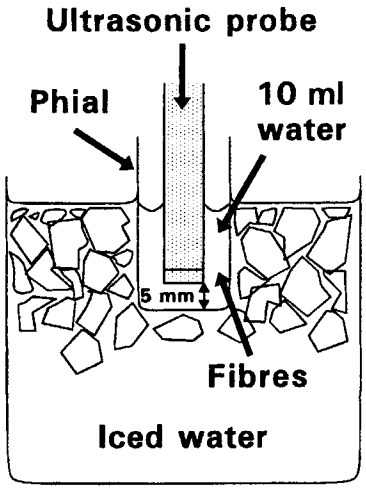


Figure 1 Apparatus for inducing fibrillation in fiber samples by ultrasonic treatment.

concerning the cellulose solution and the spin bath. A method for spinning nonfibrillable filaments on a laboratory scale will be presented.

EXPERIMENTAL

A solution of 15% dissolving pulp of $\overline{DP_V}$ 600 from International Paper Company in a mixture of 87% NMMO and 13% water was spun from a Davenport Melt Indexer at 115°C into an air gap and subsequently into a water bath (dry-jet wet spinning). Depolymerization, which can occur during dissolution and spinning, was easily controlled by adding an antioxidant such as sodium hexametaphosphate or propyl gallate. The apparatus was set up at CERMAV and specially modified for this work.[15] Five different single-hole spinnerets were used, of between 50 μm and 300 μm outlet diameter.

Air gap lengths of 20 mm, 50 mm, and 250 mm were used. When the air gap was conditioned, the temperature was varied between 0°C and 58°C and the relative humidity was varied between 0% and 100%. The draw ratio (D_R) was changed from 1 (spinning at extrusion velocity) to 41. The line speed, at constant D_R and fiber diameter, was varied from 8 m/min to 48 m/min. The cellulose solution water content was varied from 7.8% to 12.3%. The cellulose content in the solution was varied from 10% to 15%. The cellulose solution temperature was varied from 115°C to 130°C. Coagulation baths of pure water and 25% NMMO in water were used. The temperature of the bath (water) was varied from 2°C to 50°C. The diameter and birefringence of the filament were monitored using devices developed by the authors and described in Mortimer and Péguy.[15]

Fibrillation was measured by the following technique: 10 filaments of 20 mm length were immersed in 10 mL of distilled water in a 30-mL phial. These were then sonicated for 15 min on a Branson sonifier B12 ultrasonic probe while cooling the outside of the vial, as shown in Figure 1. The probe was fitted with a 13-mm flat tip. The fibrillation index (I_f) was calculated from optical micrographs of the fibrillated fibers. The lengths of the fibrils, l, over a length of fiber, L, were measured. The fibrillation index is given by

$$I_f = \frac{\frac{\sum l}{L}}{L} \quad (1)$$

Optical micrographs of fibrillated fibers with different fibrillation indices are shown in Figure 2.

The birefringence of dry fibers was measured on an Olympus optical microscope with the aid of a Berek compensator.

The crystallinity and orientation of the fibers were measured using the wide-angle X-ray diffraction (WAXD) technique described earlier.[7] Small-angle X-ray scattering (SAXS) was used to measure the lateral period in the dry and wet states, using a device described previously.[7]

Fiber tensile testing was carried out on an Instron 4301 tester, on 20 fibers from each sample, conditioned to 20°C and 65% relative humidity. Linear densities (*dtex*'s) were calculated from measurements of the fiber diameter on a Zeiss optical microscope.

RESULTS AND DISCUSSION

The Air Gap

We have seen from a previous paper[14] that the conditions in the air gap have a strong impact on the way the structure of the filament is formed, but this only translates into relatively subtle effects on the final properties and structure of the fiber. Most notably, the tenacity is affected by changes in the air gap length and humidity. Given these differences in tensile properties, what is the influence of air gap conditions on the tendency of the fiber to fibrillate?

The influence of the air gap length is shown in Figure 3. There is a very clear relationship: a longer air gap leads to much lower fibrillation. It is easy to see that with cold, dry air-gap conditioning, the fibrillation is significantly higher than in the other

