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ISSN: 1558-3724 (Print) 1558-3716 (Online) Journal homepage: http://www.tandfonline.com/loi/lmsc20

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To cite this article: Eugene F. Douglass, Huseyin Avci, Ramiz Boy, Orlando J. Rojas & Richard Kotek (2016): A Review of Cellulose and Cellulose Blends for Preparation of Bio-derived and Conventional Membranes, Nanostructured Thin Films, and Composites, Polymer Reviews, DOI: 10.1080/15583724.2016.1269124

To link to this article: http://dx.doi.org/10.1080/15583724.2016.1269124

POLYMER REVIEWS
http://dx.doi.org/10.1080/15583724.2016.1269124

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REVIEW

A Review of Cellulose and Cellulose Blends for Preparation of Bio-derived and Conventional Membranes, Nanostructured Thin Films, and Composites

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ABSTRACT
Cellulose has been used as a raw material for the manufacture of membranes and fibers for many years. This review gives the background of the most recent methods of treating or dissolving cellulose, and its derivatives to form polymer films or membranes for a variety of applications. Indeed, some potential applications of bacterial cellulose, nanofibrillar cellulose (NFC) for films showing enhanced barrier characteristics are reviewed as well as the utilization of cellulose nanocrystals (CNC) for production of highly oriented super strong films or thin films is discussed. Because of the success of the Lyocell process as well as the amine/metal thiocyanate solvent blends of cellulose and other polysaccharides like starch, chitosan, and other natural polymers. Consequently, the use of cellulose (or its derivatives) and another polysaccharide dissolved as a blend is also elaborated. It is our hope that the reader will want to follow up and investigate these new systems and use them to develop end use materials for all sorts of applications, from medical to water filtration, or electrogels for use in batteries.

KEYWORDS
Cellulose; membranes; films; NFC; CNC

1. Introduction

“A membrane is a layer of material which serves as a selective barrier between two phases and remains impermeable to specific particles, molecules, or substances when exposed to the action of a driving force. Some components are allowed passage by the membrane into a permeate stream, whereas others are retained by it and accumulate in the retentate stream.”[1] In some contexts, a membrane is another name for a film or coating, protecting one substrate or material from another. Cellulose has been used as a raw material for the manufacture of membranes and fibers for many years. Cellulose is one of the most abundant naturally occurring raw materials and has been used for all sorts of purposes for thousands of years.

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Cotton has been used as a fiber for clothing, and wood pulp/fibers have been used for paper production. Synthetic fibers have been developed for a variety of purposes, using cellulose as a raw material, with viscose rayon, cellulose acetate fibers, and membranes like cellophane, and regenerated cellulose membranes and fibers as examples. Most membranes made with cellulose have involved the solution of derivatives of cellulose, such as nitrocellulose, or cellulose acetate in common solvents and then are cast or extruded to form many different materials. Pure cellulose has been dissolved with a combination of a metal hydroxide and carbon disulfide, resulting in a derivative called cellulose xanthate, commonly called viscose rayon.[3] This process was developed in the nineteenth century. A full critical review of the dissolution of cellulose was reported by Hudson and Cuculo in 1980[4] and more recently by Liebert[5] as well as Heinze and Koschella.[6] Bacterial cellulose, nanofibrillar cellulose (NFC),[7] and cellulose nanocrystals (CNC)[8] were also recently discovered as new materials for making unique membranes.

This review gives the background of the most recent methods of treating[9] or dissolving cellulose, and its derivatives to form polymer films or membranes for a variety of applications. Cellulose can be dissolved in aqueous base with degradation. Methods with controlled cellulose degradation include the Lyocell process and variations, in Cuoxam[3] (a process using tetraaminediaquacopper dihydroxide), and amine and metal thiocyanates[10–12] systems that do not affect molecular weight during polymer dissolution and processing. Cellulose membranes can be made from cellulose derivative membranes that are treated to regenerate cellulose or can be made from wood and cotton linters or fibers.

