

# Process and Fiber Spinning Studies for the Cellulose/ Paraformaldehyde/Dimethyl Sulfoxide System

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## Synopsis

A cellulose pulp of about 550 D.P. was readily dissolved in a combination of  $(\text{CH}_2\text{O})_x/\text{DMSO}$  to afford an initial 6/6/88 cellulose/ $(\text{CH}_2\text{O})_x/\text{DMSO}$  composition solution. The concentration of formaldehyde was found to be a function of solution heating time and temperature. The solutions were microscopically free of gels and undissolved cellulose fibers. Cellulosic articles such as fibers and films are easily regenerated from these cellulose solutions in the presence of coagulants such as methanol or water. Fibers with high wet modulus, intermediate tenacity, and low elongations were produced from these regeneration systems. Fibers have been spun with conditioned and wet tenacities as high as 2.9 and 2.1 g/d, respectively, with wet modulus (at 5% elongation) as high as 1.3 g/d and solubility in 6.5% NaOH in the low range of 3.0%–15%. In many respects, these fibers are comparable to those produced in the viscose process. However, the low elongations of these fibers probably would not permit normal textile processing. The cellulose/ $(\text{CH}_2\text{O})_x/\text{DMSO}$  solutions were modified with compounds containing reactive N—H functional groups which are known to react with excess formaldehyde to yield the corresponding N-methylol derivatives. However, the resulting fiber physical properties were not significantly improved compared to those obtained from unmodified cellulose solutions. Addition of acrylic acid derivatives such as methyl acrylate, butyl methacrylate, or acrylonitrile to the cellulose solutions did not result in the formation of the expected 1,4-type adducts.

## INTRODUCTION

Today, rayon is almost universally produced by the conventional viscose process. However, in the United States this process is currently faced with several significant problems. The high investment costs and potential mill effluent pollution problems associated with viscose rayon plants indicate that this process is becoming increasingly less competitive from both an economic and environmental standpoint. Other commercial processes for producing regenerated cellulosic products include the rather hazardous cellulose nitrate process and the cuprammonium hydroxide system. This latter process is currently being reevaluated in light of the problems associated with the viscose process.

A number of alternative processes for dissolving cellulose have been reported in the literature. Most of these systems include a highly polar, aprotic organic solvent such as dimethylformamide (DMF)<sup>1,4–8,12</sup> or dimethyl sulfoxide.<sup>1–3,12</sup> These solvents are each used in combination with one or more additional compounds such as  $\text{N}_2\text{O}_4$ ,<sup>1–7,12</sup>  $\text{SO}_2$ ,<sup>8,9</sup> or an amine.<sup>10</sup> More recently, DMSO–paraformaldehyde has been reported as a solvent for cellulose,<sup>11</sup> and regenerated rayon fibers have been prepared from numerous nitrogenous and sulfur-containing compounds.<sup>13,15</sup>

While there has been much discussion of these and other solvent systems for cellulose, the literature contains little information concerning the regeneration

of films and fibers or their respective physical and chemical properties.<sup>14</sup> Although there have been substantial research efforts in this area, no economically acceptable commercial solvent-based process has as yet been disclosed for the production of fibers or films with acceptable properties while employing a totally recyclable solvent system.

## EXPERIMENTAL

The majority of the solutions were prepared using Abbé cut cellulose, i.e., a highly comminuted, defibered pulp. However, the dissolution process is not limited with respect to the degree of polymerization or the pulp form.

The solution compositions are given as weight percent in the order pulp/(CH<sub>2</sub>O)<sub>x</sub>/DMSO; for example, a 6/6/88 composition solution represents 6% cellulose, 6% paraformaldehyde, and 88% DMSO. A typical example of the solution preparation procedure is described below.

A 6/6/88 cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solution was prepared by charging 120 parts of a prehydrolyzed kraft pulp (Rayselect-J) of 550 D.P., 120 parts powdered paraformaldehyde, and 1760 parts DMSO into a 2-liter, four-neck resin reaction flask equipped with a stainless steel mechanical stirrer and a thermometer. The resulting slurry was stirred and heated to 120°C over a period of 1 hr. Although dissolution is almost complete at 120°C after about 1 hr, the heating and stirring were continued for (1) an additional hour at 120°C or (2) the length of time required to reduce the formaldehyde concentration to the desired level.

