Formation and characterization of the fibres and films from mesophase solutions of cellulose in ammonia/ammonium thiocyanate solvent*

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Fibres and films were formed from mesophase solutions of cellulose in ammonia/ammonium thiocyanate solvent. The physical properties of the fibres and films were discussed on the basis of the properties of the mesophase solutions used. Cholesteric and nematic phases were formed in the solutions. Fibres were extruded from both kinds of solution. The fibres from the nematic solutions were more highly oriented, had a more fibrillar texture and were apparently stiffer than those from the cholesteric solutions. The fibres spun from the nematic solutions using the technique of dry jet-wet spinning had moduli comparable to those of Fortisan®.

(Keywords: cellulose; mesophase solution; nematic; cholesteric; dry jet-wet spinning)

INTRODUCTION

Anisotropic spinning solutions have been recognized as being useful for forming fibres and films with high tenacity and modulus. For example, anisotropic polyamide spinning solutions such as poly(phenylene terephthalamide) have been employed for producing high tenacity aramid fibres known commercially as Kevlar® fibres.

It has been observed that cellulose and cellulose derivatives can form anisotropic solutions. Chanzy and Peguy[1], Patel and Gilbert[2] and Conio *et al.*[3] have reported that such anisotropic solutions could also be obtained from cellulose in various solvents. Gray[4] lists a number of cellulose derivatives and solvent systems which have been reported to form anisotropic cellulose derivative solutions. Anisotropic cellulose derivative solutions have also been reported to form high tenacity, high modulus cellulose fibres[5].

In accordance with previous work by Liu and Cuculo[6], cellulose in ammonia/ammonium thiocyanate (NH_3/NH_4SCN) solvent was isotropic. The isotropic solutions were wet spun to produce cellulose fibres having properties essentially equivalent to conventional rayon.

This work relates to anisotropic cellulose solutions and to fibres and films produced therefrom. Specifically, it relates to the production of anisotropic cellulose solutions in the nematic phase as the preferred precursor to high tenacity, high modulus cellulose fibres and films.

EXPERIMENTAL

Materials

Three different cellulose samples were used. Cellulose powder of DP 210 (CC 41, microgranular grade) was obtained from Whatman Chemical Ltd. Cellulose pulp sheets of DP 450 and DP 765 from Avtex fibres and ITT Rayonier, respectively, were cut into small pieces and shredded. Unless specifically stipulated otherwise, cellulose of DP 210 was used. Ammonium thiocyanate (Whitco Chemical) was dissolved in condensed anhydrous NH_3 (Air Products). Unless otherwise noted all chemicals were ACS reagent grade. The solvent compositions chosen for study were in the range of 70–80 wt% (w/w) NH_4SCN (0.33–0.47 mol fraction).

Solution preparation

A known amount of cellulose was added to NH_3/NH_4SCN solvent which had been placed in a centrifuge tube fitted with a tight cap. The mixture was evenly dispersed by use of a Vortex Genie agitator (Fisher Sci. Co.) for up to 5 min. The mixture was then placed in dry ice for 24 h followed by warming in hot water ($\sim 50°C$) to bring about flow. The solution was then observed under a polarizing microscope. When complete dissolution of the cellulose was ascertained, the samples were routinely frozen and brought to and maintained at $25.0 \pm 0.1°C$. This ensured that all samples had similar thermal histories and that a precise reference time frame was established. All solution concentrations are reported as per cent weight of cellulose per volume of NH_3/NH_4SCN (g per 100 ml solvent).

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Fibre formation

Solutions were extruded from a wet spinning apparatus (Bradford Univ. Research Ltd, equipped with six hole spinneret, hole diameter 0.23 mm) by wet or air-gap spinning with a 2.5 cm air gap. Methanol was used as the coagulant.

Film formation

A portion of 20% solution of cellulose in the solvent containing 75% NH_4SCN was poured on to a glass plate. A glass rod was carefully used to form a thin film. The thickness of the film was controlled by sticking two lengths of Scotch tape one over the other parallel to each other along the sides of the glass plate. The glass plate with the cellulose solution was then placed in a methanol coagulation bath for $\sim$15 min, followed by washing in running water for 30 min to remove all the NH_4SCN salt. Absence of the salt was verified by using i.r. and elemental analysis (nitrogen and sulphur).