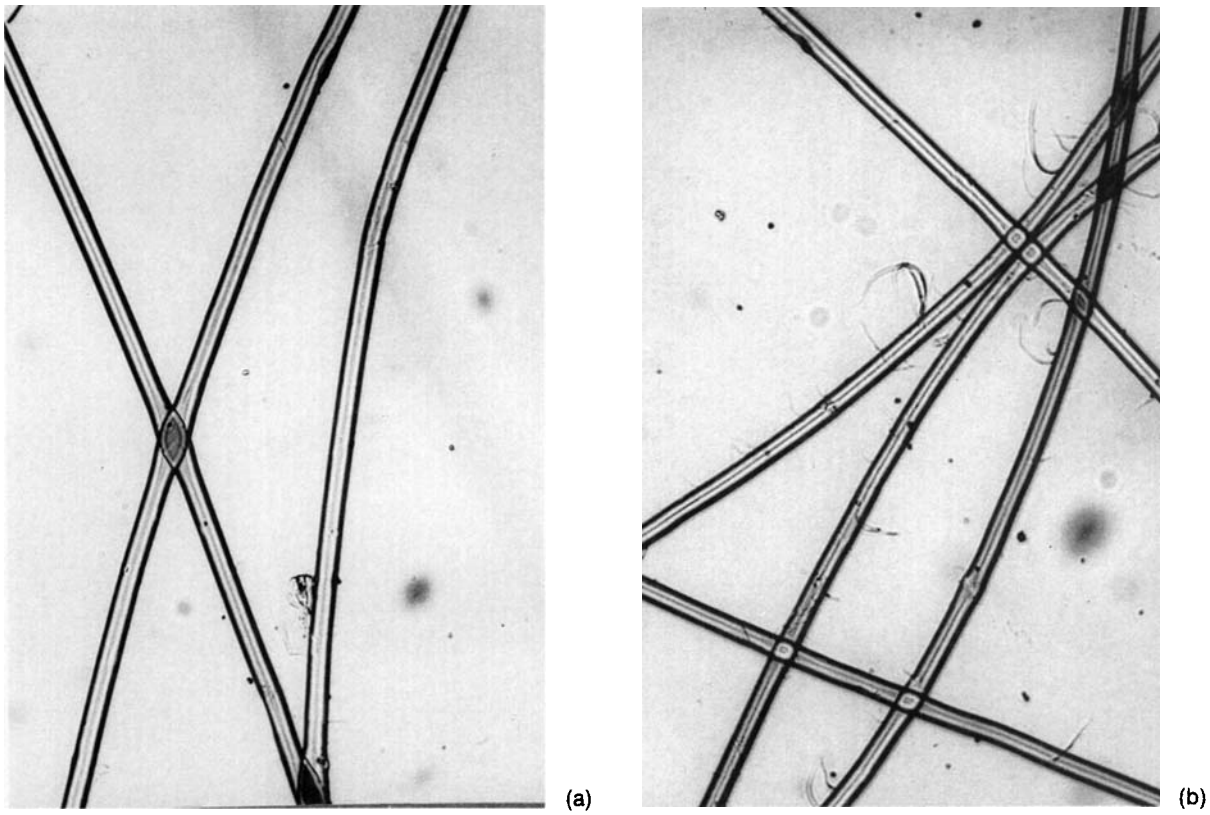


Figure 2 Photomicrographs of fiber samples with different fibrillation indices: (a) $I_f = 0$, (b) $I_f = 0.8$, (c) $I_f = 2$, (d) $I_f = 9$, and (e) $I_f = 25$.

cases. Conversely, with warm, humid air, the fibrillation is relatively low, even with a short air gap; fibrillation practically disappears with a long air gap. When spinning without conditioning the air gap, an intermediate response is observed: the fibrillation is quite high with a short air gap, but is, again, very low with a long air gap.

The effect of temperature with different air-gap lengths is shown in Figure 4. With a short air gap, there does not appear to be a highly significant effect. With a long air gap, however, increasing the temperature appears to reduce fibrillation slightly.

Table I shows the relationship between the mechanical properties and fibrillation of fibers spun in different air gap conditions. There is no apparent overall trend between tensile properties and fibrillation, but some interesting interactions may be noted. With no conditioning and with dry air, increasing the air-gap length increases both fiber tenacity and extensibility. With a short air gap, high-humidity air increases the tenacity. When a long air gap is combined with humid air, however, both the tenacity and extension at break are low. Warm, dry air appears to reduce tenacity, the effect being more marked with a long air gap. To summarize the relationship between the tensile properties and fibrillation, the strongest fibers have an intermediate fibrillation index, but the fiber with the lowest fibrillation index is the weakest.

To interpret the results presented above, we will consider the fibers' structure formation during coagulation. When the filament enters the spin bath, precipitation of cellulose occurs through diffusion of nonsolvent and solvent, which gives rise to a unidirectional network of laterally and regularly spaced fibrils. As the coagulation happens in a state of nonequilibrium, we have spinodal decomposition (the phase separation of an unstable mixture), in which an interconnected pattern of domains of a characteristic size forms and coarsens with time. This phenomenon is well explained by Gunton and colleagues.[16]

In the case of a spinning fiber, however, the quench arrives on the surface of the filament; this has been modelled by Ball and Essery,[17] who have shown that on quenching, the system is placed in either unstable or metastable states. If the system arrives in an unstable state, it decays to two coexisting metastable states leading to an interconnected structure of the two phases, one of which is rich in

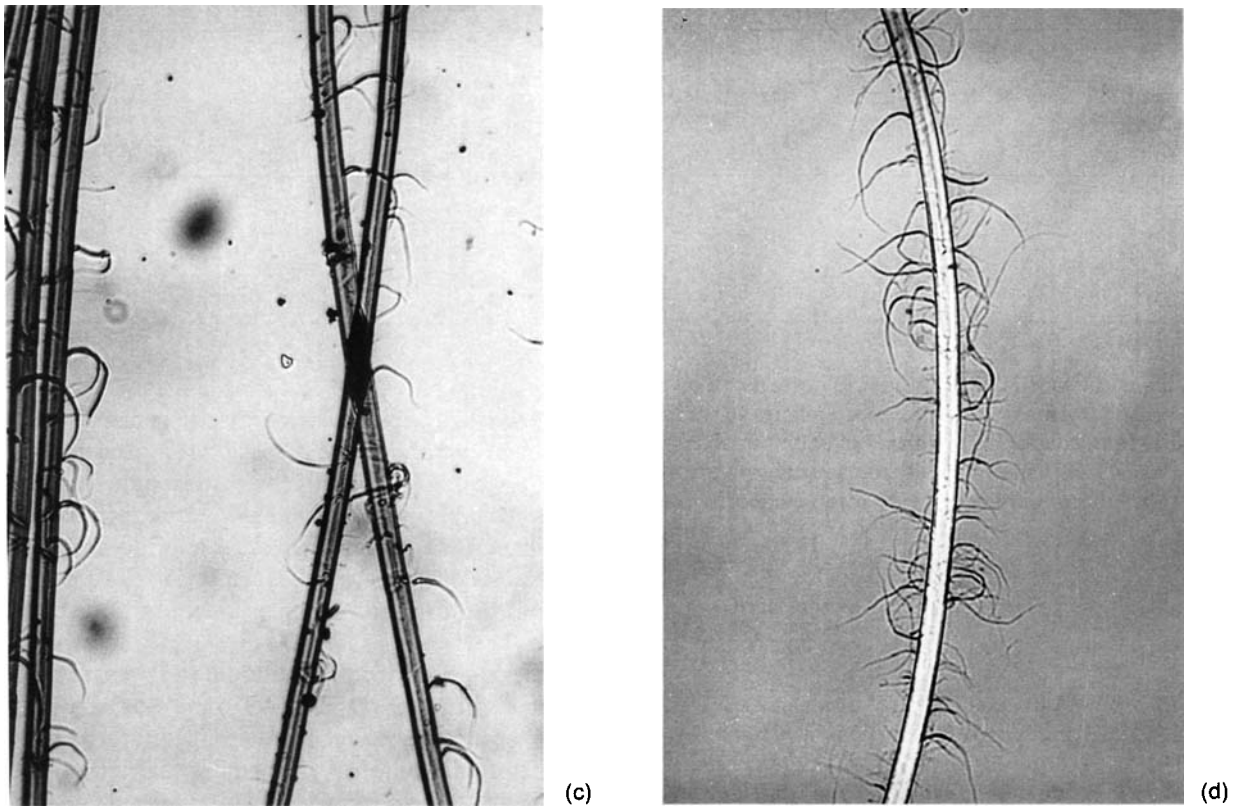


Figure 2 (*Continued from the previous page*)

solvent and the other rich in polymer. The coarseness of this structure is increased by a deeper quench. It is possible for the introduction of a nonsolvent to the surface of the system as well as a thermal quench to cause this phase separation. In this case, the depth of quench is determined by the power of the nonsolvent.