The use of cellulose (or its derivatives) and another polysaccharide dissolved as a blend is reviewed. First, the use of water soluble cellulose derivatives which were blended with starch in water solution; then, ketone soluble derivatives of cellulose and derivatives of starch were blended in the same solvent. Because of the success of the Lyocell process for dissolving cellulose, it was suggested that the Lyocell process could be used to create blends of cellulose and other polysaccharides (like starch, chitosan, and other materials). Evidence for this is provided in this study. With the success of the amine and metal thiocyanate dissolution of cellulose, it is proposed to use this method to dissolve cellulose and starch or chitosan and study the membranes that can be produced from solution.

Our work at NCSU[11,13] on making fibers and membranes from cellulose and other biomaterials (alone or in blends) using a novel ethylenediamine/salt solvent system created a new way to formulate new biomaterials with excellent physical properties. This review puts that work into a context, and will show the reader the progress that has been achieved in developing relatively non-toxic, environmentally-friendly systems. These systems can be used to manufacture cellulose membranes for a variety of applications and show the development of novel blend systems of materials previously thought to be immiscible or incompatible in a polymer matrix, fiber or film. It is our hope that the reader will want to follow up and investigate these new systems and use them to develop end use materials for all sorts of applications, from medical to water filtration, or electrogels for use in batteries.

2. Unique cellulose membranes and films

Polymer melts or viscous polymer solutions have been traditionally used to cast thin films that can be quenched or coagulated to form a variety of membranes. However, plant cellulose is a fascinating polymer exhibiting supramolecular fibrillar structure. This is a result of

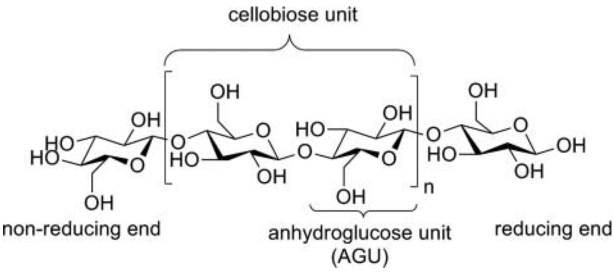

Figure 1. Molecular structure of cellulose.

biopolymerization, spinning, and crystallization that occur in a rosette-shaped plasma membrane complex (Fig. 2) with enzymatic terminal complexes (TCs) acting as biological spinnerets[14,15] Consequently, a super high degree of crystallinity is always observed for the native cellulose. giving us the opportunity to create these flat materials after separating nanofibrils or nanocrystals. Interestingly, some bacteria also can produce nanostructure polymer membranes. We shall describe both subjects in the subsequent chapters.

2.1 Bacterial cellulose membranes

Cellulose is the most abundant biological macromolecule on Earth and is harvested from plant resources such as forest trees and cotton. In addition, some microorganisms, fungi, and bacteria can also produce cellulose, which has the same molecular formula, β-1, 4-glucans, as plant cellulose.[16] Plant and bacterial cellulose, in contrast, has significantly different macromolecular properties; the degree of polymerization differs from about 13000 to 14000 for plant and 2000 to 6000 for bacterial cellulose.[17] Bacterial cellulose has very high purity, no hemicellulose or lignin, higher water holding capacity and hydrophilicity, improved mechanical properties, ultrafine network architecture, and characteristic ribbon-like microfibrils.[17–18] These advantages allow bacterial cellulose to be utilized in areas where plant cellulose can hardly be used.

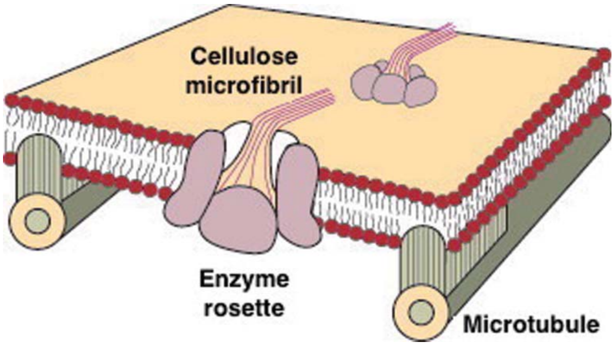

Figure 2. Orientation of microtubules controlling the orientation of cellulose in the cell wall where the microtubules act like tracks to guide the cellulose enzymes floating in the cell membrane.[15] © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