The coagulated film was lifted from the glass plate and mounted on a square frame. Further treatment included air drying or drying in an oven at 70°C for 30 min or soaking in a solution of 10% glycerol in methanol or 10% glycerol in water for 24 h, followed by air drying.

Mechanical properties of fibres and films

Tenacities and initial moduli were obtained for the fibre samples using an Instron tensile tester (model TT-B). The extension rate was 2.54 cm min^{-1} and the gauge length was 2.54 cm. The tensile properties of fibres are reported as mN per tex.

Tensile properties of the films were determined with an Instron tensile tester (model 1123) by following ASTM method D882-80A.

All the measurements were made under standard conditions, 25°C and 65% relative humidity.

RESULTS AND DISCUSSION

General behaviour of solutions

Interesting observations were made by varying the ratio of NH_3/NH_4SCN in the cellulose/NH_3/NH_4SCN system at cellulose concentrations of 12, 14 and 16 g per 100 ml. Several types of pattern, indicative of cholesteric, nematic and conjugated phases, were observed in the cellulose/NH_3/NH_4SCN mesophase solutions under a polarizing microscope. With increasing NH_4SCN concentration in the solvent, the following progression of changes was noted: the pitch size, as indicated by the increased spacings of the fingerprint pattern; the fingerprint pattern transformed to a uniformly dispersed highly birefringent pattern; and finally the latter pattern was obtained indicating a change to a combination of spherulitic patterns and uniformly dispersed birefringence.

The cellulose anisotropic solutions forming the fingerprint and spherulitic patterns were characterized as containing cholesteric mesophases. First, the anisotropic solutions showed high negative specific rotations when compared with the low specific rotation of +35° for cellobiose in the solvent with a composition of 30.0/70.0. Further, a linear relationship was found between the specific rotation and the reciprocal of the square of the wavelength of the incident light. Such a relationship is interpretable by de Vries' theory[7] to show that these mesophases were cholesteric. Second, the ring diffraction pattern of an incident He–Ne laser beam also provided evidence of a cholesteric phase[8–10]. All of the anisotropic solutions which resulted in the formation of the fingerprint pattern were turbid. The turbidity increased as the negative specific rotation increased.

Nematic phase patterns, which were observed in the cellulose solutions containing $\sim$75.5% NH_4SCN, appeared immediately following dissolution and persisted throughout a 2-week period. The uniformly dispersed birefringent patterns were the most prevalent in the nematic solutions of all DPs studied. The Schlieren (*Figure 1*) and the thread-like patterns indicating nematic phases were readily observed in the cellulose solutions of DP 450. The nematic phase patterns formed at relatively low cellulose concentrations (12, 14, 16 g per 100 ml) were transformed to the conjugated phase patterns with an increase in cellulose concentration up to 18 g per 100 ml at the same solvent composition (24.5/75.5).

The turbidity of the cellulose solution increased with increasing deviation in either direction from the solvent composition 24.5/75.5 (*Figure 2*). Increasing storage time increased the turbidity of the solutions prepared

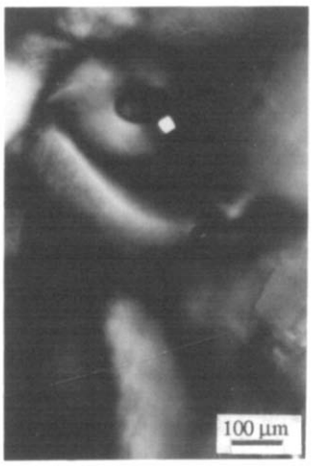

Figure 1 Schlieren texture formed in the cellulose solutions: solvent composition 24.5/75.5; cellulose concentration 14 g per 100 ml; DP 450

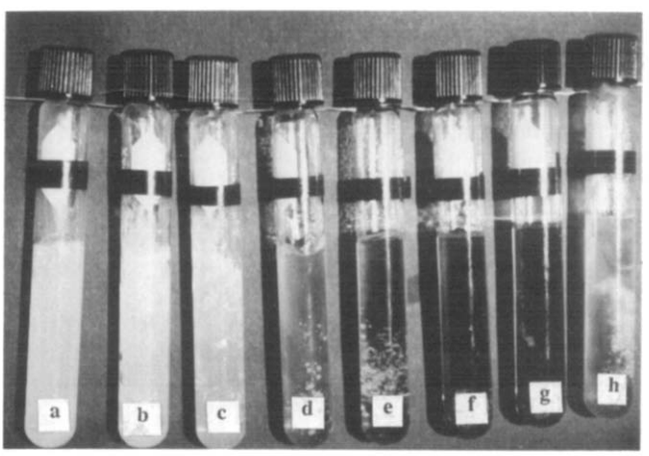

Figure 2 Turbidity dependence of cellulose solutions of solvent composition: (a) 30/70; (b) 28/72; (c) 26/74; (d) 25/75; (e) 24.5/75.5; (f) 24/76; (g) 23/77; (h) 22/78; cellulose concentration 12 g per 100 ml; DP 210