In some cases, the cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions were modified with compounds containing reactive N—H functional groups that are known to react with formaldehyde to yield N-methylol derivatives. In these cases, the reactive modifiers were added to the solution at the termination of the 2-hr heating cycle. A wide range of temperatures were employed during modification depending upon the additive employed. For the most reactive formaldehyde scavengers such as urea, a low temperature of about 70°C was employed. Higher temperatures were used in those cases where the less reactive modifiers were incorporated, for example, 120°C for phthalimide.

The cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions were also modified with acrylic acid derivatives such as methyl acrylate, butyl methacrylate, and acrylonitrile. The initial solutions were modified at 100°C following the 2-hr initial dissolution stage at 120°C. These modified solutions were then either (1) regenerated in the form of films or (2) coagulated in a Waring Blendor. The regenerated films or cellulosic solids were then subjected to infrared and nitrogen analyses in an attempt to detect a 1,4-addition product.

All of the cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions were observed to be microscopically free of gels and unreacted fibers. The solutions were deaerated prior to spinning and the viscosities measured by a Brookfield viscometer. They were found to be in the range of from 15,000 to 60,000 cps at ambient temperatures, the higher viscosities being associated with the modified cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions. The solutions were filtered through a 90-mm-diameter nylon in-line filter during spinning.

The majority of the spinning trials were performed using a bench-scale vertical spinning unit employing a 150-hole, 63.5- $\mu$  platinum-gold spinneret. The solutions were spun into the appropriate primary regeneration bath and the resulting fiber tow passed vertically to the primary glass godet and then through

a secondary regeneration bath to a secondary glass godet whose speed could be altered to produce the desired stretch conditions. Spinning speeds generally ranged between 10 and 60 meters/min although no attempt was made to optimize this parameter.

All fibers were processed as staple by treatment with 60–70°C water, 0.3% aqueous solution of a finishing agent at 50°C, and then centrifuged and oven dried at 100–110°C. The fibers were tested for physical properties according to the American Society of Testing and Materials Standards D-1577-73 and D-2101-72.

## RESULTS AND DISCUSSION

Paraformaldehyde/dimethyl sulfoxide is a convenient solvent for cellulose. The percent cellulose in the resulting solutions is dependent upon the degree of polymerization of the pulp. In general, 6/6/88 cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO spinnable solutions were prepared at 120°C over a 2-hr time period from pulps within the 400–600 D.P. range. The pulps may be either sulfate or sulfite grades and include many of the pulps that are typically employed in the viscose process. Rayselect-J, a prehydrolyzed kraft pulp of 550 D.P., was employed in the preparation of the majority of the solutions described herein.

The dissolution of cellulose in the (CH<sub>2</sub>O)<sub>x</sub>/DMSO solvent system is reported to result from the formation of a hemiacetal of cellulose, i.e., methylol cellulose.<sup>11</sup> The methylol derivative results from the reaction of cellulose with formaldehyde, the latter being formed by the in situ depolymerization of paraformaldehyde.

The final concentration of formaldehyde in the resulting solution was found to be a function of the dissolution heating time and temperature. Longer heating times or temperatures in excess of 120°C assisted the depolymerization of paraformaldehyde and thus the subsequent evolution of formaldehyde gas.

Cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions were prepared in which the final formaldehyde concentration ranged between 0.6% and 4.2%. The percent formaldehyde, as determined by the sodium sulfite test procedure, was found to affect the rate of regeneration during the spinning process. As the concentration of formaldehyde decreases, the rate of regeneration increases.

The cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions can be coagulated by employing protonic coagulants such as methanol or water. Interestingly, the fibers produced from these coagulants were found to readily redissolve in dimethyl sulfoxide in a temperature range of 50–70°C. These results indicate that (1) regeneration is incomplete, i.e., some type of methylol cellulose fiber is being obtained, or (2) the fiber is being regenerated or partially regenerated to cellulose which contains occluded paraformaldehyde. This is truly an unusual behavior for a "regenerated" cellulosic material. In fact, this coagulation followed by redissolution in dimethyl sulfoxide can be performed several times until the formaldehyde concentration in the resulting solution is <1% at which time dissolution cannot be repeated. However, this is not surprising since this level of formaldehyde is also required to maintain the stability of the cellulose in the initial DMSO/paraformaldehyde solution.

