7
Other processes

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7.1　Historical review

Ever since the discovery of the xanthate process by Cross and Bevan in 1892 and its commercialization in the early 1900s there have been many efforts to dissolve cellulose directly in non-aqueous solvents which would be both easy to use and readily recoverable. The viscose process produces good quality films and fibers. However, by the mid-1970s pollution problems and price competition from synthetic films and fibers had seriously eroded the cellophane and rayon markets. In order to remain commercially competitive it was necessary for rayon and cellophane producers to seek simpler, less polluting processes.

In the mid-1970s ITT Rayonier decided that to preserve their pulp markets it would be in their best interest to take the lead in trying to find new ways to make rayon. To their credit, Rayonier's management authorized a multimillion dollar research effort which ran for a period of 7 years at the ITT Rayonier Eastern Research Division Laboratories. The overall goals were to develop new direct cellulose solvent systems which would require lower investment costs and be readily recovered and recycled in closed loop non-polluting systems.

In order to identify potential solvent candidates that had been examined previously, an extensive literature search was made covering 80 years of cellulose solvent reports. A close examination and evaluation of these reports from a physical organic viewpoint led to a review paper which, for the first time, delineated all cellulose solvent systems into four simple categories.[1] Subsequently, several other solvent system reviews have been reported.[2,3] Rayonier reported some of their preliminary results at an American Chemical Society symposium in New Orleans in 1977.[4] As a result of Rayonier's stimulus other companies and research universities undertook cellulose solvent research projects.

Concurrently, Franks, McCorsley and Varga at the American Enka Corp were deeply involved in evaluating *N*-methyl morpholine-*N*-oxide

(NMMO).[5] The Enka NMMO technology was subsequently pursued by Courtaulds in England. Courtaulds' Tencel® NMMO solvent spun cellulose fiber technology is now a major commercial success and solvent spun cellulose films for food packaging are currently under intense investigation. Tencel® lyocell is actually not a regenerated cellulose fiber but, rather, is a *reconstituted* cellulose fiber since it was never derivatized.

7.2   Thermodynamic requirements for dissolution

No chemical reaction, including dissolution of any polymer, can proceed unless the free energy requirement for the overall solution process is negative, that is, $\Delta G_{solution}$ must have a negative value. There are several factors involved in the dissolution process and while any one of them may have a positive value, such a value must ultimately be overcome by a larger negative value of the other factors if solution is to occur, Equation [7.1]:

$$-\Delta G_{solution} = -\Delta G_{fusion} + \Delta G_{reaction/complexing} + \Delta G_{mixing} \qquad [7.1]$$

In the case of liquids the situation is simpler than it is for solids and particularly simpler than it is for polymers. Since liquids do not have sufficient molecular interaction to form solid crystals the free energy of crystallization (fusion) can be ignored and then the overall solution process can be fairly well defined by considering only the free energy of interaction (or complexing) and the free energy of mixing.

With many solids, the free energy of interaction (complexing) or wetting and swelling of the solid by the incoming liquid is sufficiently negative to weaken the crystal forces greatly and lower the free energy of fusion. The solid then dissolves if the free energy of mixing is negative. With polymers, however, the free energy of fusion is so high owing to the many points of molecular interaction along chains that the process of dissolution becomes much more difficult. This is especially true for cellulose and protein polymers which have very large positive values for ΔG_{fusion}, and do not melt.

A good example of the importance of overcoming the ΔG_{fusion} is found in the dissolution of polypropylene. There is no known solvent which will dissolve polypropylene directly at room temperature. However, once the polypropylene is heated near its melting point then many liquids that have a solubility parameter similar to polypropylene will readily dissolve the polymer. The same is true for many other thermoplastic polymers.

Therefore, in order to dissolve cellulose, the proposed solvent system must either directly or indirectly lower the large positive value of ΔG_{fusion} or raise the negative values of $\Delta G_{complexing}$ and ΔG_{mixing} to allow these other two factors to yield an overall negative result. It is obvious that $\Delta G_{complexing}$ will always have a negative value and, once complexed, will always

present a new surface for solvent interaction to improve the negative value of ΔG_{mixing}.

In trying to explain why certain solvents dissolve polymers, some authors have emphasized the requirement that the solubility parameter (δ) of the solvent must be in the same range as the solubility parameter of the polymer in question. While such statements are directionally correct, it is obvious from the above discussion that they are fundamentally incomplete. For example dimethylformamide (DMF), dimethylsulfoxide (DMSO) and several other liquids have solubility parameters that are in the range calculated for cellulose yet they do not dissolve cellulose directly. All free energy values (ΔG) are dependent upon their corresponding enthalpy (ΔH) and their entropy (ΔS). In the case of mixing this becomes, Equation [7.2]:

$$\Delta G_{mixing} = \Delta H_{mixing} - T\Delta S_{mixing} \qquad [7.2]$$

or the free energy of mixing = the heat of mixing $- T \times$ (the entropy of mixing).

Since the entropy of mixing (ΔS) will normally have a positive value it is necessary that the ΔH_{mixing} has the smallest possible value if the ΔG_{mixing} is to be negative. Hildebrand relates the solubility parameters (δ) of the solute and solvent to the heat of mixing by Equation [7.3]:

$$\Delta H_{mixing} = k(\delta_1 - \delta_2)^2 \qquad [7.3]$$

Therefore, ΔH_{mixing} will be at its lowest positive value when the solubility parameters for the solvent and the polymer are as identical as possible. This defines the extent to which the solubility parameters (δ) will contribute to the overall dissolution process.

7.3   Cellulose solvent systems

In each and every instance of dissolution of cellulose, the above described thermodynamic factors can be delineated and shown to have a significant and controlling effect on the success of the dissolution process. In each case the solvent system swells the cellulose and then modifies the molecule either by derivatizing, proton weakening or removal, or by complexing, to give a new intermediate species that can more readily react with the liquid solvent system. Thus, all cellulose solvent systems can be categorized under four mechanisms:

1   cellulose as an acid
2   cellulose as a base
3   cellulose unstable derivatives
4   cellulose stable derivatives.
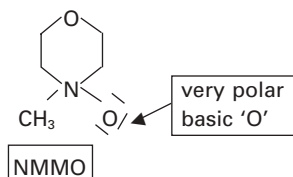
7.1 Structure of N-methyl morpholine-N-oxide.

This chapter will review selected solvent systems involving areas (1), (2), and (3). Stable derivatives (4) will not be discussed. All compounds can be considered to be acids or bases relative to some other stronger species. For example the following acid/base relationships:

(A) is an Acid	relative to	*Base (B)*
HCl, H_2SO_4		Carboxylic acids
Phosphoric		Acetic, cellulose
Phenol		NaOH, sodium carbonate
Alcohol		NaOH, sodium metal
Cellulose		NMMO, N_2N_4
$Li^{(+)}$/DMAc (dimethylacetamide)		Cellulose
Cellulose-OH		Unsolvated anhydrous Cl^-
Hydrocarbons, (isobutane)		$NaNH_2$

It may seem odd to realize that cellulose can act either as an acid or a base, yet this is exactly the case, especially in anhydrous or limited aqueous systems.

Water is an excellent swelling liquid for cellulose and opens millions of internal pores in the cellulose microfibrillar structure. However, H_2O is itself both an acid or a base depending on the other molecular species. Therefore, water normally reacts more rapidly than the cellulose with incoming molecules and this totally disrupts the effectiveness of the incoming potential dissolving moiety.