Table 1 Effects of solvent composition on fibre properties

NH_3/NH_4SCN	DP	Conc. (g per 100 ml)	tex	Tenacity (mN tex^{-1})	Modulus (mN tex^{-1})	Birefringence rank
29.3/70.7	210	16	10.9	49.4	1978	Low
25.0/75.0	210	16	12.2	86.5	3885	High

from solvent containing either more or less than 75.5% NH_4SCN. There was no noticeable change in the turbidity of the solution prepared in solvent containing ~75.5% NH_4SCN.

Properties of the fibres and films

Preliminary wet spinning experiments were performed for the purpose of comparing properties of fibres spun from cholesteric and nematic solutions. The solvent compositions chosen for preparation of the spinning dopes were 25.0/75.0 and 29.3/70.7 at which respective compositions nematic and cholesteric phases formed. A relatively low viscosity was required to sustain good spinning ability. Thus, a less viscous partly nematic solution obtained by increasing the solution temperature up to 40°C was used rather than a wholly nematic solution. The properties of fibres formed from solvent composition 25.0/75.0 were very different from those of fibre derived from solvent composition 29.3/70.0. Fibre property dependence on solvent composition is shown in *Table 1*.

These are the first fibres produced and the experimental techniques are crude. A subsequent paper will report the results of a methodical study of fibre formation from the NH_3/NH_4SCN solvent system. Nevertheless several important differences can be detected even at this stage for fibre derived from a nematic system *versus* fibre derived from a cholesteric progenitor. The tenacity and modulus of the fibre obtained from solvent composition 25.0/75.0 were twice those of the fibre from solvent composition 29.3/70.7. When compared under a polarizing microscope, the fibres prepared from the two solvent compositions showed distinct differences (*Figure 3*). The fibres from solvent composition 25.0/75.0 are more longitudinally oriented than the fibre from solvent composition 29.3/70.7, as illustrated by light extinction of the fibre from the former solvent when it is rotated by 45° in going from *Figure 3a* to *b*, and the lack of this property in the fibre from the latter solvent.

The properties of fibres produced by using the dry jet-wet spinning technique are compared in *Table 2* with those of Fortisan®. The fibre spun from the nematic phase has an initial modulus (13 160–14 750 mN tex^{-1}) very close to the lower range of Fortisan®, a regenerated cellulose fibre which is widely considered to be stiff and strong. It is recognized that tensile strength or breaking strength in the early stages of fibre development depends greatly on processing conditions and perfection of the fibre structure itself. Modulus, on the other hand, due to the small deformation, is not strongly related to perfection of the fibre structures. The moduli of crudely prepared fibres is more significant than their tenacity with respect to the ultimate achievable properties.

The cellulose films made from liquid crystalline solutions of cellulose/NH_3/NH_4SCN were transparent. They show birefringence when viewed under a polarizing

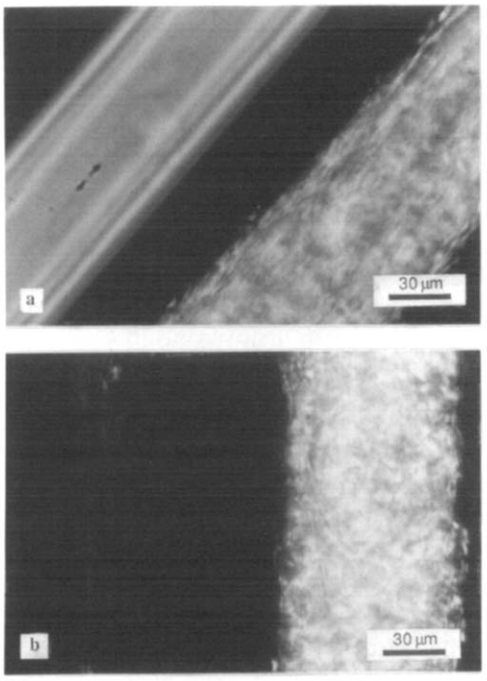

Figure 3 Polarizing micrographs comparing two fibres from two different solvent compositions: 25.0/75.0 (left); 29.3/70.7 (right); cellulose concentration 16 g per 100 ml; DP 210; (b) rotated 45° from (a)