Generally, the pattern expected is a layered surface with a granular core, but the presence of noise is sufficient to impart a granular structure to the surface. In the case of fibers spun from polymer solutions, the predicted structure is fibrillar,[18] which equates to a granular structure mapped into three dimensions along the fiber axis. The fibrils are the result of the polymer regions. The solvent regions will become microvoids.[2] As a deeper quench gives rise to a greater differentiation in composition between the two phases, there will be less polymer in the solvent-rich regions to form bridges between the polymer-rich regions. We would expect that this will increase the tendency to fibrillate.

As we have shown previously,[13,14] depending on the spinning parameters (spinneret size and temperature, draw ratio, etc.) and the air-gap conditions (air gap length, temperature, and humidity), there will be more or less thermal and nonsolvent quench and more or less orientation of the polymer chains, which will change and perturb the spinodal decomposition. These phenomena will have an influence on the final structure of the fibers. In particular, the orientation, the state of stress, and the eventual existence of interconnections between the microfibrils will affect the longitudinal and lateral cohesion of the cellulose microfibrils. Drying will bring the fibrillar elements together, but may reinforce the stress induced in the wet state. Indeed, formation of the polymer into a single unit cannot be brought about by mutual diffusion of macromolecules into neighboring microfibrils due to the kinetic immobility of the polymer chains that are already in a paracrystalline state. Only a weak network of interfibrillar hydrogen bonds can form from the collapse that occurs during drying. If the network is weakened sufficiently by stresses between microfibrils or a lack of interconnections between them, high fibrillability will result. Fibrillation will therefore be reduced by a reduction in stress, which will possibly—but not necessarily—be accompanied by a reduction in orientation.

Figure 5, from Mortimer and Péguy,[14] shows the relationship of birefringence Δn to distance from the spinneret in the air gap for fibers spun with dif-

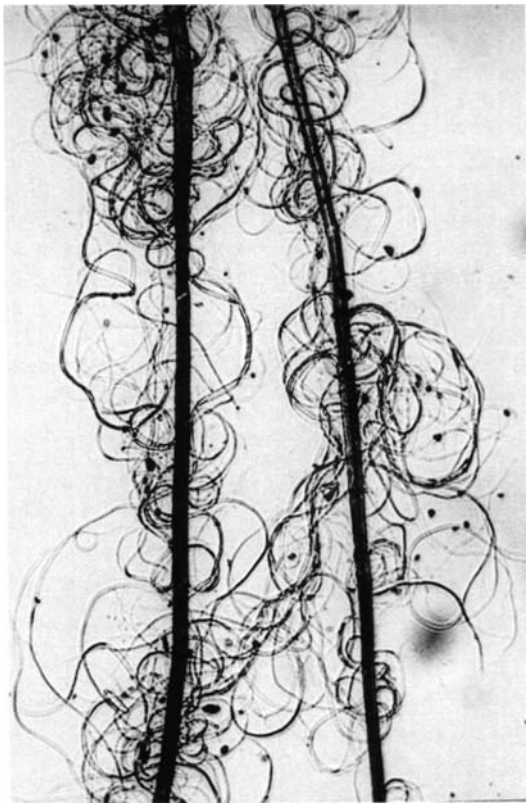


Figure 2 *(Continued from the previous page)*

ferent air-gap conditioning. With cold, dry air, the birefringence increases towards the spin bath. If this curve is extrapolated, it is possible that the Δn at the entrance to the spin bath is higher than with warm, humid air. Figure 6(a), from Ref. 14 shows the same results, but as a function of dimensionless velocity. In the case of warm, humid air, there is a smooth progression which is not totally proportional, indicating the presence of chain slippage.[14] These gentle conditions lead to relatively low fibrillation. In contrast, the curve for cold, dry air begins with a very low slope followed by sharp growth in birefringence with little increase in velocity. This indicates severe chain slippage followed by orientation induced by high stress on the supercooled, oriented polymer solution. The severity of these conditions leads to the high fibrillation with a short air gap and dry air observed in Figure 3.

A comparison between air-gap conditions with a long air gap can be made using Figure 6(b) from Reference 14. The curve for cold, dry air shows the same general form as the short air-gap case, but the initial part is less flat, followed by a smaller rise at the end. The chain slippage is thus less severe and less orientation is induced due to stress. This leads to lower fibrillation, as shown in Figure 3.

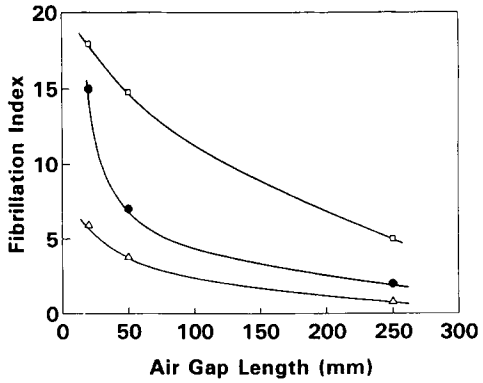


Figure 3 Fibrillation index as a function of air gap length with different air gap conditions: (□) 2% RH, 0°C; (△) 100% RH, 30°C; (●) no conditioning.