As examples of this, consider that NMMO has a very polar basic oxygen atom which will seek to abstract hydrogens (Fig. 7.1) wherever it can find them. Thus, water can be used to swell the cellulose. However, since it is a stronger acid than the cellulose (OH), the excess water must first be removed before this polar oxygen can exert its influence in abstracting or loosening the 'H' atoms from the (OH) positions on cellulose to begin the dissolution process. Similarly, the Li^+ of complexed LiCl/DMAc requires essentially anhydrous conditions before it can interact effectively as an acid toward the basic electrons on the 'O' of the (OH) on cellulose. In each case it is important to recognize that the incoming reactant has so modified the original cellulose that a negative $\Delta G_{complexing}$ has resulted and this will give the solvent a new surface species for interaction.
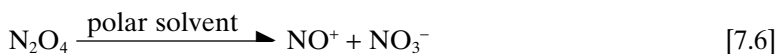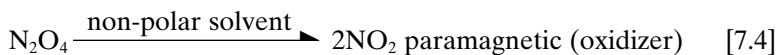
7.4   Unstable cellulose derivatives

Cellulose forms many unstable derivatives and complexes. Except for cuprammonium and xanthate very few unstable derivatives have been spun into fibers. While the literature reports include cellulose carbamates and formates as possible candidates, no fiber spinning studies have been reported from these systems. Only two extensive studies exist where good fibers were spun from solutions of cellulose nitrite in DMF and also from methylol cellulose dissolved in DMSO.
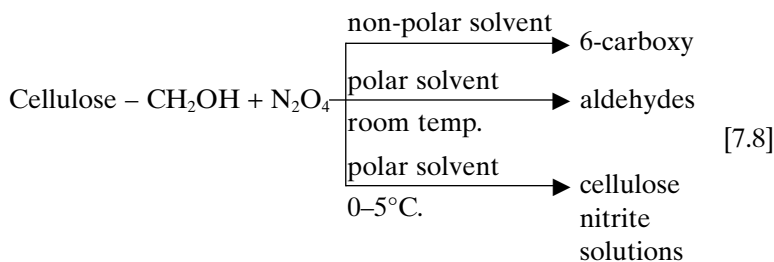
7.4.1 Cellulose nitrite

7.4.1.1   Reaction chemistry

The reaction of cellulose with nitrogen dioxide (N_2O_4) was initially studied by Kenyon, Yackel and Unruh[6,7] who found that it produced 6-carboxy cellulose in good yields. Fowler and McGee[8] then made a detailed study using 40 different solvents and found that the degree of cellulose oxidation was related to the polarity of the solvent employed – the higher the polarity, the lower the degree of oxidation. Although N_2O_4 has an O_2N-NO_2 structure it reacts homolytically or heterolytically depending on the polarity of the solvent.[9]

$$N_2O_4 \xrightarrow{\text{non-polar solvent}} 2NO_2 \text{ paramagnetic (oxidizer)} \qquad [7.4]$$

$$\text{Cellulose} – 6\text{-OH} + NO_2 \longrightarrow \text{Cellulose} – 6\text{-Carboxy} \qquad [7.5]$$

$$N_2O_4 \xrightarrow{\text{polar solvent}} NO^+ + NO_3^- \qquad [7.6]$$

$$\text{Cellulose} – OH + NO^+ \longrightarrow \text{Cellulose} – ONO + HNO_3 \qquad [7.7]$$

Equations [7.4]–[7.7] show the formation of cellulose nitrite using N_2O_4.

While good solutions of cellulose nitrite can be prepared, the temperature of the reaction is important in minimizing the amount of aldehyde that is formed. Temperatures lower than 5°C must be employed during dissolution or significant amounts of aldehyde are formed.

$$\text{Cellulose} – CH_2OH + N_2O_4 \begin{cases} \xrightarrow{\text{non-polar solvent}} \text{6-carboxy} \\ \xrightarrow[\text{room temp.}]{\text{polar solvent}} \text{aldehydes} \\ \xrightarrow[\text{0–5°C.}]{\text{polar solvent}} \text{cellulose nitrite solutions} \end{cases} \qquad [7.8]$$

Equation [7.8] shows the effect of N_2O_4 reaction conditions on cellulose reactivity.

Higher dissolving temperatures ultimately lead to fibers that have poor resistance to alkaline washing cycles. Solubility in 6.5% NaOH at 20°C ($S_{6.5}$) is an acceptable test for predicting fiber losses in alkaline wash cycles. Early attempts to find the aldehydes were not successful because the standard oxidation analytical method employed was not sufficiently sensitive. However, Hergert et al.[10] reported that when the aldehyde content was determined by the alkaline copper number method, the alkaline conditions enhanced the aldehyde sensitivity owing to the well-known alkaline peeling reaction. There is a direct correlation of $S_{6.5}$ and dissolving temperature. At 0–5°C reaction temperature only 10–15% of the fiber would dissolve in 6.5% caustic soda, while at 20°C reaction up to 80% of the fiber would subsequently dissolve in 6.5% caustic soda. Such high levels would be totally unacceptable commercially.

7.4.1.2   Fiber spinning and properties

The cellulose nitrite/DMF solutions can be readily regenerated by a wide variety of protonic liquids. In most cases the regeneration is very rapid and care must be taken to obtain some molecular alignment and stretching before the polymer is completely regenerated. Water is particularly fast, and simply exposing the nitrite solution to air will result in formation of a surface skin. To obtain good quality fibers it is necessary to have high jet stretch and high initial stretch on the first godets. Addition of bases to the alcohol regeneration bath slows the regeneration process and allows for greater stretch.

In addition to high mechanical speeds of extrusion, the nature of the protonic regenerating liquid is important. Extensive studies by Hammer and Turbak[11] demonstrated that as the molecular weight of the regenerating alcohol bath is increased, alcohol diffusion inward is decreased and the cross-sectional shape of the fiber is significantly affected. While methanol gives a round fiber, amyl alcohol and benzyl alcohol give a crenulated fiber and octanol actually gives a hollow segmented fiber. The hollow fiber results from the fact that octanol can readily form an outer skin but then cannot readily penetrate this skin to regenerate the fiber internally. Faced with this situation the lower molecular weight internal DMF diffuses towards the outer skin and the cellulose nitrite solution densifies from the inside out to give a hollow structure (Fig. 7.2).

It should be noted that this is one of the few instances, if not the only one, where a hollow fiber could be spun by controlling inside and outside diffusion without relying on the use of some type of a gaseous blowing agent.
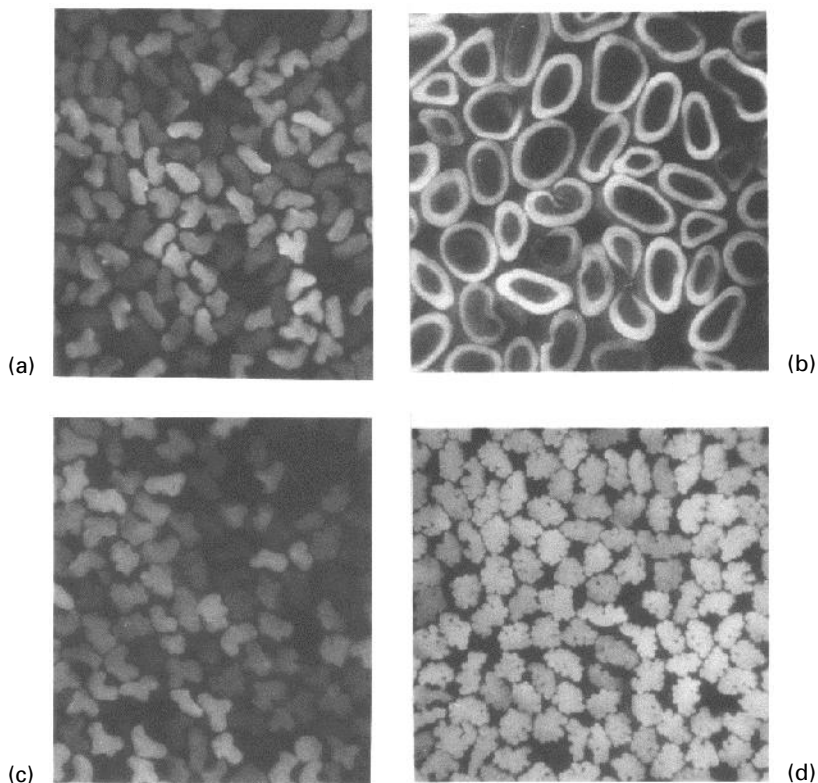
7.2 Cross-sections of N_2O_4/DMF spun fibers. (a) Precipitated in isoamyl alcohol; (b) precipitated in octanol; (c) precipitated in benzyl alcohol; (d) regular rayon.