In addition, the methanol and water regenerants may be employed in combination with dimethyl sulfoxide. However, the level of dimethyl sulfoxide concentration in the primary regeneration bath was found to critically affect the resultant fiber physical properties. For example, the dimethyl sulfoxide con-

centration in a methanol regeneration bath should be maintained below the 20% by weight range. A primary methanol regeneration bath containing >20% by weight of dimethyl sulfoxide resulted in fiber fusion, adverse fiber physical properties, and/or spinneret plugging.

The dimethyl sulfoxide concentration in a water primary regeneration bath should be maintained below 30% by weight to avoid fiber fusion. Spinneret plugging was observed when the dimethyl sulfoxide concentration exceeded 50% by weight in water.

Variations in the composition of the regeneration or spin bath did not alter the fiber cross-sectional shapes. Both methanol and water regenerants afforded rayon fibers with circular shapes. Representative cross sections of fibers spun from the cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions are illustrated in Figure 1.

The regenerated cellulosic fibers produced by spinning the cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions into methanol or water are comparable in properties to cellulosic fibers produced by the viscose process. They are particularly outstanding by the fact that they exhibit very low  $S_{6.5}$  values. The  $S_{6.5}$  values are measurements of regenerated cellulosic fiber solubility in 6.5% sodium hydroxide at 20°C. This is a useful test for determining the potential resistance of such fibers or resultant fabrics to alkaline treatment such as alkaline laundering or mercerization. Accordingly, regular viscose rayon which cannot be mercerized and is not resistant to alkaline washing (unless crosslinked) has a relatively high  $S_{6.5}$  of 25–35%. On the other hand, the high performance and polynosic rayons have superior resistance to caustic soda as evidenced by  $S_{6.5}$  values of 5–15%. Cellulosic fibers spun from the cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions have  $S_{6.5}$  values in the range of 3–15%.

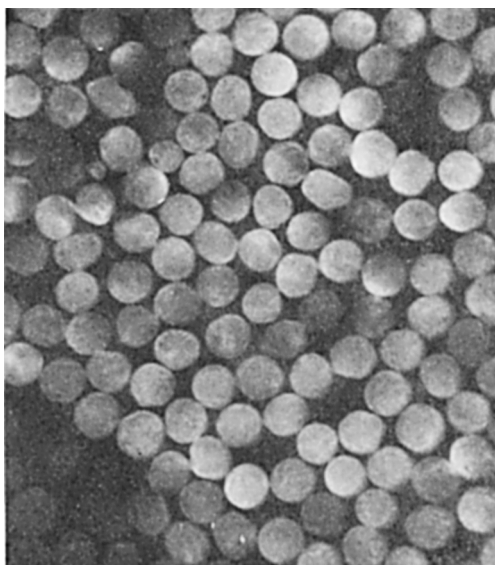
It should also be mentioned here that in this spinning system it is readily possible to obtain fibers with high wet modulus without the use of zinc or other additives which are required in a viscose spinning operation.

In Figure 2, stress-strain curves [conditioned (c) and wet (w)] for a methanol-spun fiber are shown for comparison with regular rayon and high wet modulus rayon. The shape of the wet curve is of particular importance since the yielding portion is different from that of other rayons. Low elongations in the fiber result in the steep slope of the conditioned stress-strain curve for these fibers and are an indication of stiffness. If the conditioned elongation could be increased to 10–12% or the slope manipulated to fall between that of high wet modulus rayon and cotton, for example, a superior cellulose fiber may be obtainable.