The most dramatic effect is observed with warm, humid air and a long air gap. The growth of orientation is similar to the short air-gap case shown in Figure 6(a), but after reaching a maximum, the birefringence drops off towards the end. This relaxation is due to the filament having time to absorb water from the saturated air and a subsequent drop in the viscosity of the material. This effect, as well as the different quenching conditions, leads to very low fibrillation (Fig. 3) and low tenacity (Table I).

Turning now to the effect of the air gap temperature on fibrillation, we have shown that, with a short air gap, there is no measurable effect. This is consistent with the similitude of the relationship of the birefringence to the dimensionless velocity in the three cases, as reported earlier.[14] The slight reduction in fibrillation (and tenacity) observed on increasing temperature with a long air gap can be explained in terms of Figure 7 from Ref. 14. It can be seen that, at 58°C, the material displays slippage toward the end of the air gap, owing to the high

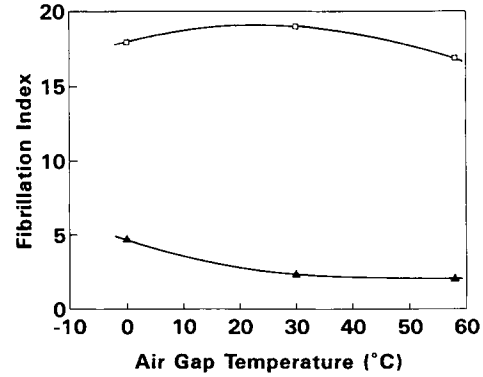


Figure 4 Fibrillation index as a function of air gap temperature; dry air gap. (□) 20 mm air gap; (▲) 250 mm air gap.

Table I Physical Properties of Fibers Spun with Different Air Gap Conditions

Air Gap Length	Air Gap Conditioning	Initial Modulus (GPa)	Tenacity (GPa)	Extension at Break (%)	Fibrillation Index
250 mm	No conditioning	20 ± 2	0.60 ± 0.03	11 ± 1	2 ± 0.5
250 mm	2°C 0% RH	22 ± 3	0.65 ± 0.03	9 ± 1	5 ± 1
250 mm	33°C 100% RH	21 ± 2	0.41 ± 0.02	6 ± 1	0.9 ± 0.1
250 mm	58°C 0% RH	19 ± 2	0.48 ± 0.01	10 ± 1	2 ± 0.7
20 mm	No conditioning	20 ± 2	0.53 ± 0.02	9 ± 1	15 ± 2
20 mm	2°C 0% RH	20 ± 2	0.56 ± 0.01	7 ± 1	18 ± 2
20 mm	33°C 100% RH	21 ± 2	0.68 ± 0.02	10 ± 1	6 ± 1
20 mm	58°C 0% RH	17 ± 2	0.51 ± 0.01	10 ± 1	16 ± 2

Spinneret size = 100 μm; D_R = 10.4.

temperature. In this case, the phenomenon allows some of the stresses in the filament to relax out just before it enters the spin bath.

Line Speed

The spinning speed was varied from 8 m/min to 48 m/min while maintaining a D_R of 10.4 by simultaneously varying the throughput of cellulose solution and the godet speed. This basically changes the rate at which things are happening, but produces a fiber of the same diameter (in this case 11 μm).

The effect of the line speed on fibrillation, shown in Figure 8, is that raising the line speed increases the tendency of the fiber to fibrillate. The ratio between the fibrillation indices for fibers spun at 8 m/min and 48 m/min is about 4 with a 250 mm air gap, but with a 20-mm air gap, it is only 2. The increase in line speed is achieved by increasing the throughput of polymer solution. As seen in a previous paper, this will change the draw length (D_L).[13]

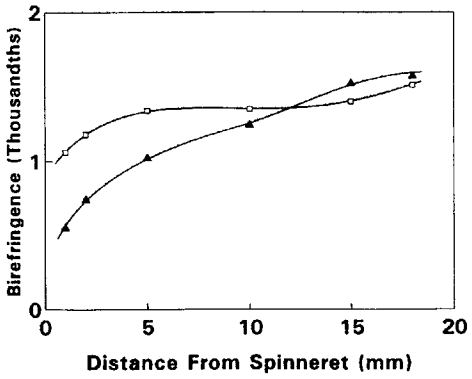
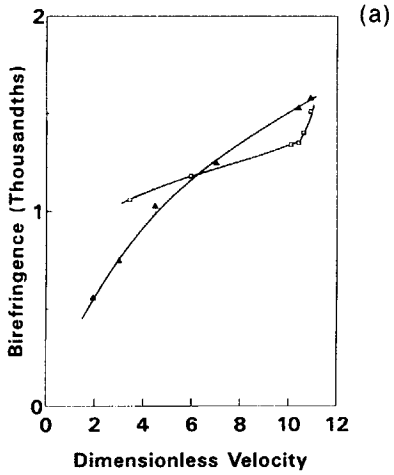


Figure 5 Birefringence of a filament in the air gap as a function of distance from the spinneret, with different air gap conditions; 20 mm air gap. (□) 2% RH, 0°C; (▲) 100% RH, 30°C.



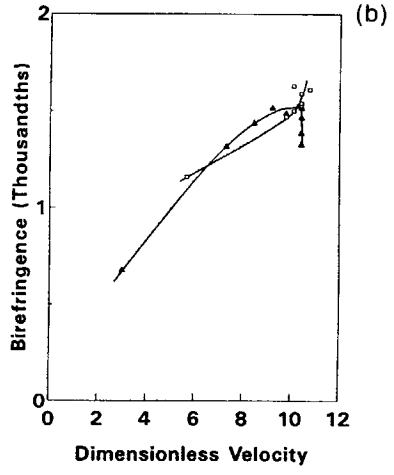


Figure 6 Birefringence of a filament in the air gap as a function of dimensionless velocity, with different air gap conditions: (a) 20 mm air gap; (b) 250 mm air gap; (□) 2% RH, 0°C; (▲) 100% RH, 30°C.