With cellulose nitrite, as essentially with all solvent spun fibers, outer skin formation is very rapid giving rise to fibers that have intermediate wet strength properties without the need for any regeneration bath additives. The comparative fiber physical properties are given in Fig. 7.3.

7.4.1.3 Recovery and recycle

One of the most important factors in deciding the fate of all cellulose solvent systems is the ability to recover and recycle all of the reactants in good yields in closed loop systems. In the case of cellulose nitrite this is a difficult and expensive sequence. McDonald[12] has proposed spinning cellulose nitrite solutions into DMF/aqueous ammonium nitrate baths then subsequently concentrating the ammonium nitrate and converting it back to
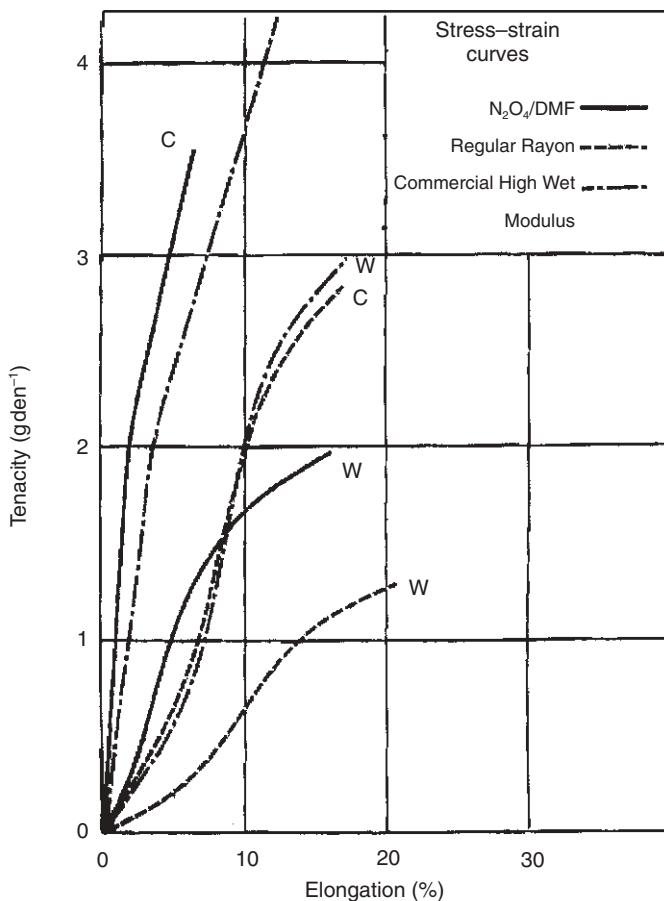
7.3 Fiber properties of N_2O_4/DMF spun fibers: Conditioned (C); Wet (W).

NO_2. However, no details are given about how such a conversion could be achieved.

Portnoy and Anderson[13] undertook a major detailed study on the recovery and recycle of NO_2 from the spinning of cellulose nitrite solution into an isopropanol regeneration bath. Their detailed scheme is given in Fig. 7.4 and demonstrates that recovery and recycle of this system would be quite complex.

7.4.2 Methylol cellulose

7.4.2.1 Reaction chemistry

The reaction of cellulose with formaldehyde to form a reasonably stable methylol derivative in the presence of DMSO was discovered and first
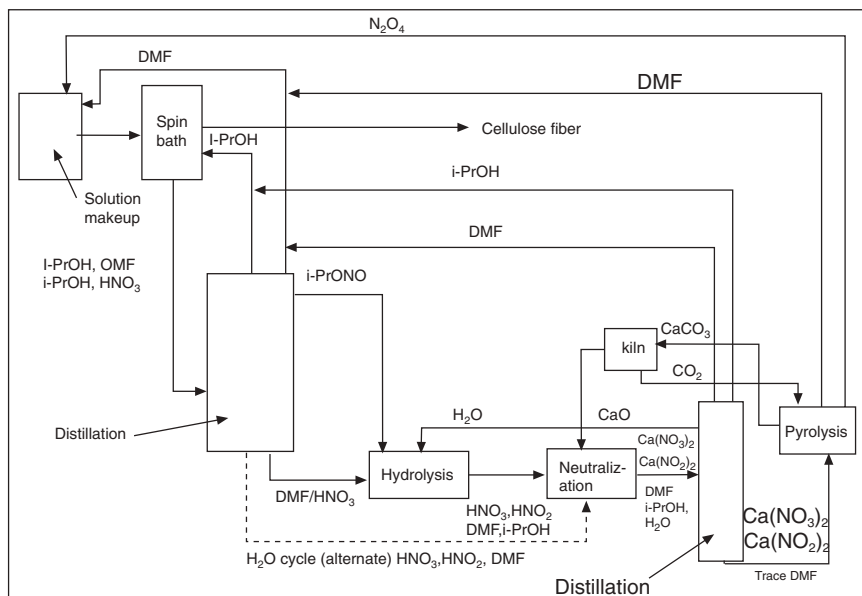
7.4 Total recovery and recycle scheme for the N_2O_4/DMF fiber system.

reported by Johnson, Nicholson and Haigh[14] at the Institute of Paper Science in 1976. This was a most interesting discovery since formaldehyde had previously been used almost exclusively to crosslink cellulose and the supposed methylol cellulose was always reported as a hypothetical non-isolatable intermediate.

Several studies have confirmed that excess formaldehyde is needed to effect the initial dissolution and that paraformaldehyde – being a polymeric form $(CH_2O)_x$ – is the best material to supply the required excess rapidly when it decomposes at higher temperatures. The paraformaldehyde (PF) is preferably used as a solid suspension. Methylation of the cellulose in the DMSO/PF solution demonstrated that the methylol formation initially occurred mostly in the C6 position of cellulose.[15–16] Figure 7.5 shows the reaction sequence for formation of methylol cellulose.

Baker, Schroeder and Johnson then reported that solvents other then DMSO could also be used in this reaction,[17,18] at low dissolving temperatures (80°C), where the amount of molar substitution (MS) could be as high as 24:1, depending on the polarity, complex-forming ability and basicity of the specific solvent. Lower polarity solvents required more formaldehde to effect solution of the cellulose.

The high MS levels dropped significantly at higher temperatures as excess formaldehde was removed. The high initial MS was probably due to the fact
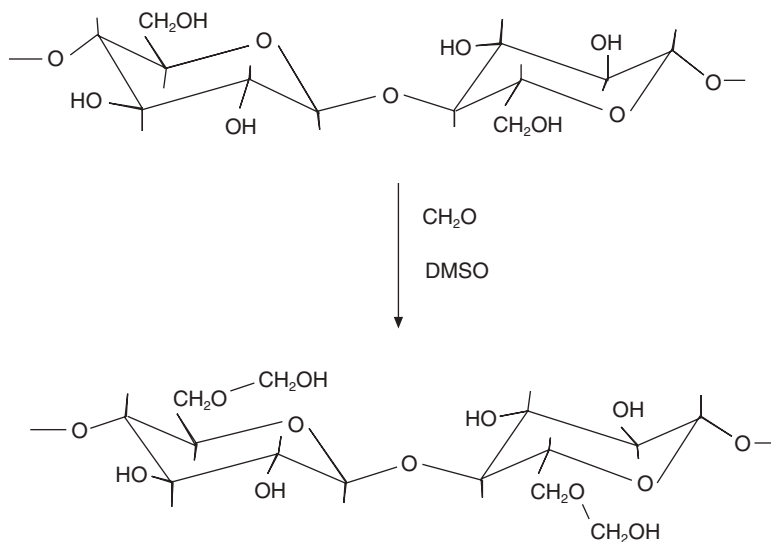
7.5 Formation of methylol cellulose in DMSO/PF.[16]
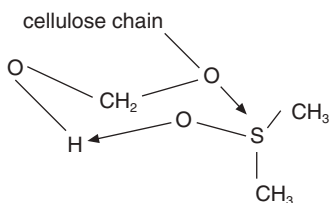
7.6 Complex formation of DMSO with methylol cellulose.[18]

that lower polarity solvents need the higher MS to act as a wedge to help keep the chains apart. Baker *et al.*[18] reported that even at high temperatures, over extended periods of time under vacuum, the DMSO to formaldehyde molar ratios in these solutions could not be lowered below a 1:1 level. This is strong evidence for the formation of a molar complex between the methylol content and the DMSO and they proposed the complex shown in Fig. 7.6.