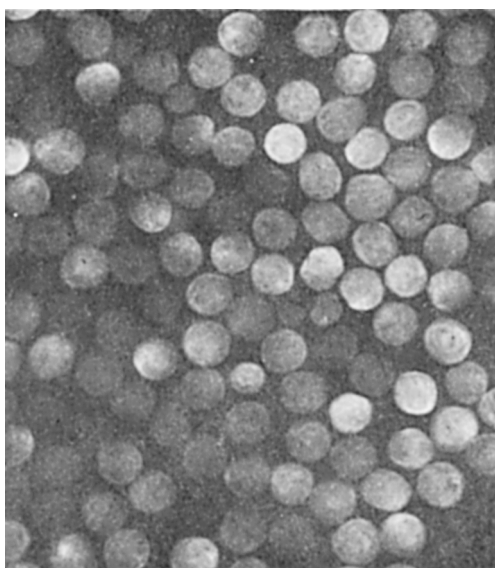
Some typical fiber physical property data are shown in Table I employing methanol and water primary regeneration baths for the production of rayon fibers from solutions of cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO containing a wide variety of formaldehyde concentrations. In general, fiber physical properties were fair to moderate. It is interesting to note that the better fiber physical properties resulted when the formaldehyde content in the cellulose solution was greater than 3.0% as determined by the sodium sulfite test procedure.

Some fiber physical property data are shown in Table II comparing some commercial rayons with those produced from spinning cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions into methanol or water primary regeneration baths. The DMSO/(CH<sub>2</sub>O)<sub>x</sub> fiber physical properties most closely resemble those of regular rayon produced by the viscose process. However, the low  $S_{6.5}$  values are similar to those associated with high wet modulus rayon fibers.

In an attempt to gain further evidence for the existence of a methylol cellulose



(a)



(b)

Fig. 1. Cross sections of cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO fibers spun from (a) methanol and (b) water (650×).

intermediate, the cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions were modified with reactive acrylic acid derivatives such as methyl acrylate, butyl methacrylate, and acrylonitrile. In this manner, it was hoped that the methylol cellulose would react with the acrylic acid derivatives to yield 1,4-addition products which may have resulted in (1) fibers with unique physical properties or (2) easier characterization of the cellulose intermediate. The cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions were modified at a 3:1 molar ratio of acrylate per glucose unit. For each acry-

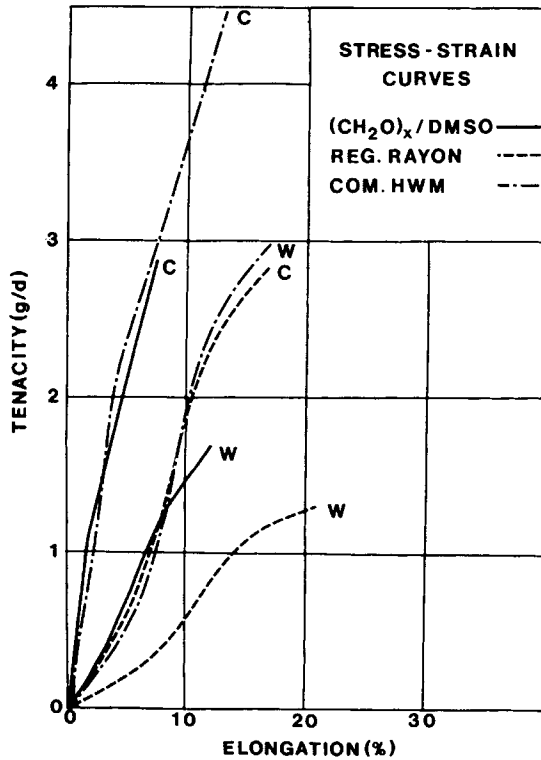


Fig. 2. Stress-strain curves of regular rayon, commercial high wet modulus rayon, and rayon produced by regenerating cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions from methanol.

late-treated solution and for an unmodified control solution, films were cast and regenerated from isopropanol and water.

Infrared spectra obtained from all acrylate-modified systems and from the unmodified control samples were very similar. Enhanced carbonyl or nitrile absorbances which would indicate bonding of the modifier were not observed. Nitrogen analyses of the acrylonitrile-treated samples showed 0.53% nitrogen, corresponding to an acrylonitrile D.S. of approximately 0.06, if indeed the nitrile