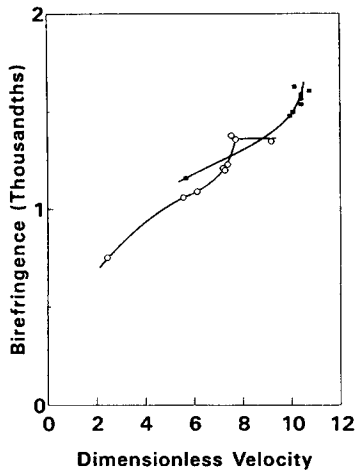


Figure 7 Birefringence of a filament in the air gap as a function of dimensionless velocity, with different air gap temperatures; 250 mm air gap. (■) 2% RH, 0°C; (○) 1% RH, 58°C.

Let us consider the 20-mm air-gap case. We have seen that with such a short air gap, and with a line speed of 24 m/min, the material has to accelerate toward the spin bath,[14] but with a low line speed, D_L will be decreased, which will allow the velocity more time to stabilize. This will allow the stresses to relax out, all the more since the residence time of the filament in the air gap is longer (230 ms versus 70 ms, as computed from draw profiles in previous experiments.[13,14] We would therefore expect, with a line speed of 8 m/min, to have a lower I_f than at 24 m/min, which is what we observe.

Increasing the line speed to 48 m/min, we will significantly increase D_L, causing more rapid acceleration and less time to relax since the residence time in the air gap is lower (58 ms against 70 ms). The stress induced in the material should lead to a high I_f, as we observe. With a long air gap, the effect of shortening the residence time, combined with the increase in D_L greatly decreases the time left for the macromolecules to relax. This leads to a stronger effect than with a 20-mm air gap.

The physical properties of fibers spun with different line speeds are shown in Table II. There does not appear to be an effect on fiber tenacity and initial modulus, but on raising the line speed, the extension at break is reduced along with the increased fibrillation, which means that the fiber is fragilized since the lateral and longitudinal cohesion are diminished.

We have seen that the residence time of the filament in the air gap can affect the formation of the structure and hence the fibrillation index. Therefore, the air-gap residence time was computed from the draw profiles of fibers spun with different line speeds, air gap lengths, and conditioning, and this was plotted against the fibrillation index. The results are shown in Figure 9.

There appears to be a very good correlation. The effects discussed above can be summarized by stating that fibrillation is reduced by increasing the residence time of the filament in the air gap, for reasons that have already been considered. With wet conditioning, a significant decrease in I_f is observed. It is clear that water vapor in the air gap further reduces fibrillation and that there is an interaction, confirming what was observed above.

Using optical birefringence, WAXD, and SAXS measurements, we have studied the structures of filaments spun with different air-gap residence times. All the results were very similar: the birefringence was always between 0.040 and 0.042; the crystalline index was always between 43% and 46%; the crystalline orientation factor was between 0.93 and 0.95; and the dry and wet lateral periods were approximately 45 and 104 Å, respectively. Nevertheless, when the fibers are swollen for 24 h in zinc chloride solution and crushed between microscope slides, as described previously,[7] the way they break up laterally is different (Fig. 10). The fibers with a high fibrillation index have more voids and appear to split apart more easily. Although the microcrystalline structure is identical in the two cases, it is this lack of lateral cohesion which causes the fibers to fibrillate.

Draw Ratio (D_R)

It is well known that lowering the D_R reduces the orientation of the polymer in the resulting fiber.[19] One of the main reasons (described in the INTRODUCTION) for the high fibrillation of lyocell fibers

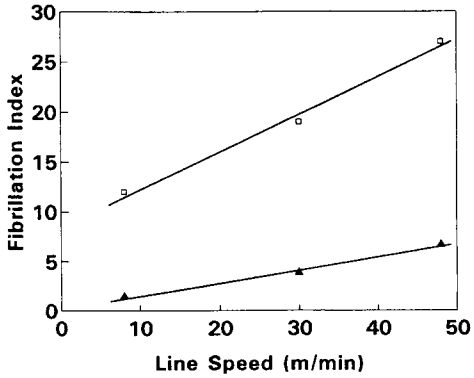


Figure 8 Fibrillation index as a function of line speed: (□) 20 mm air gap; (▲) 250 mm air gap.

Table II Physical Properties of Fibers Spun with Different Line Speeds

Line Speed	Initial Modulus (GPa)	Tenacity (GPa)	Extension at Break (%)	Fibrillation Index
8 m/min	22 ± 2	0.61 ± 0.02	11 ± 1	12 ± 2
30 m/min	23 ± 2	0.59 ± 0.02	7.4 ± 0.4	19 ± 4
48 m/min	24 ± 2	0.60 ± 0.02	7.7 ± 0.4	27 ± 5

Spinneret = 100 μm; D_R = 10.4; air gap = 20 mm.

compared to other cellulosics is their high orientation. It may thus be expected that the D_R has an influence on fibrillation.

Figure 11(a) shows the fibrillation index of fibers spun with different D_Rs, keeping constant the spinneret size and the throughput Q. As a consequence, the final diameter of the fiber will change as the D_R is varied. The general trend observed is one of increasing fibrillation with increasing D_R. With a long air gap, however, below a D_R of about 10, the D_R has relatively little influence on the fibrillation index. With a short air gap, on the other hand, the fibrillation increases rapidly up to a D_R of 10, after which we note a tendency for the fibrillation to decrease with increasing D_R.

Still keeping the flow rate constant, a second series of fibers was spun with spinneret sizes from 50 μm to 200 μm in order to keep a constant final diameter of 11 μm (Fig. 11[b]). The effect of D_R on fibrillation is very similar to what was observed in Figure 11(a).

Once again, increasing the D_R significantly above 10 does not lead to an associated increase in fibrillation when the air gap length is short: there is a levelling off. This is due to the attainment of full chain extension and the onset of chain slippage as described in Mortimer and Péguy.[13]

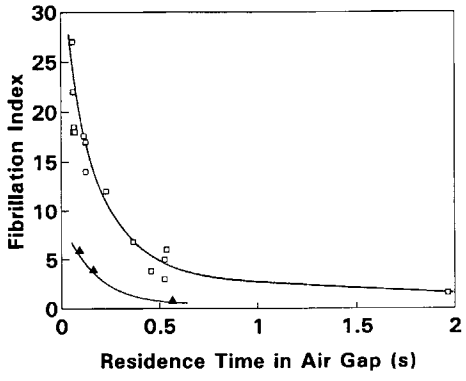


Figure 9 Fibrillation index as a function of the residence time of the filament in the air gap: (□) ≤2% RH, various temperatures (0–58°C); (▲) 100% RH, 30°C.