When properly cultured, some bacteria especially *Acetobacter* and *Acanthamoeba* or *Achromabacter* form cellulose membranes. These membranes have multiple uses and applications. The processing of such membranes to form either wet membranes or dry membranes for a variety of applications is discussed. The wet membranes can be used as is, without going through dehydration phase. Alternatively, the membranes can be dehydrated and used in some medical applications to protect and absorb moisture. A combination of dehydration and pressing processes, from solvent exchange and then drying, to using pressing equipment to squeeze out the solvents while heating can be used to form a useful membrane. Authors are usually unconcerned with the forming and retention of micro-porous structures, as they seem more interested in nanoporous or nonporous membranes that become functional when hydrated.

The study of cellulose produced by bacteria goes back to Brown[19] in 1886, and also scientists publicized their processes in 1931, 1936, 1947, and 1951. The food for the bacteria is glucose, which is added to a culture medium to produce cellulose. A wet sheet made of cellulose microfibrils is developed in 6 to 8 hours. As seen in Fig. 3(a), during the extrusion of cellulose in the interior of the bacterial cell, the cellulose synthase enzyme catalyzes the addition of uridine diphosphate glucose (UDP glucose) to the end of the growing cellulose chain to form a protofibril of ca. 2–4 nm diameter (Fig. 3b) and spontaneously assembles in the culture medium to form a cellulose fibril mesh via forming a ribbon-shaped microfibril of ca. 80 × 4 nm.[17,20,21] The formation of 100 glucose molecules into cellulose can be done in an hour by a single cell; therefore, millions of bacteria together with many synthesized fibrils can generate a ribbon of crystalline cellulose for crystallization and polymerization of the elementary fibrils by the self-assembly process.[17,21] The polymerization catalyzed by cellulose synthase can be explained by starting the β-(1- 4) linkage with the formation of cellobiose as an intermediate at a dual UDP glucose binding site.[21] Furthermore, the activator of cellulose synthase is observed, and it is cyclic diguanylmonophosphate (c-di-GMP).[125] The emerging fibrila become linearly extended structures, are highly hydrated, and are as wide as 100 nm. Then, still suspended in the liquid medium, they gradually form a consolidated mesh of

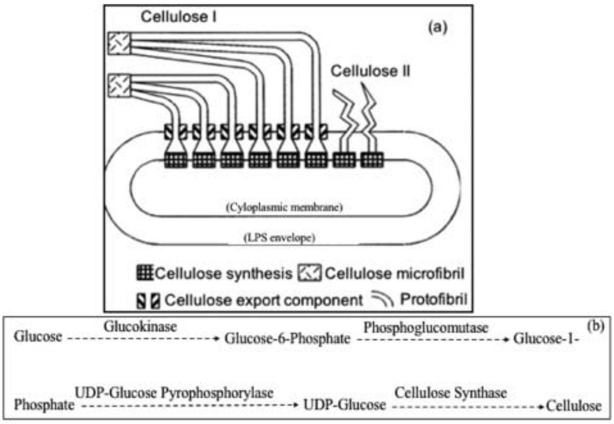

Figure 3. (a) Schematic diagram showing cellulose fibrils forming from the bacteria cell through the cell wall.[20] (b) Biochemical model for cellulose synthesis in *Acetobacter xylinum*.[17] (a) © Springer. Reproduced by permission of Springer. (b) © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholders.

fibrils. These cellulose fibrils aggregate at random, resulting in a wet sheet that floats in the culture medium. By playing with the process conditions, for example, the bacterial strain, additives, substrates, carbon and nitrogen sources, pH, temperature, and cultivations make it possible to control the cellulose properties with adjusting molar mass with distribution, and the supramolecular structure.[17,21]

Bacterial cellulose (BC) has unique properties; for example, it shows good biocompatibility, high water-holding capacity, ultrafine network structure, transparency, and high mechanical properties which can be used as materials in various biomedical fields. Kim et al.[22] have obtained BC nanofibrillar patch for a wound-healing application. In this study, *Gluconacetobacter xylinus* was used to obtain BC gels after a certain time period of cultivation. After washing with deionized water, BC nanofibrillar structures were purified with 1 wt% NaOH for 2 h at 90°C, and washed again with deionized water. The resulted transparent nanofibrils demonstrated good mechanical properties of the tensile strength and Young's modulus of 11.85 ± 2.43 and 11.90 ± 0.48 MPa, respectively, with the thickness of 10.33 ± 0.58 μm.