Seymour and Johnson[19] studied this reaction and developed a chart showing the optimum conditions under which cellulose will dissolve in the DMSO/PF system and their chart is shown in Fig. 7.7.

All of these studies clearly indicate that cellulose dissolves readily in the presence of a polar solvent, that DMSO is the preferred polar solvent because it forms a strong 1:1 complex with the dissolved methylol
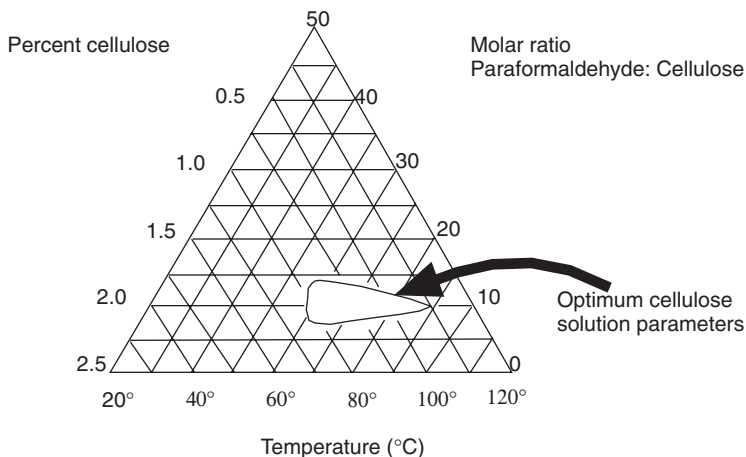
7.7 Optimum dissolving conditions for cellulose in DMSO and formaldehyde.[19]

cellulose and that excess formaldehyde is needed initially to help keep the chains apart. The formaldehyde favors formation of the 6-methylol and the large amount of formaldehyde that can be released from paraformaldehyde as it decomposes at temperatures above 120°C greatly accelerates the dissolution reaction.

7.4.2.2 *Fiber spinning and properties*

Hammer, O'Shaughnessy, Strauch, Portnoy and Turbak[20,21] made extensive spinning studies with clear particle-free polymer dopes containing from 4–15% cellulose prepared from pulps having a degree of polymerization (DP) from 1000 down to 300. Swenson[22] has reported the viscosity versus pulp DP relationships for DMSO/PF solutions. For most spinning studies 6–8% cellulose/CH_2O/DMSO solutions were prepared at 120°C using paraformaldehde. These solutions were spun and coagulated into protonic solvents such as water or methanol. Surprisingly, these fibers were coagulated but were not regenerated and could be readily redissolved in fresh DMSO at 50–70°C.

This demonstrated that the DMSO/methylol complex was much stronger than first expected and was not being broken down by simple dilution and coagulation with protonic liquids. In fact, this type of coagulation followed by redissolution in fresh DMSO could be repeated several times until the formaldehyde level of the cellulose solution fell below 1% which corresponds to the level required to maintain the stability of the methylol cellulose in the initial DMSO/PF solution.
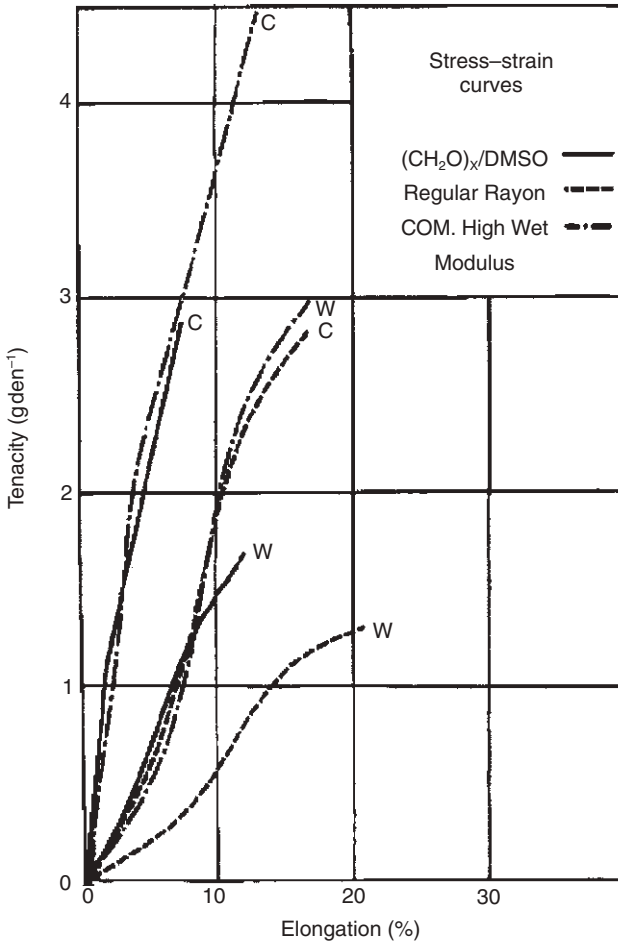
7.8 Fiber property comparisons for DMSO/PF spun fibers: Conditioned (C); Wet (W).

Figure 7.8 shows how the DMSO/PF fibers compare with known rayon fibers. One of the big advantages of the DMSO/PF fibers is their low $S_{6.5}$ levels of 3–15% which puts them in the range of high wet modulus (HWM) premium rayon fibers.

Various nitrogen compounds (urea, melamine, etc.) that are known to react with formaldehyde were added to the cellulose/DMSO/PF solutions to try to convert the excess formaldehyde into known crosslinking agents. While the expected compounds were formed, they all came out in the spinning baths and were not retained for possible further internal fiber reaction. A large range of synthetic fiber polymers which were soluble in DMSO were also added and spun into fibers but they acted mostly as fillers

in the final fibers with no apparent tendency to give improved fiber properties.

In order to achieve more rapid regeneration of the cellulose/DMSO/PF dopes, various additives which are known to react with formaldehyde were added to the regeneration bath. These included ammonia, various amines, sodium sulfide, sodium sulfite and sodium thiosulfate. These coagulation bath additives did, indeed, increase the regeneration rate and in some cases gave improved fibers. However, the problem with such additives was that they would later have to be recovered and recycled. Rodier at Rhone Poulenc[23,24] has issued several US and British patents dealing with the area of fiber spinning into various coagulation baths. Lenoni at Snia Viscosa[25] has taken advantage of the coagulated fibers and then stretched them extensively before they were regenerated, thereby improving the fiber properties.

7.4.2.3   Recovery and recycle

With the DMSO/PF solvent system, as with all solvent systems, the overall potential commercial success is fundamentally determined by how simply and completely the dissolving materials can be removed, recovered and recycled.

The complex recovery system noted for the N_2O_4/DMF system essentially eliminated it from commercial consideration.

For the DMSO/PF system the recovery of the formaldehyde in a readily reusable form is absolutely mandatory. Unfortunately, the strong complex formation of the DMSO to the formaldehyde greatly limits the ease of CH_2O recovery. Further, the formaldehyde that is recovered is not in the paraformaldehyde form, but rather in some other solid form that does not lend itself to ready use for redissolving purposes. If some way could be found to overcome this recovery and recycle problem, this system could hold significant promise in the future.