The slight decrease in fibrillation above a D_R of 10 shown in Figure 11(a) may, at first, appear surprising, especially since the line speed was not held constant and the residence time in the air gap was decreased. We could explain this by noting that, with a high D_R, the strain rate will be high, leading to relatively low viscosity in the material. This will cause a large amount of chain slippage, which will affect the spinodal decomposition in the spin bath (possibly due to the reduction of local concentration fluctuations).

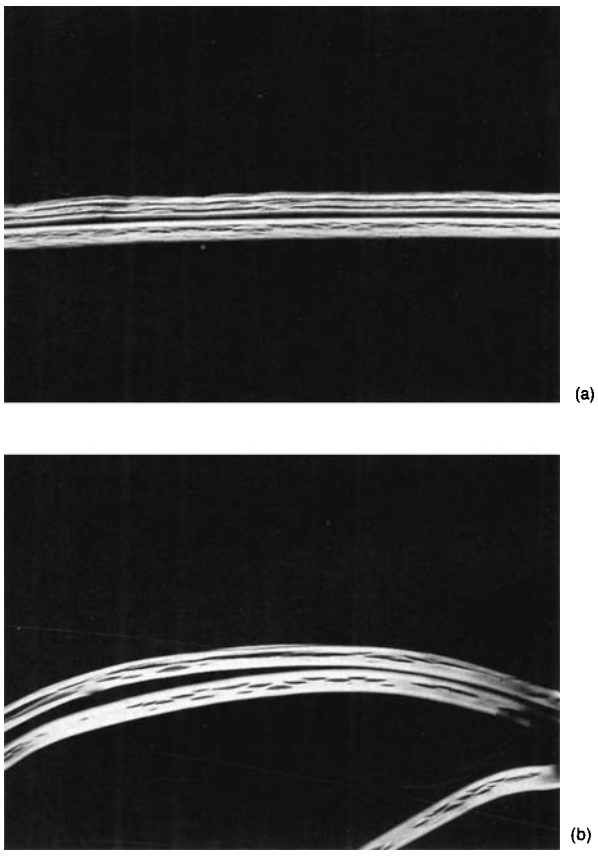


Figure 10 Photomicrographs showing fibrillar structures of fibers with different fibrillation indices, revealed by light crushing (×220): (a) high fibrillation; (b) low fibrillation.

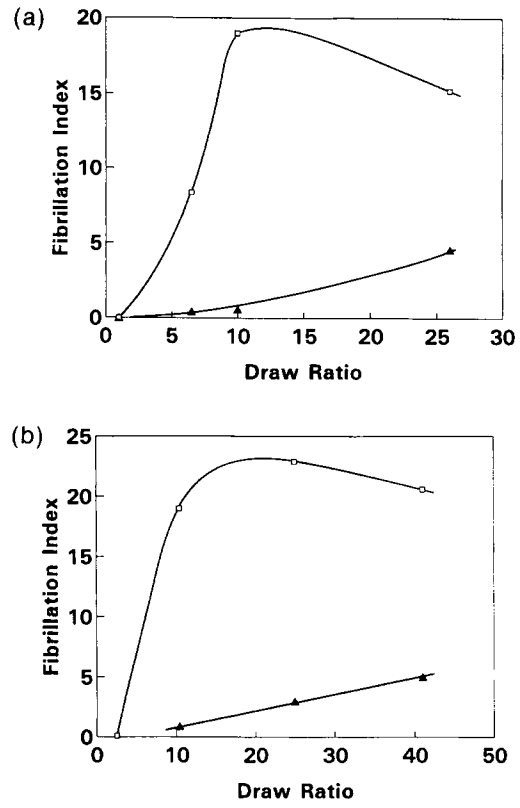


Figure 11 Fibrillation index as a function of draw ratio: (a) constant spinneret size (100 μm); (b) constant fiber diameter (11 μm) and line speed (30 m/min); (□) 20 mm air gap; (▲) 250 mm air gap.

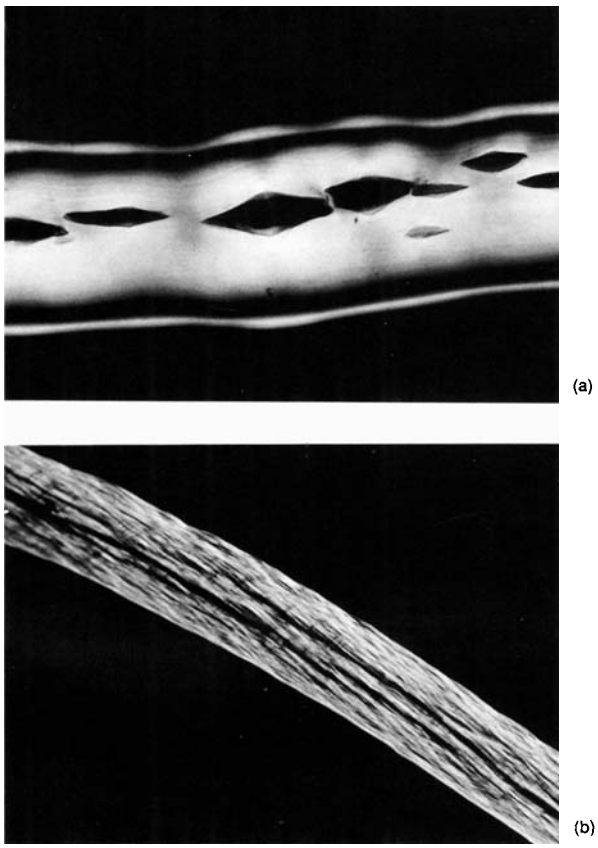


Figure 12 Photomicrographs showing fibrillar structures of fibers spun with different draw ratios, revealed by severe crushing (×220): (a) D_R = 1; (b) D_R = 10.4.

