Spinning of cellulose from *N*-methyl morpholine *N*-oxide in the presence of additives

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A series of ten additives were mixed with cellulose solutions in *N*-methyl morpholine *N*-oxide (MMNO). Each of these solutions was spun to produce cellulose fibres which were tested for their properties. Most additives had no effect but the addition of NH_4Cl led to fibres where the tensile strength and modulus had almost doubled when compared to fibres made without additive. Fibres prepared with $CaCl_2$ were also stronger, but not as much as in the case of NH_4Cl. Tentative explanations are presented to account for such improvements.

(Keywords: Cellulose spinning; high strength fibres; *N*-methyl morpholine *N*-oxide)

INTRODUCTION

At present, the viscose system is the process the most widely used to dissolve cellulose in order to spin it back in the form of rayon[1]. Viscose has now been spun for more than 90 years and when one compares its production to the spinning of synthetic polymers, one is struck by the complexity and inefficiency of the viscose process. Further, its production generates extensive pollution which needs to be confined and this is very expensive. This is why so many viscose plants are being shut off and the production of rayon is decreasing in the countries where the quality of the environment has become a critical issue.

Despite these problems and because rayon still presents many attractive properties[2], new processes for preparing rayon-like cellulose fibres are being actively researched both in industrial and academic laboratories. From these investigations, it now appears that the spinning of cellulose from organic solvents will be one of the main methods of preparing cellulose fibres which may eventually replace viscose. Several organic solvents useful for dissolving and spinning cellulose have been investigated during the last two decades[3–5]. Among them the cellulose–cyclic amine oxide system, in particular when the amine oxide is *N*-methyl morpholine *N*-oxide (MMNO), stands out as being the most promising[6–17]. In fact, such a system is now being considered seriously for commercial operation.

The dissolution and spinning of cellulose in MMNO is remarkably simple as compared to that of viscose. Solutions of underivatized cellulose, with a concentration as high as 15% (for DP 600 cellulose) are easy to produce in a matter of minutes. These solutions are then spun in air and coagulated in a water bath, using the conventional dry jet/wet spinning technique. Although produced in such a simple way, at speeds of several hundreds of metres per minute, these cellulose fibres (named Newcell by Enka and Tencel by Courtaulds) have tensile strengths comparable to those of intermediate modulus rayon[1]. In the case of rayon prepared in the classical way, obtaining such properties requires substantial amounts of additives such as $ZnSO_4$ as well as other chemicals, which must be added either to the viscose solution or to the various baths of the spinning line. In particular, the subsequent elimination of Zn is difficult and costly. In contrast, the MMNO celluloses have good mechanical properties that are readily obtained without the help of any additive and with a unique spinning bath filled only with water. In our laboratory using a crude bench top spinning device, cellulose fibres with tensile strength of 1 GPa†, Young's modulus 40 GPa, elongation at break 5% are commonly obtained at 100/200 m/min with DP 5000 cellulose; these values become 0.5, 20 and 16%, respectively, when rayon grade cellulose pulp of DP 600 is used[14,16].

Even if the spinning of cellulose from organic solvents such as MMNO, seems to lead to cellulose fibres of substantially improved mechanical properties, these are nevertheless far from the theoretical values reported in the literature for the ultimate mechanical properties of cellulose. Regarding the theoretical elastic modulus of regenerated cellulose, several authors seem to agree on the value of 90 GPa for cellulose II[18,19], *versus* values ranging from 130 to 170 GPa for cellulose I[19–21]. This is more than double that which has been reached so far in the MMNO system or in any commercial or experimental viscose. As a rule of thumb the theoretical strength of a fibre is about 1/10 of its theoretical elastic modulus[22]. This would give a value of 9 GPa for cellulose II and values in the range of 13 to 17 GPa for cellulose I. It is clear that even the best cellulose fibres do not achieve these values and large improvements can be envisaged.