7.4.3   Cellulose/urea systems

While the solutions of cellulose heated with urea apparently form a derivative with above average stability, they are included under this heading of unstable derivatives since they ultimately can be broken and spun under viscose-like conditions.
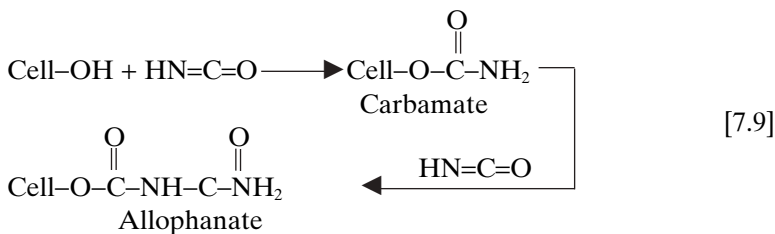
7.4.3.1   Reaction chemistry

The reaction of excess urea with cellulose preswollen in liquid ammonia was first promoted in the early and mid-1980s in Finland by Turunen *et al.*[26]
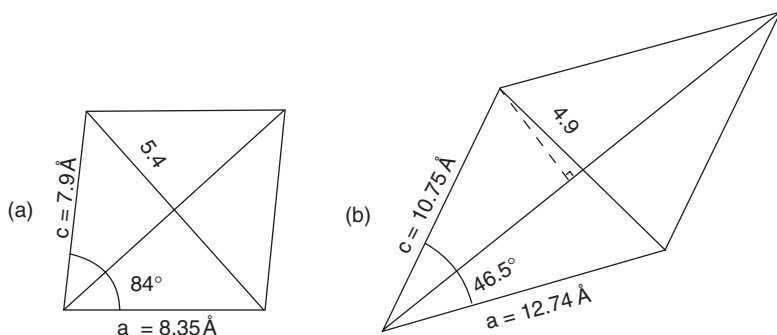
7.9 (a) Unit cell of cellulose I; (b) unit cell of ammonia–cellulose I.

and by Huttunen et al.[27] who subsequently filed a series of patents for their work. Evidently, one of the major factors in achieving a satisfactory product lies in having a high degree of swelling of the cellulose in order for the urea to obtain good and even penetration. The ability of liquid ammonia to swell the cellulose and to alter the crystal structure is vividly demonstrated in the comparison of cellulose crystal structures shown in Fig. 7.9.

The swollen cellulose is impregnated with a high concentration of urea also dissolved in liquid ammonia. Following evaporation of the liquid ammonia, the cellulose/urea material is heated to 120°C, a temperature sufficient to cause decomposition of the urea to isocyanic acid (HN=C=O) which then reacts with the cellulose (OH) supposedly to form a cellulose carbamate. The carbamate when washed free of excess urea (and by-products) and dissolved in 6% caustic soda gives a spinnable solution. Since most carbamates that have terminal NH_2 groups are quite unstable, this author questions whether the supposed carbamate is, indeed, the derivative formed. Most terminal carbamates readily undergo further reaction with more isocyanic acid to form much more stable 'allophanates'.

$$
\begin{array}{c}
\text{Cell–OH} + \text{HN=C=O} \longrightarrow \underset{\text{Carbamate}}{\text{Cell–O–}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{–NH}_2} \\[2em]
\underset{\text{Allophanate}}{\text{Cell–O–}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{–NH–}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{–NH}_2} \xleftarrow{\quad \text{HN=C=O} \quad}
\end{array}
$$

[7.9]

Equation [7.9] shows reactions of cellulose with isocyanic acid.

Since there obviously is an excess of HN=C=O available for further reaction one must wonder why such reaction would not occur in this case. Also, HN=C=O should react with liberated NH_3 and with urea.

Sol. %
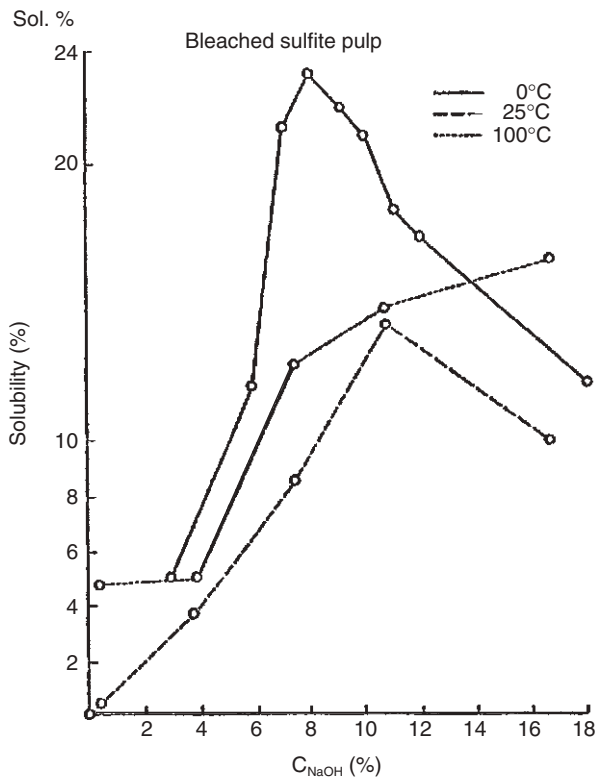
7.10 Swelling solubility of pulp versus NaOH and temperature.

The possibility of running this reaction without the need for liquid ammonia was reported by Struszczyk in Poland.[28] Mercerizing strength caustic (18%) was used to swell the cellulose in the presence of excess urea. The excess caustic was removed and the dry urea saturated cellulose was heated to generate the desired HN=C=O. The derivative was then dissolved in more dilute caustic soda and spun into an acid coagulation/regeneration bath similar to viscose.

Bridgeford and Rahman[29,30] realized that 18% caustic soda was not necessary to obtain good swelling of cellulose and filed several patents showing how much lower levels of caustic soda could be used if the temperature of swelling was kept cold. The use of cold temperatures to achieve maximum swelling is well known in the pulping industry and has been used extensively to remove low ends of cellulose along with hemicelluloses in the S_{10}–S_{18} tests and to prevent mercerization during pulping operations. Figures 7.10 and 7.11 demonstrate the theoretical soundness of the Bridgeford/Rahman approach.
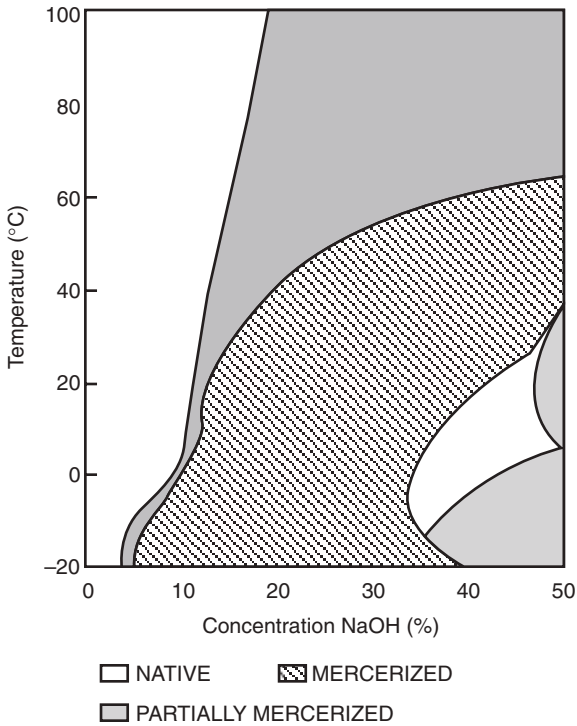
7.11 Caustic temperature and concentration to achieve mercerization.

7.4.3.2   *Fiber properties and recovery and recycle*

For the cellulose/urea system very little has been published regarding the quality of the fibers that might be expected and even less regarding the possible economics of recovery and recycle for the reagents. Struszczyk[28] has reported spinning 1.6 dtex fibers having strengths of 15–22 cN tex^{-1}, with 12% elongation. No overall recovery scheme has been made available but removal and handling and recovery of liquid ammonia would involve significant investment costs. The recovery and separation of purified urea and by-products along with the standard recovery of acid and salts for the alkali swelling method would also be of some consequence. Obviously much more needs to be done in the recovery/recycle area if this approach is to become competitive.