Another more general bacteriological process has been used in Asian countries for the production of an edible coconut gel. This gel is made by cooking the wet cellulosic sheet in sugar syrup. The culture medium is coconut water or coconut milk, and it takes weeks for the materials to be fermented / prepared for use. It is a public domain process where the temperature and humidity are not controlled. The bacteria used are not specific, but ones already present in the environment.

Levy and Kurokawa[23] developed a process for obtaining a cellulosic wet sheet and a membrane from a bacteriological process. Levy describes as background the preparation of a bacterial cellulose wet sheet as pictured in Fig. 4. This sheet is processed to replace the culture medium with water, and then the WET membrane is applied to an injury to protect a wound. This membrane is kept wet and then replaced periodically as the wound heals.

Levy and Kurokawa's invention involves the wet sheet being dehydrated and then applied to the wound in dry form giving a naturally adhering material that can serve as a template for tissue regeneration. The patent describes a process to obtain compound wet sheets, and

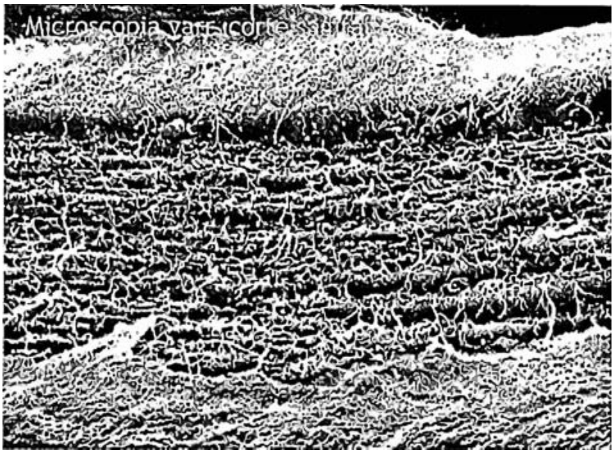

Figure 4. SEM dried bacterial cellulose sheet.[23]

then blending those sheets with other materials, and then drying them to do future physical tests to characterize the materials.

The use of these cellulose-wet sheets in various products is described. A few examples are stabilizers and thickeners in milk, juices, and food products, replacing chemical stabilizers and thickeners. Once obtained through the claimed process, these wet membranes are then dried with the equipment proposed to obtain dried cellulosic membranes. The resulting membranes are extremely fine, and include features like gas permeability, imperviousness to liquids, and are ideal for *in vivo* tissue regeneration.

The process for dehydrating these membranes, using specific machinery is described. Diagrams are used to show the basics of the machinery for this process. Some examples are seen in Fig. 5. The cellulosic wet sheet is placed between felt fabrics to start the extraction of water, then the sheets are sent through a series of rollers to squeeze out the water. The rollers can be heated, if desired, depending on end uses. Then, the drying process for the sheets continues under ambient conditions.

The discussion includes other uses of pressing and novel dehydration processes that result in a uniform sheet of cellulose that can be used in medical applications. The diagram (Fig. 5) shows their invention. The cellulosic wet sheet is placed between felt pads and then transported through a series of rollers to remove the water and other solvents.

The issue with dehydration of wet cellulose membranes is that the dehydration is irreversible, since once it is hydrated on forming, the membrane has no crystalline regions, and once the water or swelling solvent is removed, the chains move closer to one another and form crystalline regions. The crystalline regions now have a different crystal structure than the original. The above patent application describes one unique process used to gain a usable dehydrated membrane for wet applications. The drying conditions significantly alter the membrane morphology.