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† 1 N/Tex = 1.5 GPa for cellulose of density 1.5 g cm^{-2}

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In recent patents, two experimental cellulose fibres produced by mesophase spinning of cellulose esters, followed by saponification have been disclosed: a fibre reported by Du Pont has a tensile strength and Young's modulus as high as 2.3 and 46 GPa, respectively[23], whereas a Michelin fibre is described with properties of 1.6 GPa and 59 GPa[24]. Both fibres display elongations at break of the order of 4 to 5%.

The present work[25] is part of an attempt to determine the type of modifications that can be brought to the spinning of cellulose in MMNO in order to improve the mechanical properties of the fibres spun with this type of system. Following the route of the rayon pioneers and their quest for stronger fibres, we undertook a survey of the influence of a series of additives to the MMNO system. This paper describes how the addition of specific salts to the cellulose solutions affect the solution properties in such a way that fibres of higher strength are readily produced without any other modification of the spinning system.

EXPERIMENTAL

Materials

N-methyl morpholine N-oxide (MMNO). Aqueous MMNO from Texaco was used throughout the study. It had a water content of 40%, determined by refractometry. For this, a calibration curve of the index of refraction of aqueous MMNO as a function of water content was established by titration of specific samples using the Karl Fischer technique[26].

Cellulose samples. Two cellulose samples were used in this study: a sample of dissolving pulp V60 from the Buckeye Cellulose Co (DP = 600) and a sample of Menoufi cotton (DP = 5000). Both samples were dry disintegrated with a Thomas shredder and screened through a 1 mm mesh grid. It was verified that such treatment did not diminish the DP of the celluloses that were used.

Additives. Ten additives were selected in this study: $CaCl_2$, P_2O_5, $C_6H_5B(OH)_2$, $(CH_3)_4NCl$, NH_4Cl, $ZnSO_4$, $Na_2B_4O_7(10H_2O)$, $MgSO_4$, $LaCl_3$ and LiCl.

Methods

Preparation of cellulose solutions. The preparation of the cellulose solutions was achieved as follows. To a 250 cc spherical flask containing 14 g of aqueous MMNO and 80 mg of n-propyl gallate (an anti-oxidant that stabilizes the DP of cellulose in this process[27]) were added various amounts of cellulose ranging from 170 mg to 1.7 g in the case of V60 cellulose and 80 mg to 210 mg in the case of cotton. Various amounts of additives, ranging from 0 to 1.5 g were then mixed. The flask was hooked up to a Büchi rotavapor operated at 100°C and connected to a water pump giving a vacuum of 15 mm Hg. Within 7 to 15 min of rapid rotation, a yellowish film of transparent cellulose solution was formed on the inner wall of the flask. This film was bubble free and had a thickness of between 1 and 2 mm. The flask was then brought to atmospheric pressure and immersed for 5 min inside an oil bath kept at 130°C. The solution flowed freely at the bottom of the flask. Its perfection, i.e. absence of bubbles and insoluble particles, was checked by sampling a drop of solution and positioning it on a preheated glass slide for observation with a polarizing optical microscope.

Solution spinning and fibre production. The solutions were extruded with a Melt Indexer Davenport No. 3 fitted with either a 300 or a 500 μm one hole spinnerette and operating between 50° and 110°C. Cellulose fibres were produced according to the dry jet/wet spinning technique. After leaving the orifice, the cellulose solution was deformed in a 10–15 cm air gap by applying a high take-up speed relative to the extrusion velocity. The liquid filament was coagulated in a 2 m water bath from which it emerged as a continuous cellulose fibre. Linear speed of winding, ranging from 20 to 200 m/min were commonly achieved with such a device. The fibres, still on their bobbins, were washed overnight under tap water, air dried and processed for testing. Chemical element analyses showed that they were devoid of any trace of solvent, antioxidant or additive.