Table III shows the physical properties of fibers spun with different spinning conditions and having different fibrillation indices. The reduction in fibrillation with decreasing D_R is accompanied by differences in structure and properties of the fibers. Regarding the fibers' fine structure, the fibrillation index appears to be changing independently of the

Table III Physical Properties of Fibers Spun with Different Draw Ratios and Air Gap Lengths

Air Gap	Fiber Diameter	Draw Ratio	Δn	Initial Modulus (GPa)	Tenacity (GPa)	Extension at Break (%)	Fibrillation Index	Crystalline Index (%)	Cryst Orientation Factor
250	33	1	0.023	6.2 ± 0.5	0.25 ± 0.01	80 ± 8	0	43	0.67
140	11	2.5	0.041	16 ± 1	0.46 ± 0.01	18 ± 1	0.9 ± 0.1	—	—
250	15	6.5	0.040	20 ± 2	0.53 ± 0.02	11 ± 1	0.4 ± 0.1	43	0.91
250	11	10.4	0.041	20 ± 2	0.60 ± 0.03	11.3 ± 0.5	0.9 ± 0.2	46	0.94
250	11	25	0.042	21 ± 2	0.60 ± 0.01	11.9 ± 0.5	3 ± 0.5	44	0.95
250	11	41	—	19 ± 2	0.56 ± 0.02	11.4 ± 0.4	5 ± 0.5	—	—
20	15	1	0.034	10 ± 1	0.35 ± 0.01	40 ± 3	0	—	—
20	11	2.5	0.041	12 ± 2	0.47 ± 0.04	28 ± 2	0.1 ± 0.02	—	—
20	15	6.5	—	17 ± 2	0.46 ± 0.03	14 ± 1	8.4 ± 1	—	—
20	11	10.4	0.041	20 ± 2	0.53 ± 0.02	9.1 ± 0.6	19 ± 2	43	0.94
20	11	25	0.042	22 ± 2	0.56 ± 0.03	11.3 ± 0.5	23 ± 2	45	0.95
20	11	41	—	21 ± 2	0.52 ± 0.02	8.1 ± 0.4	21 ± 2	—	—

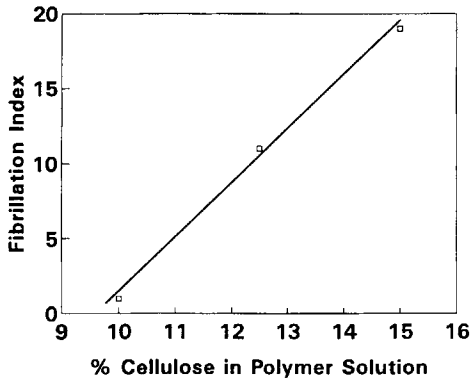


Figure 13 Fibrillation index as a function of percent cellulose in the polymer solution; air gap length = 20 mm.

polymer crystallinity. For a long air gap, it does seem to be related to the crystalline orientation, however, as evidenced by the crystalline FWHM: fiber with a lower crystalline orientation fibrillates less because its structure is less fibrillar for a low D_R. This can be seen in Figure 12, which shows fibers that were soaked in zinc chloride solution for 24 h and crushed between microscope slides.

For a D_R of 1, the highly fibrillar structure seen with a D_R of 10 disappears completely. This makes it very hard for the fiber to delaminate. The condition for low fibrillation, in this case, appears to be that the structure is completely without visible parallel fibrils.

A point of interest shown by Table III is that it is possible to maintain acceptable mechanical properties for fibers with low fibrillation. In terms of the initial modulus and extension at break, there is very little difference between the fibers above a D_R of about 6.5, but a relatively high tenacity can be maintained down to a D_R of 2.5. Regardless of the air gap, fibers spun with this D_R have a very low fibrillation index. With a short air gap, it is not possible to use a D_R much above 2.5 before the fibrillation increases significantly, so, in this case, about 0.47 GPa is approximately the maximum tenacity that can be expected for a fiber with low fibrillation. With a long air gap, however, the D_R can be increased up to 10.4. These fibers have very good mechanical properties.

Polymer Solution Cellulose Content

Braverman and colleagues[20] and Loubinoux and Chaunis[21] have shown that there is a very strong dependence of the solution viscosity on the cellulose concentration: reducing the cellulose content reduces the solution viscosity. We have studied the effect of the polymer solution cellulose content on the fibrillation and mechanical properties of the fibers; results are shown in Figure 13 and Table IV. This figure shows that reducing the solution cellulose content significantly reduces the tendency of the fiber to fibrillate. It is suggested that this is due to the lower elasticity and relaxation time[20] of the more diluted solution, allowing some of the stress and orientation to relax out at the entrance to the spin bath. This is reflected in the lower mechanical properties of the fibers (Table IV).

A highly significant trend in initial modulus and extension to break is hard to identify. Reducing the cellulose content clearly gives rise to lower tenacity, however, at the same time as lower fibrillation.

Polymer Solution Water Content

Decreasing the solution water content has been shown in a previous work[14] to increase the birefringence (and hence the orientation) of the polymer at the entrance to the spin bath when using cold, dry air conditioning. It is expected that this increase in orientation will produce highly fibrillating fibers. This is what we observe in Table V, but the difference that can be effected is much smaller than what can be achieved by varying the air gap or D_R. The increase in fibrillation is accompanied by better tensile properties.

The suggested reason for the effect of water content on fibrillation is that reduced water in the solution increases its viscosity, as evidenced by its higher birefringence during drawing.

Table IV Physical Properties of Fibers Spun With Different Cellulose Concentration in the Solution

% Cellulose in Solution	Initial Modulus (GPa)	Tenacity (GPa)	Extension at Break (%)	Fibrillation Index
10	20 ± 2	0.45 ± 0.02	11 ± 1	1 ± 0.05
12.5	19 ± 2	0.52 ± 0.02	7 ± 1	11 ± 2
15	21 ± 2	0.56 ± 0.02	9 ± 1	19 ± 2

Table V Physical Properties of Fibers Spun with Different Solution Water Contents (20 mm Air Gap)

% Water in Solution	Initial Modulus (GPa)	Tenacity (GPa)	Extension at Break (%)	Fibrillation Index
7.8	21 ± 2	0.63 ± 0.01	7.2 ± 0.5	24 ± 2
12.3	20 ± 2	0.56 ± 0.01	7.7 ± 0.5	13 ± 1

Spin Bath Concentration

Fibers were spun using distilled water and solutions of NMMO in water with a concentration of 25%, and the results are shown in Table VI. As explained previously, pure water coagulant will give a deeper non-solvent quench than a solution of NMMO in water. Using 25% NMMO in the coagulant instead of the usual water should therefore reduce fibrillation. This is what we observe in Table VI, the magnitude of the effect being similar to that of a 4–5% increase in solution water content. The tenacity of the fiber with lower fibrillation is also somewhat lower.