7.5   Cellulose as an acid or a base

7.5.1   Lithium chloride/dimethyl acetamide

7.5.1.1   Reaction chemistry

In this system the complexed positive Li⁺ ion exerts a strong interaction with the (O) electrons of the cellulose (OH) while simultaneously releasing a strongly negative Cl⁻ ion to pull the (H) atom away from the (OH) on cellulose. While Cl⁻ ions are not normally considered to be strong bases, in anhydrous media they have sufficient electron density to exhibit strong base behavior. This is supported by the fact that the much larger bromide ion in lithium bromide does not dissolve cellulose under these identical conditions, nor do other lithium salts.

Lithium, being a small atom, has a very high positive charge density. In aqueous electrolyis measurements this small lithium ion moves much more slowly than the much larger sodium ion. This has been shown to be due to the six associated water molecules that Li⁺ carries with it while sodium carries none. The LiCl/DMAc system has received considerable research attention.

LiCl/DMAc was first used as a polymer solvent system by DuPont for dissolving and spinning synthetic fibers. Later, Austin at the University of Delaware[31] used this solvent system to dissolve chitin. Subsequently, McCormick[32] reported the use of low levels of cellulose (less than 3%) to run various derivative reactions on cellulose in Li/DMAc. However, it was not until the research team at Rayonier[33] discovered how to get higher amounts of cellulose into solution that this solvent system could possibly be considered for commercialization. This group also demonstrated that *N*-methylpyrrolidone could also be used in place of the DMAc.

The Rayonier group found that activating the cellulose was a critical step prior to dissolution. If the cellulose was not preactivated, then temperatures of 150°C were required, at which temperature the solutions become brownish in color indicating significant decomposition. The best and simplest way to improve the dissolution process was to preswell the cellulose with water (or steam) and then maintain the swollen state by exchanging the water down to less than 2% with DMAc prior to adding the LiCl/DMAc mixture.

Liquid ammonia preswelling could also be used. If the water level was too high the cellulose did not dissolve because the LiCl would be interacting with the excess water. In this way clear solutions containing up to 16% cellulose/12% LiCl/72% DMAc at DP 400–600 could be readily obtained within 4–6 hours at temperatures of 85°C. At DP levels of 800–1700 up to 4% cellulose could be dissolved with less than 30 DP unit losses. Ekmanis[34] at Waters Labs used the LiCl/DMAc solvent system to develop a totally
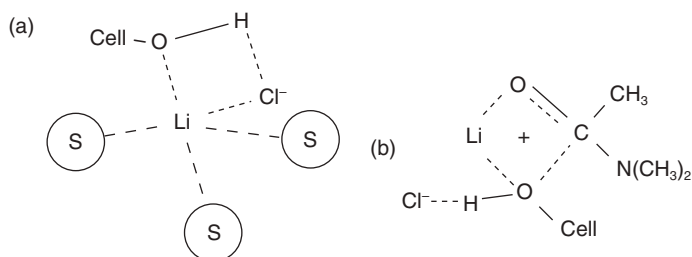
7.12 Proposed LiCl/DMAc/cellulose complex, (a) by Morgenstern and (b) by El-Kafrawy.

new simple and rapid GPC technique for determining molecular weight distributions of cellulose. This method has been adopted by many industrial laboratories.

The exact nature of the dissolving species has been investigated. El-Kafrawy[35] reported a ^{13}C-NMR study which demonstrated that the LiCl/DMAc did not form a derivative, meaning it was a complex with the cellulose. Morgenstern and Werner-Kammer[36] have also studied the nature of the complex formation and dissolution mechanism using ^{7}Li-NMR. Both studies agree that a complex is formed between the lithium ion and the DMAc. They differ, however, about what happens to this complex in the presence of cellulose. The two model proposals are given in Fig. 7.12.

Morgenstern reports that a large ^{7}Li-NMR shift occurs when the LiCl/DMAc complex first encounters cellulose suggesting that the cellulose (OH) is replacing the DMAc. Yet, one must wonder if this observed shift isn't exactly what might be expected when the Li$^+$/DMAc complex moiety starts to share its charge with the cellulose (OH) without break-up of the Li$^+$ complex structure. Further, if close continued DMAc complex interaction was not crucial at this contact stage, then many other solvents should be just as effective as DMAc once their Li$^+$/solvent complex met the cellulose (OH). This is simply not the case. Regardless of which concept of interaction is more nearly correct, the Li/DMAc system is capable of producing excellent quality fibers.

7.5.1.2   Fiber spinning/properties

Extensive spinning studies were made with the Li/DMAc system dopes by Hammer, Snyder, Kafrawy and associates.[37] They spun fibers by all three fiber spinning methods, that is, (a) wet spinning, (b) dry spinning and (c) dry jet-wet spinning (or air gap spinning). The effects of jet stretch, godet stretch, temperature, residence time, dope concentration and regeneration bath variations were evaluated for each spinning system. In general
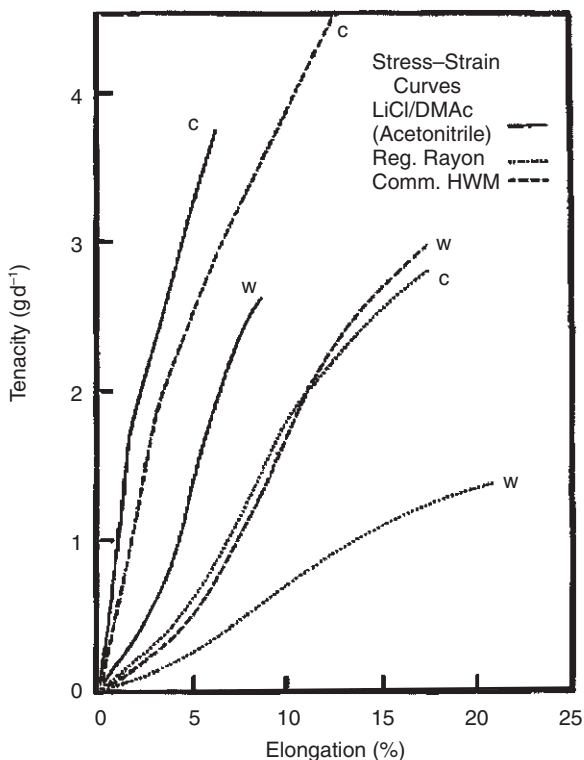
7.13 Stress-strain curves for LiCl/DMAc fibers and rayon fibers: Conditioned (C); Wet (W).

6–10% cellulose dopes gave good spinning performance. With polar regeneration baths good quality intermediate wet strength fibers could be spun at over $200\,m\,min^{-1}$. Physical properties of fibers spun into an acetonitrile bath are shown in Fig. 7.13.

Fibers spun into organic liquids like methanol, acetone or acetonitrile had round shapes. Fibers spun into saturated aqueous salt baths containing NaCl or LiCl had a 'peanut' shape or a 'C' shape. Fibers spun into organic polar liquids typically had slightly higher conditioned tenacities and about equivalent conditioned elongations.