Fibre testing

Mechanical properties. Tenacities, moduli and elongations at break were measured with the help of an Instron tester on an average of 20 fibres, equilibrated at 65% r.h. at 20°C. The linear densities were either deduced from measurements with a vibroscope (from Centralp Automatisme) operated under constant tension and variable frequencies or by weighing a given length of fibre.

Scanning electron microscopy (SEM). Observations were made on intact and fractured fibres. In the latter case, the fibre fragments were collected directly on the Instron tensile testing machine. They were glued with silver paint and positioned in a special fibre holder that allowed simultaneous observations of the lateral as well as the fractured surface. Both fractured and intact samples were then coated with a small amount of gold and examined with a Jeol 35CF SEM operated at 7–10 kV.

RESULTS

Selection of the best additive

The first experiments involved the preparation of a series of cellulose solutions in MMNO, each of them doped with a different additive. These solutions were spun and fibres were produced at increasing winding speeds, while maintaining constant the extrusion flow. As a rule, the fibres that were wound the fastest were the strongest. In each case the mechanical properties of the best fibres made with each additive were compared with those made without. The preliminary results, presented in *Table 1* indicate clearly that when NH_4Cl was added, one could obtain fibres with a substantial increase in mechanical properties. With $CaCl_2$, an increase was also observed but was somewhat smaller than that in the case of NH_4Cl. The fibres made with LiCl, $MgSO_4$, $(CH_3)_4NCl$, $C_6H_5B(OH)_2$ and P_2O_5 did not show significant modifications. On the other hand, the mechanical properties were reduced when the additives $LaCl_3$, $ZnSO_4$ or $Na_2B_4O_7$ were added to the solution prior to spinning. These first trials prompted us to investigate in greater detail the effect of NH_4Cl. Several further trials were also achieved with $CaCl_2$.

Table 1 Influence of various spinning additives on the mechanical properties of the cellulose fibres. Each solution contained 2% (w/w solution) of DP 5000 cellulose, 2% (w/w) additive and around 10% water

Additives	Mechanical properties (tensile strength, Young's modulus)
NH_4Cl	strongly increased
$CaCl_2$	increased
LiCl	no change
$MgSO_4$	no change
$(CH_3)_4NCl$	no change
$C_6H_5B(OH)_2$	no change
P_2O_5	no change
$LaCl_3$	decreased
$ZnSO_4$	decreased
$Na_2B_4O_7$, $10H_2O$	decreased

Table 2 Mechanical properties of cellulose fibres spun with the addition of NH_4Cl

Cellulose DP 5000[a]		Young's modulus (GPa)	Tenacity (GPa)	Elongation at break (%)
No additive		40	0.85	4
NH_4Cl	1%	39	0.6	3
	2%	37	0.7	4.5
	3.5%	55 (65[b])	1.31 (1.85[b])	4.5
	5%	53 (57[b])	1.20 (1.50[b])	5

[a] In this series of experiments, the concentration in cellulose was kept at 2% (w/w solution)

[b] These values correspond to particular tests obtained with one or two fibres

Effect of the addition of NH_4Cl and $CaCl_2$

The fibres which were spun with the addition of NH_4Cl displayed mechanical properties that were substantially improved. These properties, together with those of the fibres prepared without additive are presented in *Tables 2* and *3*. *Table 2* corresponds to trials made with DP 5000 cellulose. With these specimens, the addition of 3 to 5% NH_4Cl leads to fibres where both the tensile strength as well as the Young's modulus have increased. In particular, a solution doped with 3.5% NH_4Cl leads to fibres having a tenacity of 1.35 GPa and a Young's modulus of 55 GPa. These values present a 1.4 increase on the initial values obtained from solutions without additive. In *Table 2*, one also sees that the values of the elongation at break remain constant and seem unaffected by the addition of such salt to the cellulose solutions prior to spinning.