Table 2 Comparison between cellulose fibres spun from nematic solution and Fortisan®

Characteristics	Fibre sources: NH_3/NH_4SCN (24.5/75.5)	Fortisan®[15]
DP	765	
Spinning method	d.j.-w.s.	
tex (tex f^{-1})	0.96	
Tenacity		
Dry (mN tex^{-1})	263–301	529–706
Wet (% dry)	73	75–85
Elongation		
Dry (%)	8	
Wet (%)	9	
Initial modulus (mN tex^{-1})	13 160–14 750	15 000–22 075

d.j.-w.s., Dry jet-wet spinning
[a]Taken from reference 16

microscope. Using a quartz compensator, the birefringence was estimated to be 0.003. The fracture surface of the film edge (*Figure 4*) seems to indicate that the film has a bilayer structure. The thinner upper layer of the film (6% total thickness) is the side sheared with the glass rod during the formation of the film. The molecular orientation of the upper layer seems much higher than

that of the lower layer. This might have resulted from shear-induced molecular orientation. The value of the birefringence of the films is believed to originate mainly from the thinner, oriented upper layer.

Considering the limited depth of shear effect, finding appropriate conditions (viscosity, anisotropy of the solution) for film formation will be important factors for the introduction of molecular orientation throughout the whole depth of film.

Moisture regain values of the retrieved cellulose films from NH_3/NH_4SCN are 7–8% at 25°C and 65% relative humidity (*Table 3*). Since water molecules do not penetrate the crystalline regions of cellulose, the moisture must be absorbed in the less ordered regions and on the surface of crystallites[11,12]. The moisture regain of the retrieved films is lower than that of viscose fibre and is within the same range as that of cotton. Cellophane® is normally finished with a water-proofing agent[13]. Considering these facts, the low values of moisture regain of the retrieved film also suggest a rather highly ordered structure of the cellulose films.

The ratio of absorbance at 1372 cm^{-1} (C–H bending) to the absorbance at 2900 cm^{-1} (C–H stretching) in the i.r. spectrum can be used for measuring the crystallinity in cellulose materials[14]. The average value of the i.r. crystallinity index (a_{1372}/a_{2900}) calculated from spectra as shown in *Figure 5* was found to be ~0.5 (*Table 3*), which is in the range of mercerized cotton as reported by Nelson and O'Connor[14]. *Table 3* shows that the crystalllinity index is larger than that of any other cellulose II materials. The unexpectedly low density of the retrieved film (*Table 4*) at this stage of development cannot be unequivocally explained. It could result from an inherent situation or simply from voids or bubbles captured in the cellulose film.

Table 4 compares the physical properties of films derived from cellulose/NH_3/NH_4SCN with a commercial film. These data show that the films from liquid crystalline solutions of cellulose in the NH_3/NH_4SCN solvent have similar tensile properties with Cellophane® as suggested by their close values of tensile strength and modulus. The elongation was found to be 5–8% for the cellulose films compared to 17–21% for the commercial films. The difference might be caused by the properties peculiar to cellulose films derived from the anisotropic NH_3/NH_4SCN solution and crystallinity, and by the simple addition of softeners or plasticizers in the commercial films. Experimental results have shown that the elongation of cellulosic films from NH_3/NH_4SCN can increase three times after treating with 10% glycerol solutions.

Heat treatment can have a positive effect on the tensile properties of polymeric products. More recent experiments, involving heating the films at higher temperatures in ethylene glycol, appear to be very encouraging.