7.5.1.3   Recovery and recycle

In this case, as is the case with all solvent spun rayon systems, the ease of complete recovery and recycle of reactants and solvents is the controlling factor for possible commercial success. The N_2O_4 recovery was very complex. The $CH_2O/DMSO$ system presented significant problems in the recovery of re-usable paraformaldehyde owing to possible strong com-
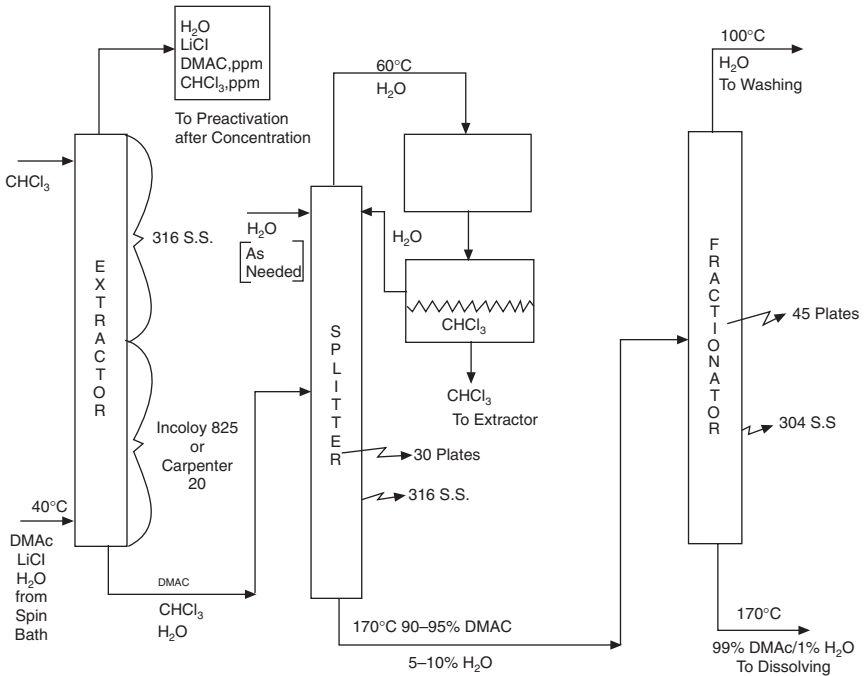
7.14 LiCl/DMAc recovery/recycle process for spinning cellulose into concentrated aqueous LiCl coagulation bath.

plexing with the DMSO. The LiCl/DMAc system is much more friendly. The recovery and recycle of DMAc has been quite thoroughly worked out by the DuPont company and they were more than willing to help anyone interested in using their DMAc as a potential solvent.

Figure 7.14 is a diagram of the overall recovery process for spinning 12% cellulose dopes into an aqueous saturated LiCl bath followed by extraction of the DMAc with $CHCl_3$, fractionating, recovery and recycle of all starting materials. This system produced very good quality fibers. A detailed analysis was made of the overall costs of such a system with the following achievable process parameters:

1   £100 million/year greenfield plant
2   99.50% DMAc recovery/recycle
3   99.85% LiCl recovery/recycle
4   99.90% $CHCl_3$ recovery/recycle.

For the above parameters, the overall manufacturing costs would be 11% lower than the viscose rayon process and would be non-polluting. This system appears to have possible commercial potential.

Films were also cast from these regeneration baths. Films from LiCl/DMAc had significantly better tenacity, elongation and tear strength than cellophane. For example, the LiCl/DMAc films cast into methanol had 34% higher conditioned tenacity, 62% higher conditioned elongation and 162% higher tear strength compared to cellophane. When properly cast and coagulated these films had a dense dye resistant skin indicating that such films may have potential as membranes for various uses.

7.5.2 Cellulose/hydrazine system

7.5.2.1 *Reaction chemistry*

Hydrazine is a rather unstable chemical and has been used as a rocket fuel. Therefore, extreme caution is necessary when running reactions with a carbon source like cellulose. Hydrazine has a boiling point of 113.5°C, a flash point of 52°C, an auto ignition temperature of 270°C in air and glass; 156°C in air and stainless steel and 23°C in air and rust. A special composition of stainless steel must be used to prevent explosion at higher temperatures. The vapors are very toxic at 1 ppm with continued exposure. Hydrazine has a strong irritating ammonia-like odor. Hydrazine is a strong enough base to dissolve cellulose at higher temperatures. Such solutions suffer significant DP loss.

Dissolution of cellulose in hot hydrazine has been reported by Litt and Kumas[38] and studies on the morphology of cellulose regenerated from hydrazine solutions have been reported by Kolpak, Blackwell and Litt.[39] Owing to the overall danger of try to spin such solution, no fiber data is available.

7.5.3 Cellulose/phosphoric acid

Cellulose readily dissolves in 85% phosphoric acid at room temperature with little loss of DP. At this high acid concentration the (OH) of cellulose is protonated and dissolution results. These clear dopes are readily prepared and they could form the basis of a potential commercial spinning system if some way could be found to recover the phosphoric acid easily without neutralizing the H_3PO_4,. In this respect, water is a sufficiently strong base to make distillation of the water to reconcentrate the H_3PO_4 too expensive. A previously reported approach tried by this writer was to coagulate a 6% cellulose solution in H_3PO_4 into a weaker base such as strong acetic acid. This worked fairly well and acetic acid recovery was reasonably effective, but the coagulation rate was quite slow. Finding the proper volatile weak acid might well develop into a novel system. Simple systems such as this are worth more investigation.

[Editors note: Patents[40,41] published in February 1996 describe anisotropic cellulose solutions at concentrations up to 40% in a 'solvent containing from 72 to 79 wt% of phosphorous pentoxide'. Claiming a highly economical route for the production of tyre yarns, the process described therein appears to be simple and elegant.

A twin-screw extruder is fed with dry fluff-pulp and the phosphoric acid solvent. The first cooled zone mixes the cellulose into the solvent and reduces the particle size, the second hotter zone starts the dissolution and the third zone provides further blending and dissolution time, its temperature being controlled to achieve the desired reduction in cellulose DP. A final low-pressure zone allows deaeration and dewatering (or the injection of additives) as necessary, and filters remove particles before spinning.

While 'all available types of cellulose' can be used, dissolving pulps are preferred for best spinning and fibre properties. The solvent preparation involves mixing orthophosphoric acid with polyphosphoric acid, in 80/20 ratio at around 50°C and then cooling and storing for several hours to arrive at the desired concentration of anhydride.

After less than 15 min in the extruder, the cellulose solution, typically containing 20% cellulose, is spun like lyocell, through a similar-sized air gap, but into cold acetone, followed by water washing, sodium carbonate or soda neutralization, and a final water washing. Tyre yarn with a breaking tenacity of 76 cN tex^{-1}, an elongation at break of 6.5%, capable of sustaining a load of 20 N tex^{-1} without extending by more than 2%, was obtained at 120 m min^{-1} spinning speed.

A similar process[41] from Michelin Research appeared in March 1996.

Further work at Akzo-Nobel[42] showed that if extra water is injected with the solvent, or added to the anisotropic solutions described above, isotropic solutions of cellulose could be obtained at concentrations of 7–20%. A 7.6% cellulose solution could be spun to give fibres with tenacities of 18–38 cN tex^{-1} (extension at break declining from 17.4% to 8.4%) as draw ratios were increased from 60–150%.

One of the key requirements for making high quality high modulus fibres using the phosphoric acid approach is to keep the level of phosphorous bound to cellulose at a minimum. Allowing it to rise from the <0.5% level preferred in the above process to more than 3% by increasing the phosphorous pentoxide level in the solvent, or by increasing the storage temperature of the solvent prior to introduction of the cellulose, resulted in weaker, hard-to-handle gel fibres with very high absorbency. Akzo-Nobel therefore postulated the production of superabsorbent fibres using a variation of the phosphoric acid route.[43] While the resulting patent covers conventional fibre production, perhaps in recognition of the difficulties of cleaning up such fibres, it also covers the production of fibrids by extrusion into a high shear mixer to obtain a fibrous slurry. Water absorbencies of up to 100 g g^{-1} are

claimed if the fibres that contain more than 6% bound phosphorous are crosslinked with ethylene glycol diglycidyl ether in a 70/30 ethanol/water mixture.

Centrifugal spinning of phosphoric acid solutions of cellulose was also explored,[44] and found capable of producing mixtures of filaments with linear densities ranging from 1 to 23, and tenacities of 4–90 cN tex^{-1} and extensions at break up from 1–15%.

In an attempt to remove the problems associated with the acetone coagulation bath, fibres were air-gap spun into aqueous salt solutions, for example up to 25% of diammonium hydrogen phosphate or potassium phosphate or 5% zinc sulphate.[45] This patent also makes it clear that the corrosive nature of the solution is an issue in spinneret design.

None of the above patents address the crucial solvent recovery issues, and at the time of writing, work at Akzo-Nobel (now Acordis) appears to have ceased. We can only conclude that once again the process economics, especially those related to solvent recovery, have compared unfavourably with the lyocell approach.