A small percentage of NH_4Cl is also beneficial to improve the mechanical properties of the fibres spun from DP 600 cellulose (*Table 3*). Typically, one sees that the addition of 2% NH_4Cl to a solution containing 14% cellulose will lead to fibres where the mechanical properties are nearly two times greater than those of the fibres made without additive. These fibres display a tensile strength reaching 0.9 GPa for a Young's modulus of 36 and elongation at break of 8%. Such properties are comparable to those measured on Fortisan 36, one of the strongest commercial cellulose fibres made so far and commonly used as standard of high strength/high modulus rayon.

A survey of *Table 3* indicates that the optimum fibre properties are obtained when a small amount of NH_4Cl is used. In fact, there is a marked disadvantage of adding more than 2% of this chemical because the solubility of cellulose in MMNO seems inversely related to the NH_4Cl concentration. Furthermore, the mechanical properties of the cellulose fibres have a tendency to decrease when an excess of NH_4Cl is used. In particular, the elongation at break is only of 6% (as opposed to 16% for the fibres made without additives) when 10% salt is added to the solutions. This decrease in the elongation at break is not compensated by an increase in strength and modulus which are slightly lower than those measured on the fibres made with 2% additive.

The addition of $CaCl_2$ to the cellulose solutions in MMNO will also lead to fibres that have better modulus and tensile strength than those made without additive. The results for cellulose of DP 5000 are shown in *Table 4*. One sees that it is essentially the Young's modulus which is increased, from 40 GPa for the fibres without additive to 55 when 2% $CaCl_2$ is added. The tensile strength of the fibres is slightly improved, from 0.85 to 1 GPa. This is not as much as in the case of NH_4Cl, which, in this respect, appears to be a superior additive to $CaCl_2$. As in the case of *Table 2* for DP 5000 cellulose, the elongation at break appears unaffected by the addition of $CaCl_2$.

Morphological observations

The addition of NH_4Cl to the solutions of cellulose in MMNO has a strong influence on the internal morphology of the fibres. This is revealed by studying the fracture surface of the fibres broken in the Instron tester. In *Figures 1a* and *1b* typical SEM micrographs of fractured fibres made with DP 600 cellulose are presented. *Figure 1a* corresponds to a fibre prepared without additive

Table 3 Mechanical properties of cellulose fibres spun with the addition of NH_4Cl

Cellulose DP 600	Young's modulus (GPa)	Tenacity (GPa)	Elongation at break (%)
No additive, 14% cellulose	21	0.5	16
2% NH_4Cl, 14% cellulose	36	0.9 (1.1[a])	8
4% NH_4Cl, 10% cellulose	36 (40[a])	0.8	7
10% NH_4Cl, 4% cellulose	31	0.7	6

[a] These values correspond to particular tests obtained with one or two fibres

Table 4 Mechanical properties of cellulose fibres spun with the addition of $CaCl_2$

Cellulose DP 5000[a]	Young's modulus (GPa)	Tenacity (GPa)	Elongation at break (%)
No additives	40	0.85	4
$CaCl_2$ 1%	45 (49[b])	0.85	3.5
$CaCl_2$ 2%	55 (62[b])	0.95	2.6
$CaCl_2$ 5%	45 (51[b])	1	4
$CaCl_2$ 7%	48 (58[b])	0.9	4.5

[a] In this series of experiments, the concentration in cellulose was kept at 2% (w/w solution)