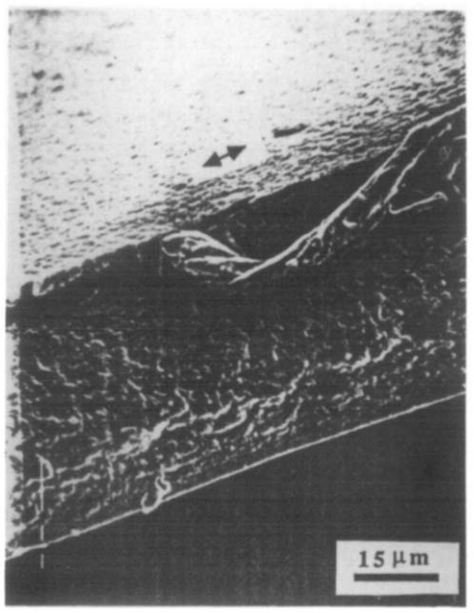

Figure 4 Fracture surface of the film edge: (↔) shear direction; solvent composition 25.0/75.0; cellulose concentration 20 g per 100 ml; DP 210

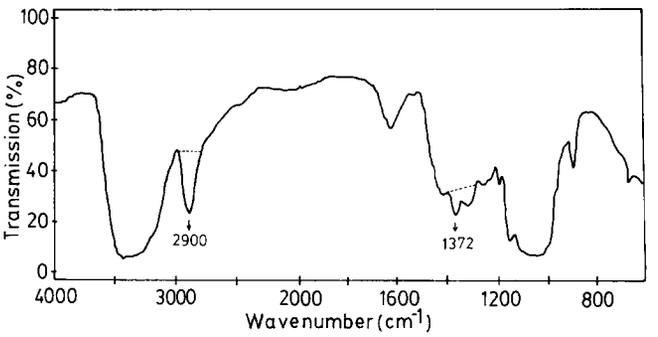

Figure 5 I.r. spectra of the cellulose film cast from a liquid crystalline solution: solvent composition 25.0/75.0; cellulose concentration 20 g per 100 ml; DP 210

Table 3 I.r. crystallinity index (a_{1372}/a_{2900}) and moisture regain measured for various types of cellulose materials

Cellulose source	I.r. crystallinity index (a_{1372}/a_{2900})	Moisture regain (%)[a]	References
Cotton	0.62	7–8	6
Mercerized cotton	0.54–0.58	–	14
Pulp	0.49	–	6
Viscose fibre	0.41	13	6
Protofibre	0.18	–	6
Cellulose/NH_3/NH_4SCN fibre (spun from isotropic solution)	0.44	–	6
Cellophane® (duPont)	0.23	7–8	
Cellulose/NH_3/NH_4SCN film (cast from liquid crystalline solution)[a]	0.50	7–8	

[a]Tested at 22°C and 65% relative humidity
[b]Solvent composition 25.0/75.0; cellulose concentration 20 g per 100 ml, DP 210

Table 4 Physical properties of cellulose films cast from solution[a]

	Films from anisotropic cellulose/NH_3/NH_4SCN				
	Parallel to the shearing direction		Normal to the shearing direction		
	Air dry	Oven dry[b]	Air dry	Oven dry[b]	Cellophane® (duPont)
Elongation (%)	7–8	7–8	5–6	5–6	17–21
Tensile strength (kN m^{-2}) × 10^{-3}	76–83	90–96	65–69	76–83	83–96
Elastic modulus (kN m^{-2}) × 10^{-5}	45–48	48–55	38–41	41–45	34–41
Tear strength (mN mm^{-1}) × 10^{-2}	19–23	19–23	19–23	19–23	19–23
Density (23°C) (g ml^{-1})			1.484		1.495

[a]Solvent composition 25.0/75.0, cellulose concentration 20 g per 100 ml, DP 210. Tested at 22°C and 65% relative humidity
[b]Dried at 70°C for 30 min

The retrieved cellulose films show unbalanced behaviour in the directions parallel and normal to the shear direction. The respective values of the ratio of the former to the latter directions for the tensile strength and modulus are both only 1.2, indicating that there is relatively little preferred orientation in the films. This low ratio may be related to including the nature of the cholesteric structure of the anisotropic solutions used and/or to the method of film formation at relatively high cellulose concentration of 20 g per 100 ml.

CONCLUSIONS

A nematic phase is formed in solution with NH_3/NH_4SCN in what are presumed to be good solvent compositions. The comparable moduli of the fibre spun from a nematic solution with those of Fortisan® may represent high uniaxial orientation of cellulose molecules in the fibre spun from the ordered structure of the nematic solutions.

Films made from mesophase solutions of cellulose without any additives, have a good appearance and strength that is competitive with Cellophane®. It is felt that their structure and, therefore, the physical properties can be further enhanced or modified by incorporating a plasticizer using a continuous casting process followed possibly by heat treatment.

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