Spin-Bath Temperature

Fibers were spun with spin-bath temperatures of 2°C (using floating ice on the spin-bath surface), 20°C, and 50°C and the results are shown in Table VII. There does not appear to be a significant trend. It was expected that a low temperature spin bath should cause the fibrillation index to increase, since the thermal quench will be higher and, consequently, the spinodal decomposition effect will be stronger. In view of this, our result is rather surprising.

Despite this near independence of the fibrillation index on the spin-bath temperature, there is a relatively strong effect on the physical properties of the fibers. There is a very clear trend toward higher tenacity and extension at break with a lower spin-bath temperature. This effect has also been described elsewhere.[22]

CONCLUSIONS

This paper has shown how to modify the structure and influence the fibrillation tendency of Lyocell fiber. We have shown that cold, dry air-gap conditioning significantly increases the fibrillation. Conversely, with warm, humid air, the fibrillation is relatively low with a short air gap and practically disappears with a long air gap. The residence time of the filament in the air gap has been demonstrated to have an effect on the comparative fibrillation index: the longer this time, the lower the index. The mechanisms by which these parameters affect the structure of the fiber are by altering the amount of stress on the material as it is coagulated and by the way it is quenched. For a short air gap, an increase in the D_R strongly increases the fibrillability, but at a D_R of 2.5, it is possible to produce fibers of high tenacity and low fibrillation. With a long air gap, on the other hand, fibers showing little fibrillation and having very good mechanical properties can be produced with a D_R up to 10. The polymer solution cellulose content and water content, as well as the spin-bath concentration, also prove to be parameters that influence the fiber structure and its tendency to fibrillate. To conclude our study, we present a method for spinning non-fibrillable Lyocell fibers on a laboratory scale: a solution of 10% dissolving pulp in a mixture of 85.5% NMMO and 14.5% water is spun at 115°C into an air gap of 100 mm conditioned to 30°C and 100% relative humidity with a D_R of 5. The fiber is coagulated in a solution of 25% NMMO in water. Although academic, this example

Table VI Fibrillation and Physical Properties of Fibers Spun with Different Spin Bath Concentrations (20 mm Air Gap)

Spin Bath NMMO Concentration (%)	Initial Modulus (GPa)	Tenacity (GPa)	Extension at Break (%)	Fibrillation Index
0	21 ± 2	0.56 ± 0.02	9.0 ± 0.8	19 ± 2
25	21 ± 2	0.50 ± 0.02	6.8 ± 0.7	11 ± 1

Table VII Physical Properties of Fibers Spun with Different Spin Bath Temperatures (20 mm Air Gap)

Spin Bath Temperature (°C)	Initial Modulus (GPa)	Tenacity (GPa)	Extension at Break (%)	Fibrillation Index
2	23 ± 2	0.63 ± 0.03	11.1 ± 0.4	16 ± 2
20	21 ± 2	0.56 ± 0.02	9.0 ± 0.8	19 ± 2
50	23 ± 2	0.48 ± 0.02	7.1 ± 0.3	16 ± 2

opens the way to the production of new fibers via the NMMO process.

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REFERENCES

1. C. C. McCorsley and J. K. Varga, U.S. Patent 4,142,913, 1979.
2. M. Dubé and R. H. Blackwell, *Tappi Proceedings*, 111–119, (1983).
3. I. Quenin, Doctoral Thesis, UJF Grenoble, 1985.
4. J. Lenz and J. Schurz, *Cellulose Chem. Technol.*, **24**, 679 (1990).
5. J. M. Taylor, International Patent Application WO 92/01724, 1992.
6. J. M. Taylor, International Patent Application WO 92/19807, 1992.
7. S. A. Mortimer and A. A. Péguy, *Cellulose Chem. Technol.*, to appear.
8. N. Drisch and R. Priou, *Bulletin ITF*, **101**, 667 (1962).
9. N. Drisch, *Pure Appl. Chem.*, **14**, 317 (1967).
10. Y. Uchida, *Pure Appl. Chem.*, **14**, 461 (1967).
11. N. Drisch, P. Herrbach, and H. Rodier, French Patent 1,226,492, 1961.
12. D. Gagnaire, D. Mancier, and M. Vincendon, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 13 (1980).
13. S. A. Mortimer and A. A. Péguy, *Cellulose Chem. Technol.*, to appear.
14. S. A. Mortimer and A. A. Péguy, *J. Appl. Polym. Sci.*, to appear.
15. S. A. Mortimer and A. A. Péguy, *Textile Res. J.*, **64**(9), 544 (1994).
16. J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, Vol. 8, C. Domb and J. L. Lebowitz, Eds., Academic, London, 1983, p. 267.
17. R. C. Ball and R. L. H. Essery, *J. Phys. Condensed Matter*, **2**, 10303 (1990).
18. R. L. H. Essery and R. C. Ball, *Europhys. Lett.*, **16**(4), 379 (1991).
19. A. Ziabicki, *Fundamentals of Fibre Formation*, John Wiley & Sons, London, 1976, p. 102.
20. E. Braverman, V. V. Romanov, O. B. Lunina, T. P. Belasheva, and G. G. Finger, *Khim. Volokna*, **6**, 32 (1990).
21. D. Loubinoux and S. Chaunis, *Textile Res. J.*, **57**, 61 (1987).
22. D. Eichinger, R. Jurkovic, S. Astegger, H. Firgo, P. Hinterholzer, K. Weinzerl, and S. Zikeli, U.S. Patent 5,216,144, 1993.

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