[b] These values correspond to particular tests obtained on one or two fibres

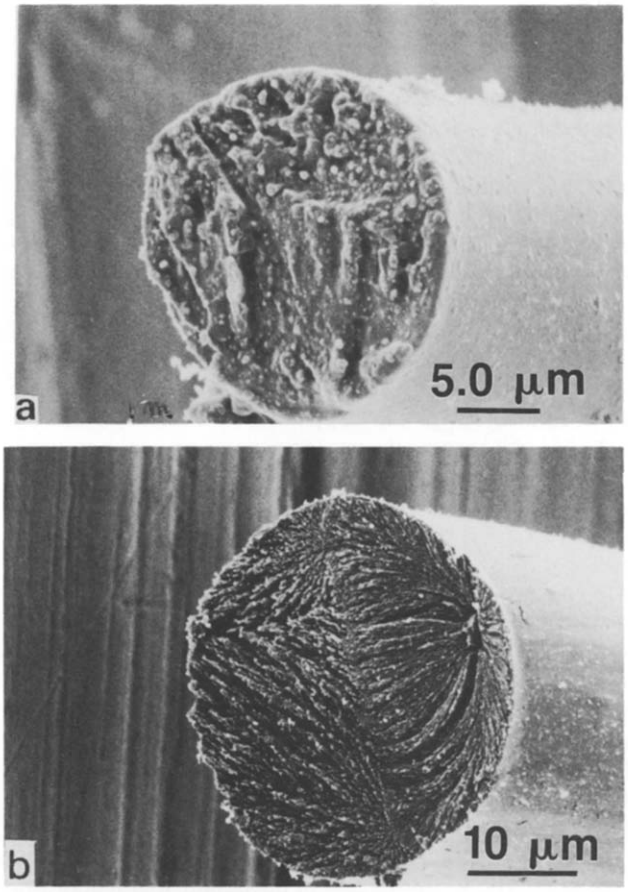

Figure 1 Scanning electron micrographs of fractured cellulose fibres spun (a) without additive and (b) with 2% NH_4Cl. In both cases, the fibres resulted from the solution of DP 600 cellulose in MMNO

whereas *Figure 1b* shows a fibre spun with 2% NH_4Cl. In both cases, the fibres have a round section, are of constant diameter and do not display any skin-core morphology. Both have a smooth external surface which does not have any noticeable features. In contrast, their inner structure is quite different. In *Figure 1a*, the inner structure of the fibre consists of a series of globular elements around 0.3 μm in diameter, embedded in a smooth and apparently structureless matrix. In *Figure 1b*, the situation is quite different because the inner structure appears entirely made of packets of microfibrils aligned parallel to the axis of the fibre. In addition, these microfibrils are organized in sectors, where they adopt an arrangement radiating from the sector centre.

For fibres spun with DP 5000 cellulose, the microfibrillar structure of the fibres made with NH_4Cl is even more pronounced. Microfibrils can be seen occasionally protruding at the fibre surface (*Figure 2*) as a consequence of a 'self-peeling' effect. This phenomenon is usually correlated with highly oriented polymer structures. In particular, it is observed with kevlar or high strength polyethylene fibres produced by the gel spinning technology. It is interesting to note that the fibres (not shown here) that were made from the same cellulose sample but without additive effect had a smooth and structureless surface devoid of any self-peeling effect. This denotes a somewhat smaller degree of orientation of the cellulose chain within the fibre and explains why the mechanical properties of the fibres made without additives are also smaller.

DISCUSSION

In the conventional MMNO process, the cellulose fibres that are produced are comparable to rayons of intermediate wet modulus[1]. As described in *Table 2*, the DP 600 cellulose fibres spun from MMNO solutions have a Young's modulus of 20 GPa, a tensile strength of 0.5 GPa, and an elongation at break of 16%. These values, which are easy to obtain, match both our previous experiments[14] and measurements from other laboratories[12,17]. The MMNO cellulose fibres are strongly oriented and for this reason, they crease and fibrillate easily[28].

This study shows how the addition of a small amount of $CaCl_2$ or NH_4Cl to the cellulose solution in MMNO is able to further improve the mechanical properties of the cellulose fibres, with the drawback of a further reduction in their lateral cohesion. As presented in *Table 2*, the spinning of a solution containing 14% cellulose and 2% of NH_4Cl leads readily to fibres having properties comparable to those of Fortisan 36, one of the best commercial cellulose fibres made so far[29]. One must stress that these properties are obtained in a simple one-step system, using a very crude bench top spinning line that does not even include a filtration device. In contrast, the Fortisan process requires the preparation of cellulose acetate, its dissolution in organic solvent, its spinning and steam stretching followed by saponification under tension. We believe that the present simple system could be quite attractive to prepare Fortisan-like cellulose fibres for which mechanical strength is of paramount importance.