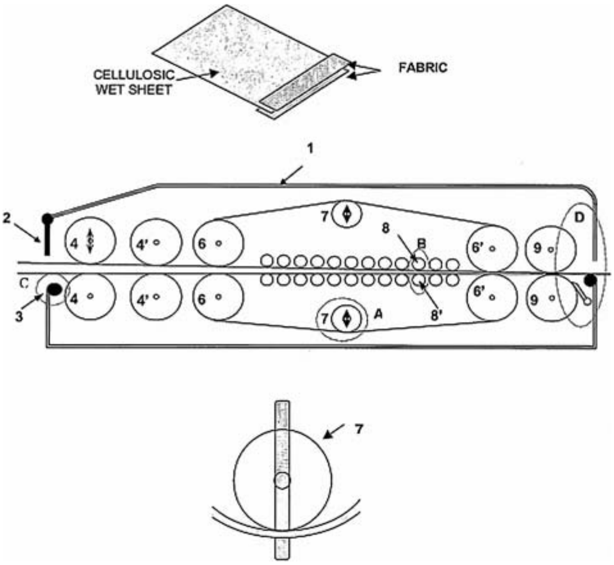

Figure 5. Schematic of invention for drying a cellulose membrane.[23]

One paper illustrating this issue is by Clasen and coauthors.[24] Clasen et al. studied the effects of different drying processes on the physical properties of bacterial cellulose membranes. The purpose of the study was to determine the best process for the manufacture of a membrane for medical applications with a few main attributes: a moist climate to transport fluid away from a wound, sufficient gas transport to the wound to provide oxygen for healing tissue, while at the same time providing a barrier to protect against microorganisms, and prevention of too much water evaporation from the wound (evaporative cooling) so that the body retains heat and prevents localized hypothermia.

Bacterial cellulose membranes can be used as electronic paper display,[25] pervaporative separation membranes for aqueous organic mixtures,[26–27] carrier material for metal catalysts,[28] artificial blood vessels,[29] and as acoustic membranes in loud speakers.[30] An excellent review of bacterial cellulose applications is by Iguchi et al.[30] Bacterial cellulose membranes as a wound dressing are already available commercially dry as Biofill (from Brazil), and in a wet state as X-Cell (Xylose Corp. USA) and Veloderm CRYSTALCELL 77 (Fig. 6). The prime advantage of cellulose membranes versus other commercial membranes (such as polyurethane) is high water permeability and increased wound healing capability.

The unique physical properties of microbial cellulose allow excellent molding, displaying a high degree of adherence even to the moving body parts (Fig. 7).[32]

The high swellability of bacterial cellulose membranes prevents them from adhering to the wound ground. Bacterial cellulose can easily be imbued with antibacterial agents, to prevent infection, in contrast to chitosan membranes that are naturally antimicrobial.

The specific bacterial cultures used for Clasen's study was *Gluconacetobacter xylinus*. Different processes are described to either partially dehydrate the membranes via a mechanical process like using a roller device, or to fully dehydrate the membrane for use on strongly exuding wounds like burns, where a highly absorbent membrane is desirable. These processes have different effects on the physical properties of the resulting cellulose membrane.

Table 1 represents the different strains of bacteria used for this study. Two main processes are used to remove the water;

Figure 6. Semi-transparent Veloderm® membrane.[31] © BTC Ltd. Reproduced by permission of BTC Ltd., Ancona, Italy. Permission to reuse must be obtained from the rightsholder.

Figure 7. Microbial cellulose dressing applied on a wounded hand (image courtesy of Center of Burn Healing, Siemianowice Slaskie, Poland).[32] © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

1) 60°C for 6 hours (called "normal dried"), and
2) shock frozen with liquid nitrogen and then freeze-dried under vacuum (called "freeze dried").

For SEM study, the membranes were dehydrated with a "shock-frosting" process using liquid nitrogen and then freeze drying at −70°C under high vacuum, or ambient drying.

As seen in Fig. 8 with freeze drying the authors obtained a micro-porous structure; however, a more solid membrane structure resulted with evaporation-drying.

The rheological tests showed that the different strains show comparable swelling ratios Q, the never dried membrane of around 80 (v/v size compared to raw dry material), freeze dried membrane at 25, and the normally dried membrane of 4. The freeze-drying process retains much of the original porous structure of the membrane, whereas in the normally dried membrane the porous structure disappears due to aggregation of the polymer strands as the water disappears. Permeability tests were done using a custom built device for different gases (H_2, O_2, CO_2, and N_2) and is shown in Fig. 9, and they seem to confirm the SEM results that show a much tighter porous structure with the evaporation dried membranes than the freeze-dried ones.