Boerstoel's work on fibres from liquid crystalline solutions of cellulose in phosphoric acid is also referred to below in Chapter 8.]

References

1 A F Turbak, R B Hammer, R E Davies and H L Hergert, 'Cellulose solvents', *Chemtech*, Jan 1980 **10** 51–57.

2 S M Hudson and J A Cuculo, 'The solubility of unmodified cellulose: a critique of the literature', *J Macromol Sci*, 1980 **18**(1) 1–82.

3 D C Johnson, *Solvents for Cellulose, Cellulose Chemistry and its Applications*, Ellis Horwood, Chichester, 1985.

4 A F Turbak, *Solvent Spun Rayon, Modified Fibers and Derivatives*, ACS Symposium Number 58, American Chemical Society, Washington, D.C., 1977.

5 N E Franks, C C McCorsley and J K Varga, 'Process for making a precursor for a solution of cellulose', US Patent 4142913 March, 1979; 'Process for making a shaped cellulose and shaped cellulose products', US Patent 4196282 April, 1980.

6 C C Unruh and W Kenyon, 'Investigation of the properties of cellulose oxidised by nitrogen dioxide', *J Am Chem Soc*, 1942 **64** 127.

7 W Kenyon and E Yackel, 'Reactions of cellulose with nitrogen dioxide', US Patent 2448892, 1945.

8 W Fowler, P McGee, C C Unruh and W Kenyon, 'Solubility of cellulose in mixtures of nitrogen tetroxide with organic compounds', *J Am Chem Soc*, 1947 **69** 1636.

9 P Gray and A D Yoffe, *The Reactivity and Structure of Nitrogen Dioxide*, Chemical Reviews, American Chemical Society, 1955 1069–1154.

10 H L Hergert, R B Hammer and A F Turbak, 'New methods for preparing rayon', *Tappi J*, 1978 **61**(2) 63–67.

11 R B Hammer and A F Turbak, *Production of Rayon from Solutions of N_2O_4 and DMF*, ACS Symposium Series Number 58, 1977, 40–51 and 71–80.

12 D M MacDonald, *Unconventional Cellulose Solutions*, ACS Symposium Series Number 58, 1977 25–39.

13 N A Portnoy and D P Anderson, *Chemistry of the Cellulose N_2O_4–DMF Solution, Recovery and Recycle of Raw Materials*, ACS Symposium Number 58, 1977 52–70.

14 D C Johnson, M D Nicholson and F C Haigh, *Dimethyl Sulfoxide/Paraformaldehyde: A Non Degrading Solvent for Cellulose*, Applied Polymer Symposium No 28, J Wiley and Sons, NY, 1976 911–943.

15 D C Johnson and M D Nicholson, *Solvent System for Cellulose*, US Patent 4 097 666 June 1978.

16 M D Nicholson and D C Johnson, 'Carboxymethylation and methylation of cellulose in DMSO/PF solvent system', *Cell Chem Tech*, 1977 **11** 349–359.

17 T J Baker, L R Schroeder and D C Johnson, 'Dissolution of cellulose in polar aprotic solvent via formation of methylol cellulose', *Carbohydrate Res*, 1978 **67** C4–C7.

18 T J Baker, L R Schroeder and D C Johnson, 'Formation of methylol cellulose and its dissolution in polar aprotic solvents', *Cellulose Chem Technol*, 1981 **15** 311–320.

19 R B Seymour and E L Johnson, 'The effect of solution variables on the solution of cellulose in dimethyl sulfoxide', *J Appl Polym Sci*, 1976 **20** 3425–3429.

20 R B Hammer, M E O'Shaughnessy, E R Strauch and A F Turbak, 'Process and fiber spinning studies for the cellulose/paraformaldehyde/dimethyl sulfoxide system', *J Appl Polym Sci*, 1979 **23** 3485–3494.

21 R B Hammer, A F Turbak and N A Portnoy, 'Solvent spun rayon, modified cellulose fibers and derivatives', *Production of Rayon Fibers from Solutions of Cellulose in $(CH_2O)_x$ – DMSO*, ACS Symposium Series Number 58, American Chemical Society, 1977, pp 71–80.

22 H A Swenson, *Solution Properties of Methylol Cellulose in Dimethyl Sulfoxide*, Applied Polymer Symposium Number 28, John Wiley & Sons, 1976, 945–952.

23 H Rodier, *Cellulose Fiber Process*, US Patent Nos. 4 145 391, 1979; 4 129 640, 1978; 4 173 613, 1979.

24 J Menault and H Rodier, *Spinnable Cellulose Solution and Process for Making Same*, US Patent 4 129 451, 1978.

25 R Lenoni, G Angelinin and A Baldini, *Regenerated Cellulose Filaments and Films*, British Patent 2 026 934, Feb 1980.

26 O Turunen, L Mandel, V Eklund, K Ekman and J Huttunen, 'Process for producing soluble cellulose derivatives', US Patent No 4 486 585, 1984; 'Procedure for treating cellulose derivative fibers', US Patent 4 583 984, 1986; O Turunen, J Huttunen, J F Selin, J Fors and V Eklund, 'Cyclic process for producing an alkali solution of cellulose carbamate and precipitating the carbamate', US Patent 4 639 515, 1987.

27 J Huttunen, O Turunen, L Mandel, V Eklund and K Ekman, 'Method for producing alkali-soluble cellulose derivative', US Patent 4 404 369, 1983.

28 H Struszczyk, *Cellulose Carbamate and its Utilization*, ACS Meeting, New Orleans, 1990.

29 D J Bridgeford and M Rahman, 'Cellulose aminomethanate sausage casings', US Patent 5 295 514, 1994.

30 M Rahman and D J Bridgeford, 'Preparation of cellulose aminomethanate', US Patent 5 229 506, 1993.

31 P R Austin and C J Brine, 'Chitin films and fibers', US Patent 4 029 727, June 14, 1977; 'Solvent for purification of chitin', US Patent 4 062 921, Dec 13, 1977.

32 C L McCormick, 'Novel cellulose solutions', US Patent 4 278 790, July 14, 1981.

33 A F Turbak, A Kafrawy, F Snyder and A B Auerbach, 'Solvent system for cellulose', US Patent 4 302 252, Nov 22, 1981; 'Process for forming shaped cellulose product', US Patent 4 352 770, Nov 24, 1981.

34 J Ekmanis, *GPC Analysis of Cellulose*, Pittsburgh Analytical Conference, Atlantic City, 1986, paper number 251.

35 A El-Kafrawy, 'NMR studies of the cellulose/LiCl/DMAc system', *J Appl Polym Sci*, 1982 **27** 2435.

36 B Morgenstern and H Werner-Kammer, 'Solvation in cellulose-LiCl-DMAc solutions', *Trends Polym Sci*, 1996 **4**(3) 87–92.

37 A F Turbak, *Newer Cellulose Solvent Systems, Wood and Agricultural Residues*, Academic Press, 1983, pp 87–99.

38 M H Litt and N G Kumar, *Cellulose Solutions and Products Prepared Therefrom*, US Patent 40 280 132, June 1977.

39 F J Kolpak, J Blackwell and M H Litt, 'Morphology of cellulose regenerated from hydrazine solution', *Polym Let Edition*, 1977 **15** 655–658.

40 H Boerstoel, B M Koenders and J B Westerlink, WO9606208 to Akzo-Nobel, 29 Feb, 1996.

41 R Huston *et al.*, WO9609356 to Michelin, 28 March, 1996.

42 J B Westerlink, H Maatman and H Boerstoel, WO9728298, to Akzo-Nobel, 7 Aug, 1997.

43 J B Westerlink, H Maatman and H Boerstoel, WO9730090, to Akzo-Nobel, 21 Aug, 1997.

44 S J Rusticus and E Van Andel, WO9730196, to Akzo-Nobel, 21 Aug, 1997.

45 M Ypma, H Boerstoel and H Maatman, WO9830741 to Akzo-Nobel, 16 July, 1998.