Other properties, such as the lateral cohesion of the fibres, will be substantially decreased when the strength of the fibres is increased upon addition of NH_4Cl. This is well shown by comparing *Figures 1a* and *1b*, where the fibre made with NH_4Cl adopts a well defined microfibrillar inner structure which was absent in the reference sample (*Figure 1a*). Any rubbing, bending or repeated handling will lead to a severe delamination of the fibre with the release of a microfibrillar fuzz. Such behaviour rules out any clothing application but is acceptable for technical fibres, especially if the fibres are embedded in a solid matrix.

Further increase in the mechanical properties of the cellulose fibres spun from MMNO are likely to be

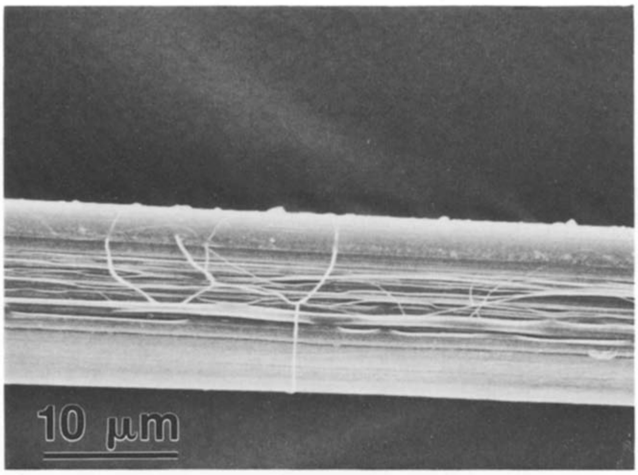

Figure 2 Scanning electron micrograph of a cellulose fibre spun with the addition of 2% NH_4Cl. The fibre resulted from the solution of DP 5000 cellulose in MMNO

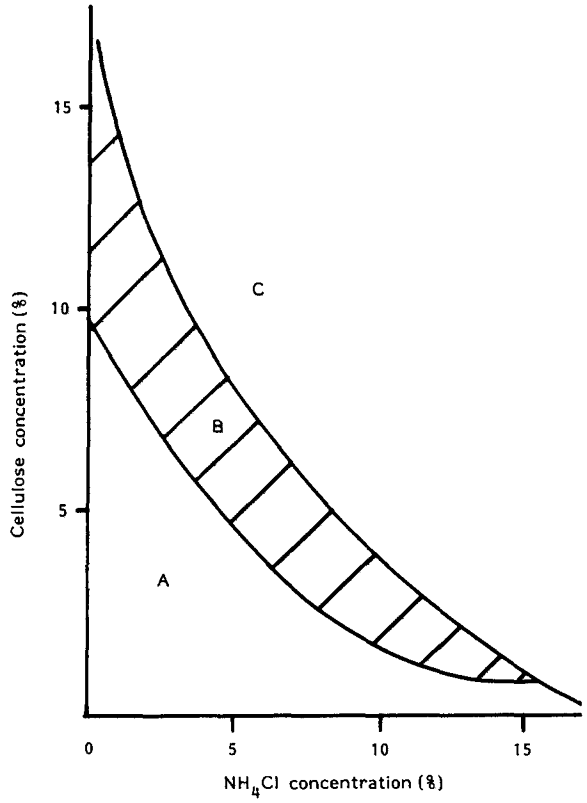

Figure 3 Spinning properties of DP 600 cellulose solutions in MMNO as a function of their concentration in cellulose and NH_4Cl. In (A) the solutions are too liquid to yield any continuous filament. In (B) the solutions can be spun and give continuous filaments. In (C) the solutions cannot be prepared because the cellulose remains insoluble