It is clear that the freeze dried material has a greater permeability, two decades larger due to the micro-porous structure. The open symbols show this distinctly.

The Clasen group showed that membrane tensile properties varied with the bacterial strain and did not show the same trends as the permeability. Only one strain, namely ATCC

Table 1. Parameters of Bacterial Strains *Gluconaceobacter Xylinus* and the Produced Membranes after Seven Days of Culturing.[24]

Membrane	Strain Name	Thickness (mm)	Dry Weight (mg)	M_w (kg/mol)
1	ATCC 14851	0.245	23.3	—
2	ATCC 10245	1.132	95.2	1420
3	ATCC 11142	1.569	100.2	1450
4	ATCC 23768	0.970	68.5	—

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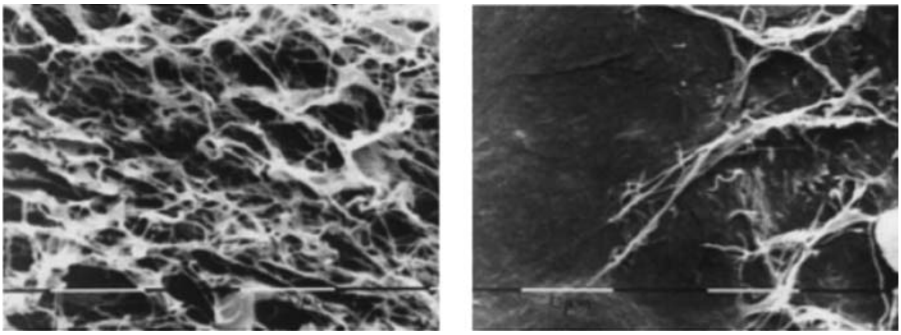


Figure 8. Freeze dried (left), and evaporation dried (right) bacterial cellulose membranes surface SEM pictures.[24] © John Wiley and Sons. Reproduced by permission of John Wiley and Sons. Permission to reuse must be obtained from the rightsholder.

14851, showed the capability to synthesize membranes that met the requirements for an application as a wet wound dressing. This useful flexible membrane had Young's modulus lower than the empirical critical value of 755 MPa.

The differences in structure between the never dried, freeze dried, and evaporation dried membranes are clearly delineated due to the high hydrogen bonding forces pulling the cellulose into crystalline regions. The authors believe it is confirmed by the significantly lower swellability of the dried membranes, a factor of 5 for the freeze-dried, and a factor of 50 for the evaporative drying procedure. Surprisingly they did not use X-ray analysis to study the changes in crystallinity with each process; because their IR analysis seemed questionable, they suggest small changes in the fingerprint regions to be determinative of the differences in the membranes. They also change the conditions of the "never dried" membrane as a "control," by doing the IR in a nonpolar solvent after water is removed with successive solvent extraction. Previous publications were used to justify their conclusions but ignored the fact that those studies were done on different materials.

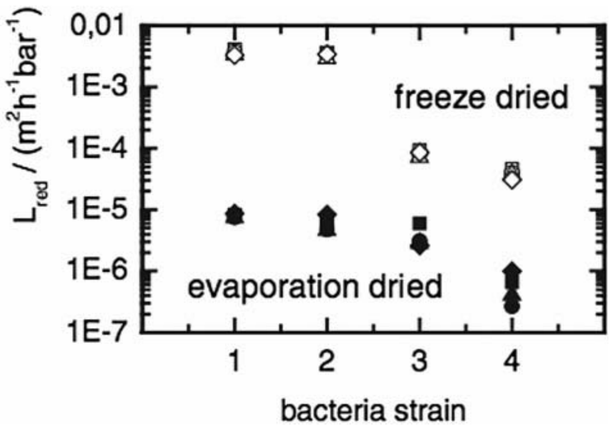


Figure 9. Comparison of reduced gas permeability for freeze-dried (open symbols), evaporation dried (closed) from 4 different strains.[24] © John Wiley and Sons. Reproduced by permission of John Wiley and Sons. Permission to reuse must be obtained from the rightsholder.