TABLE I  
Fiber Physical Properties

	0.5-1.5% <sup>a</sup>		1.6-3.0%		3.1-4.5%	
	MeOH <sup>b</sup>	H <sub>2</sub> O <sup>b</sup>	MeOH	H <sub>2</sub> O	MeOH	H <sub>2</sub> O
Tenacity, g/d						
Conditioned	1.2-2.3	1.8-2.0	1.5-2.6	1.4-2.4	1.6-2.9	1.5-2.5
Wet	0.8-1.2	0.6-1.0	0.6-1.5	0.8-1.2	0.8-2.1	0.8-1.5
Elongation, %						
Conditioned	5-16	9-28	6-14	5-15	5-13	5-14
Wet	6-20	11-26	8-16	6-18	7-26	7-16
Wet tenacity at 5% extension, g/d	0.5-0.7	0.1-0.3	0.2-0.9	0.2-0.7	0.2-1.3	0.3-0.9
S <sub>6.5</sub> , %	2.4-6.3	2.6-5.5	2.1-5.6	2.9-3.4	2.6-3.9	3.1-3.6

<sup>a</sup> (CH<sub>2</sub>O)<sub>x</sub>.

<sup>b</sup> Coagulant.

TABLE II  
 Rayon Physical Properties

	Regular	IWM	HWM	(CH <sub>2</sub> O) <sub>x</sub> / DMSO fiber
Tenacity, g/d				
Conditioned	1.5-2.8	3.5-5.0	3.5-8.0	1.2-2.9
Wet	1.0-1.8	2.5-3.5	2.5-6.0	0.6-2.1
Elongation, %				
Conditioned	14-25	12-19	6-14	5-28
Wet	18-35	18-24	9-18	6-26
Wet tenacity at 5% extension, g/d	0.2-0.3	0.4-0.6	0.7-3.0	0.1-1.3
S <sub>6.5</sub> , %	20-35	15-20	5-10	3-15

is bound. Analysis of a pyridine-catalyzed, acrylonitrile-treated solution showed a 0.29% nitrogen content, corresponding to an acrylonitrile D.S. of ~0.03%. These levels are not considered significant and indicate little reactivity between the acrylic acid derivative and the proposed cellulose methylol intermediate in question.

During the course of these investigations, methods were sought for reducing the concentration of formaldehyde in the final cellulose solution. One method previously mentioned involved the use of a prolonged heating cycle following dissolution. The cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions could simply be stirred and heated until the desired formaldehyde concentration was obtained as determined by the sodium sulfite test procedure.

A second method investigated in our laboratory concerned the use of compounds which contained reactive N—H functional groups. Such compounds are known to react with formaldehyde to yield the corresponding N-methylol derivatives. In this manner, it was hypothesized that reactive N—H compounds such as urea, melamine, phthalimide, and others could be added as modifiers to the cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions. In effect, these compounds could offer advantages such as (1) lowering the concentration of the free formaldehyde, and (2) result in the production of regenerated films and fibers which exhibit unusual physical properties. N-Methylol compounds have been used as cross-linking reagents and are universally employed by the textile finishing industry for producing smooth-drying, wrinkle-resistant, and shape-retentive cotton and rayon/polyester blend fabrics for garment end use.

Cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions of varying compositions were modified under different conditions with various reactive N—H compounds and polymeric additives. The reactive N—H containing modifiers evaluated in this solvent system are summarized in Table III. The polymeric additives studied in the cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO system are listed in Table IV.

In all cases, films were cast from the modified solutions and then regenerated

 TABLE III  
 Reactive Modifiers Evaluated in the Cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO System

Compound	Compound
Isopropyl carbamate	Phthalimide
Dihydroxyethyleneurea	Benzoguanamine
Ethyleneurea	Melamine
Urea	2,4,6-Triazinetriol

TABLE IV  
Polymeric Additives Evaluated in the Cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO System

Name	Chemical compound	Supplier
Ameripol-600	<i>cis</i> -polyisoprene rubber	B. F. Goodrich
Ameripol-1006	butadiene-styrene copolymer	B. F. Goodrich
Butvar-B76	poly(vinyl butyral)	Monsanto
Ca-394-60S	cellulose diacetate	Tennessee Eastman
Cymel-370	melamine formaldehyde resin	Cyanamid
Epon 828	epoxy resin	Shell
Estane-5715	polyurethane	B. F. Goodrich
Estane-5716	polyurethane	B. F. Goodrich
Hycar-CTB	butadiene rubber	B. F. Goodrich
Hycar-CTBN	butadiene-nitrile rubber	B. F. Goodrich
Hydrin-100	polyepichlorohydrin	B. F. Goodrich
Hydrin-200	epichlorohydrin-ethylene oxide copolymer	B. F. Goodrich
Valox	poly(butylene terephthalate)	General Electric
Vinac	poly(vinyl acetate)	Air Products and Chemicals
Vynathene-905	polyethylene-poly(vinyl acetate) mixture	U.S. Industries
Vynathene-907	polyethylene-poly(vinyl acetate) mixture	U.S. Industries