discovered because the gap is still quite large between the present measurements and the theoretical mechanical properties of cellulose II. In view of the present work and its correlation with the science of rayon, it seems clear that any gain in strength and modulus will be compensated by a decrease in elongation at break and lateral cohesion. In this respect, the results presented with DP 5000 cellulose are quite explicit. With such fibres the mechanical properties have been increased by a factor of 1.4 with respect to equivalent fibres made with DP 600. This is counterbalanced by the fact that their elongation at break is only 5%. In addition, their fibrillation is extensive because it is even apparent in as-produced fibres (*Figure 2*).

The last question which is raised concerns the role of NH_4Cl or $CaCl_2$ in improving the properties of the fibres spun from MMNO. Several explanations can be put forward to account for this occurrence, ranging from specific solvation of cellulose to sequestration of the 8 to 10% water that is always present in the MMNO process. We believe that the action of salts such as NH_4Cl or $CaCl_2$ must be sought somewhere else, namely at an increase in molecular association of the solvent molecules. Such behaviour can be deduced from *Figure 3* where the spinnability of DP 600 cellulose is studied as a function of concentration in cellulose and salt. Without salt, cellulose solutions with concentrations ranging from 12 to 16%, are relatively viscous and display a remarkable spinnability. For instance, with solutions containing 14% cellulose, fibres having several metres in length can be readily obtained by plunging a spatula in the solution and pulling it out quickly. Below 10%, the solutions are too liquid to yield any continuous filaments. When NH_4Cl or $CaCl_2$ are added, a substantial increase in viscosity is noticed and the solutions become spinnable, even at a cellulose concentration lower than 10%. In *Figure 3*, one sees that a solution containing up to 14% NH_4Cl and only 2% cellulose of DP 600 can be spun to yield a continuous fibre. This must reflect a drastic increase in molecular association, either of the solvent or of cellulose. Because NH_4Cl is not known to have any particular effect on cellulose, it is likely that it interacts essentially with the solvent. Thus the increase in viscosity must reflect a strong increase in molecular association of the MMNO molecules through NH_4Cl or $CaCl_2$.

From previous crystallographic studies achieved in one of our Institutes[30–33], it was shown that the N–O moiety of the MMNO molecule was the active part of the solvent, responsible for the solvation of cellulose. One N–O is able to hydrogen bond with the hydrogen from one or two hydroxyl groups. In particular, in the MMNO monohydrate, polymeric forms were found where the MMNO molecules were able to structure linear associations of water molecules[30]. This situation was also found with the 1,2 *trans* cyclohexane diol[32]. In that case, the polymeric association was through the oxygen of the N–O moiety linked to two OH of different diol molecules. In the MMNO process, it is believed that the associative character induced by MMNO is responsible for the viscosity properties of the solutions. When NH_4Cl or $CaCl_2$ are added, the associative character of the solvent is substantially increased. This explains the increase in viscosity of the solutions and in particular why a solution containing as little as 2% of cellulose of DP 600 can be spun to yield a continuous cellulose fibre.

One of the drawbacks of the present MMNO process is that it produces only one type of cellulose fibre, namely an intermediate modulus rayon-like fibre. In this study we have shown how a simple modification could lead to fibres that are substantially different. Other modifications giving a variety of fibres are still to be found. Their discovery depends on further fundamental investigations of the MMNO–cellulose system. In particular, the molecular description of the physico-chemical properties of the MMNO molecules and their association with other chemicals, in the presence or absence of cellulose and water needs to be better understood. Basic studies, in particular studies of crystallography on complexed crystals of MMNO and a variety of polar molecules, should give some clues to describe such association at the molecular level.