Another interesting study describing the characterization of both bacterial and Lyocell cellulose membranes was directed towards a specific end product: membranes containing ferrites to give magnetic properties. Sourty[33] discovered some important aspects of cellulosic membranes directed towards their use as frameworks for the holding of iron compounds for ferromagnetic property enhancement. The preparation of the materials for study and the tests performed are the most interesting aspects of their study.

Bacterial cellulose membranes from *Acetobacter xylinum*, produced at the surface of the culture medium, were provided for their use by a Japanese company. The membranes were produced at the interface between the liquid culture medium and the air. The membranes were washed in distilled water, and then boiled in 4% solution of NaOH to destroy any protein present, and then washed to neutrality to remove any excess base. The purified gel bacterial celluloses (about 2 mm thick, swollen with water at 99%) were stored in aqueous ethanol, and then, when used, were solvent exchanged to 100% distilled water. These membranes were kept WET.

The Lyocell membranes of uniform thickness were cast from solutions of cellulose pulp in N-methylmorpholine N-oxide (7.5% w/v), and coagulated in 60°C water. The coagulated membranes were then washed and used in the water swollen state to prepare nanocomposites 1 mm thick, and with an 80% weight of water.

The bacterial cellulose has a high degree of crystallinity when dried (about 70%), but if never dried the membrane is a very swollen nascent gel. The cellulose coagulated from the Lyocell process formed a tough membrane when dried, with a degree of crystallinity of 40–45%. Both cellulosic membranes contract significantly on drying and form a much smaller, tough film, due to removal of water and the formation of crystalline regions.

The two images in Fig. 10 show the swollen nature of the membrane on the left and then how the gel membrane collapses upon drying on the right.

The samples after special chemical treatment to form ferrites *in situ* were either dried on Teflon, or on glass. The Teflon prevents adhesion, but results in film shrinkage and curling. Using glass prevents the membrane from curling due to drying. To study the samples with a transmission electron microscopy, the bacterial samples were solvent exchanged with ethanol and then propylene oxide; the swollen gel was either embedded in Spur resin or dried to form a dried parchment and then ultrathin sectioning was performed with a Reichert Ultra cut E

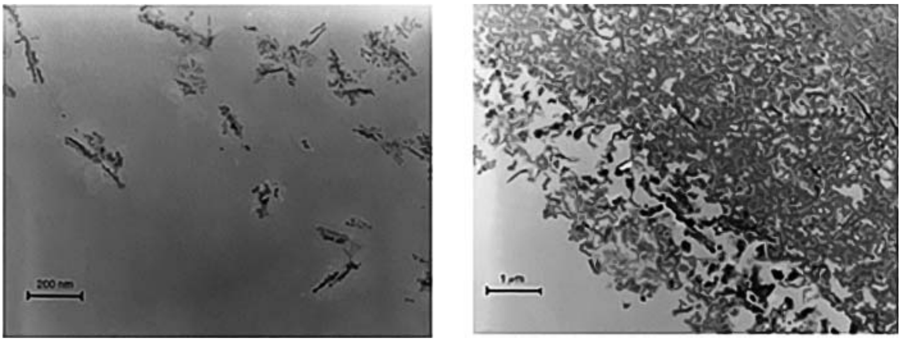


Figure 10. Never dried bacterial membrane (left), dried bacterial membrane (right) scanning electron micrographs.[33] © Springer. Reproduced by permission of Springer. Permission to reuse must be obtained from the rightsholder.

Microtome equipped with a diamond knife. The dried Lyocell membrane was ground in distilled water with a mortar and pestle and then placed on a TEM grid and allowed to dry.