in the presence of protonic coagulants such as alcohols or water. Regenerated fibers were prepared from cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions modified with those additives which exhibited the most potential in the corresponding film studies. The reactive modifiers were added in various amounts sufficient to scavenge the excess free formaldehyde.

For each modified solution and for unmodified control solutions, films and/or fibers were analyzed by infrared spectroscopy and nitrogen determinations. Infrared spectra obtained from the modified systems and from unmodified control samples were very similar.

In the case of the nitrogen-containing adducts, nitrogen analysis of regenerated fibers and films revealed little or no retention of the modifier or its corresponding N-methylol derivative. The reactive N—H compounds did react with formaldehyde to form the N-methylol analogs which were isolated, characterized, and identified by melting point and infrared spectra comparisons with the known derivatives. The known compounds were synthesized independently by reacting the parent nitrogen compound with formalin. The results indicate that the modifiers and/or their derivatives are almost completely removed during the regeneration process or in the subsequent processing steps. Therefore, the reactive and polymeric additives did not significantly alter film and fiber physical properties. It is interesting that neither the in situ-formed urea and melamine methylol compounds nor added commercially prepared melamine resins were retained or reacted with the reported cellulose methylol intermediates.

## CONCLUSIONS

A wide range of pulps can readily be dissolved in the (CH<sub>2</sub>O)<sub>x</sub>/DMSO system including experimental pulp samples. The pulps may be used in either a fluffed, Abbé cut, shredded, or diced form without encountering dissolution problems.

The concentration of pulp which can be used depends upon the degree of polymerization. At 600–1000 D.P. up to 4% solutions can be spun while 400–600



D.P. up to 6% solutions were feasible. In the range of 200–400 D.P., 6–15% cellulose solutions can be prepared.

The cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions were clear and essentially free from gels or unreacted fibers, thus requiring only a single-stage polishing filtration during spinning. The reaction and dissolution process was found to be very specific to the paraformaldehyde and DMSO components.

Coagulation and regeneration of the cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions are fairly rapid in the presence of protonic systems such as alcohols and water. However, the "regenerated" material was observed to redissolve in DMSO. Fibers with good wet moduli can be spun without the need for spin bath additives.

One unique feature of these fibers is the fact that they exhibit unusually low  $S_{6.5}$  values.  $S_{6.5}$  values in the range of 3–15% can readily and consistently be obtained.

Conditioned fiber elongation generally was between 5% and 28% but usually too low for normal textile processing. The upper limits were obtained by proper control of jet stretch and godet stretch ratios. Fiber cross-sectional shapes are circular in appearance when water and methanol are employed as primary bath regenerants.

Addition of acrylic acid derivatives such as methyl acrylate, butyl methacrylate, or acrylonitrile to the cellulose solutions did not result in the formation of the expected 1,4-type adducts.

Modification of the cellulose/(CH<sub>2</sub>O)<sub>x</sub>/DMSO solutions with reactive N—H compounds and polymeric additives to scavenge and reduce the free formaldehyde level resulted in no significant improvements in film or fiber physical properties. Although the corresponding N-methylol derivatives were formed, they were apparently extracted during regeneration or in the subsequent processing steps.

Comparison of the overall processing steps involved in the DMSO/(CH<sub>2</sub>O)<sub>x</sub> solvent system reveals some distinctive averages over the complicated viscose process. For example, viscose processing steps such as steeping, pressing, aging, xanthation, ripening, and filtration may be eliminated or simplified in a solvent spinning system.

However, it should be pointed out that the commercialization of any solvent process for rayon production will depend to a large extent on the development of a suitable recovery system, that is, one that is totally recyclable, economic, and nonpolluting.

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