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REFERENCES

1 Turbak, A. F. in 'Encyclopedia of Polymer Science and Engineering' (Eds H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges), Wiley, New York, 1987, Vol. 14, p. 145
2 Chemical weeks, 25. 29 July 1981
3 Turbak, A. F., Hammer, R. B., Davis, R. E. and Portnoy, N. E. in 'Solvent Spun Rayons, Modified Cellulose Fibers and Derivatives' (Ed. A. F. Turbak), American Chemical Society: Washington DC (1977), ACS Symp. Ser. No. 58, p. 12
4 Hudson, S. and Cuculo, J. *J. Macromol. Sci.* 1980, **C18**, 1

5 Philipp, B., Schleicher, H. and Wagenknecht, W. *Cellulose Chem. Technol.* 1977, **11**, 702

6 Johnson, D. L. US Patent 3 447 956 (1969)

7 McCorsley, III, C. C. and Varga, J. K. US Patent 4 142 913 (1979)

8 McCorsley, III, C. C. US Patent 4 144 080 (1979)

9 Franks, N. E. and Varga, J. K. US Patent 4 145 532 (1979)

10 Franks, N. E. and Varga, J. K. US Patent 4 196 282 (1980)

11 McCorsley, III, C. C. and Varga, J. K. US Patent 4 211 574 (1980)

12 Armstrong, R., McCorsley, III, C. C. and Varga, J. K. *Proc. 5th Tappi International Dissolving Pulp Conference*, Vienna, 1980, p. 100

13 Chanzy, H., Chaunis, S., Péguy, A. and Monzie, P. *Proc. 5th Tappi International Dissolving Pulp Conference*, Vienna, 1980, p. 105

14 Chanzy, H., Nawrot, S., Pérez, S. and Smith, P. *Proc. 1983 Int. Dissolving and Specialty Pulps Conf.*, Boston, 1983, p. 127

15 Chanzy, H., Noé, P., Paillet, M. and Smith, P. *J. Appl. Polym. Sci., Appl. Polym. Symp.* 1983, **37**, 239

16 Nawrot, S. *PhD Thesis*, University of Grenoble, 1982

17 Navard, P. and Haudin, J. M. *Polym. Process Engng* 1985, **3**, 291

18 Sakurada, I., Ito, T. and Nakamae, K. *Die Makromol. Chem.* 1964, **75**, 1

19 Northolt, M. G. and de Vries, H. *Die Angew. Makromol. Chemie* 1985, **133**, 183

20 Sakurada, I. and Nukushima, Y. *J. Polym. Sci.* 1965, **57**, 65

21 Tashiro, K. and Kobayashi, M. *Polym. Bull.* 1985, **14**, 213

22 Cottrell, A. H. *Proc. Royal Soc., Ser. A* 1964, 282

23 O'Brien, J. P. US Patent 4 501 886 (1985)

24 Villaine, P. and Janin, C. US Patent 4 839 113 (1989)

25 Chanzy, H. and Paillet, M. French Patent 87 09 583 (1987)

26 Fischer, K. *Angew. Chem.* 1935, **48**, 394

27 Buijtenhuijs, F. A., Abbas, M. and Willeveen, A. J. *Das Papier* 1986, **40**, 615

28 Dubè, M. and Blackwell, R. H. *Proc. 1983 Int. Dissolving and Specialty Pulps Conf.*, Boston, 1983, p. 111

29 Mitchell, R. L. and Daul, G. C. in 'Encyclopedia of Polymer Science and Technology' (Eds H. F. Marks, N. G. Gaylord and N. M. Bikales), Interscience, New York, 1969, Vol. 11, p. 833

30 Maia, E., Péguy, A. and Pérez, S. *Acta Crys.* 1981, **B37**, 1858

31 Maia, E. and Pérez, S. *Acta Crys.* 1982, **B38**, 849

32 Chanzy, H., Maia, E. and Pérez, S. *Acta Crys.* 1982, **B38**, 852

33 Maia, E. and Pérez, S. *Nouveau J. Chimie* 1983, **7**, 89