An interesting study of *Acetobacter xylinum*, was performed by Phisalaphong et al.[34] where the full characterization of their cellulose membranes were conducted. The nonporous membranes were formed after mixing bacterial cellulose (BC) solution with alginate (A), a naturally occurring polysaccharide, solution to obtain mixtures as substrates materials having different weight ratios of BC/A. These mixtures were then spread over a Teflon plate to adjust thickness of these solutions by controlling manually of the height of the casting blade and then the casting solutions were coagulated. The surface morphology, pore structure, tensile strength, water absorption, and water vapor permeability were measured. The results were interesting. They were successful at blending various levels of alginate in the bacterial cellulose, 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100. To form the nanoporous structure from a coagulated membrane they used a successive solvent exchange using increasing amounts of ethanol, and then super critical CO_2. The ethanol was flushed out and the system slowly depressurized to remove the CO_2, leaving a nanoporous structure behind.

Figure 11 shows the increase of water absorption capacity as the alginate amounts increase, suggesting the presence of alginate disrupts the crystalline regions of the cellulose, allowing more water to penetrate and be absorbed.

The blending of the bacterial cellulose (BC) with the alginate reduced the hydrogen bonding between the cellulose chains and allowed more water to penetrate and be absorbed by both the cellulose and the alginate. Klemm et al.[29] got water absorption values of wet state BC, freeze-dried BC, air-dried BC (100°C), and cotton linters which were 1027, 629, 106, and 60% respectively; this is in comparison to the current authors, who got the corresponding value of 509% at 30°C for air dried BC films, and with the fabricated regenerated BC films of about 50% in Fig. 11.

The mechanical tests (Fig. 12) were interesting, as they show the very strong character of the pure cellulose membranes, and the fact that adding alginate decreases both tensile strength and elongation to break, consistent with their theory of the nature of the blend.

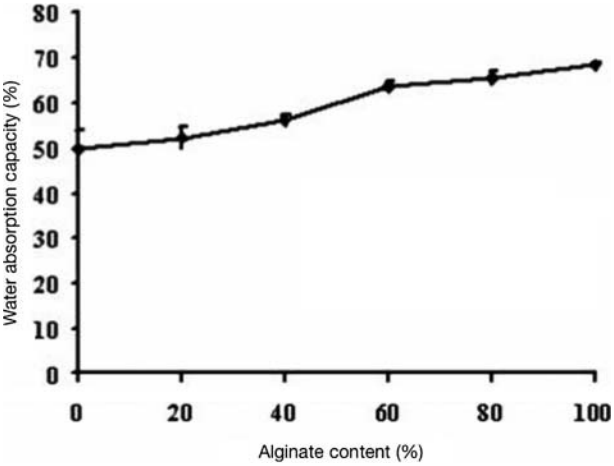


Figure 11. WAC (%) of the RBC/Al blend membranes as a function of the Al content.[34] © John Wiley and Sons. Reproduced by permission of John Wiley and Sons. Permission to reuse must be obtained from the rightsholder.

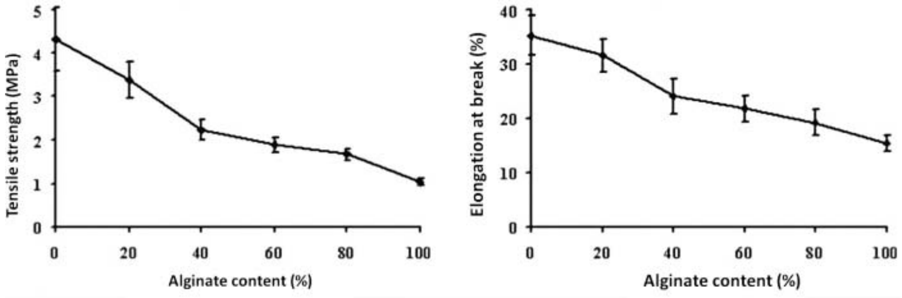


Figure 12. Tensile strength (left), elongation at break (right) of the BC/Al blend membranes as a function of the Al content.[34] © John Wiley and Sons. Reproduced by permission of John Wiley and Sons. Permission to reuse must be obtained from the rightsholder.

The surface morphology of the BC and the blend shows up very well in the SEM images shown in Fig. 13.

The nature of the fibrils after reswelling with water and then super critical drying of the membranes, which locks the porous structure in place, show up clearly in these pictures. The most interesting results were for the RBC membrane, where the tensile strength was 4.32 MPa, 35.20% elongation at break, compared to the 80/20 blend which was 3.38 MPa,

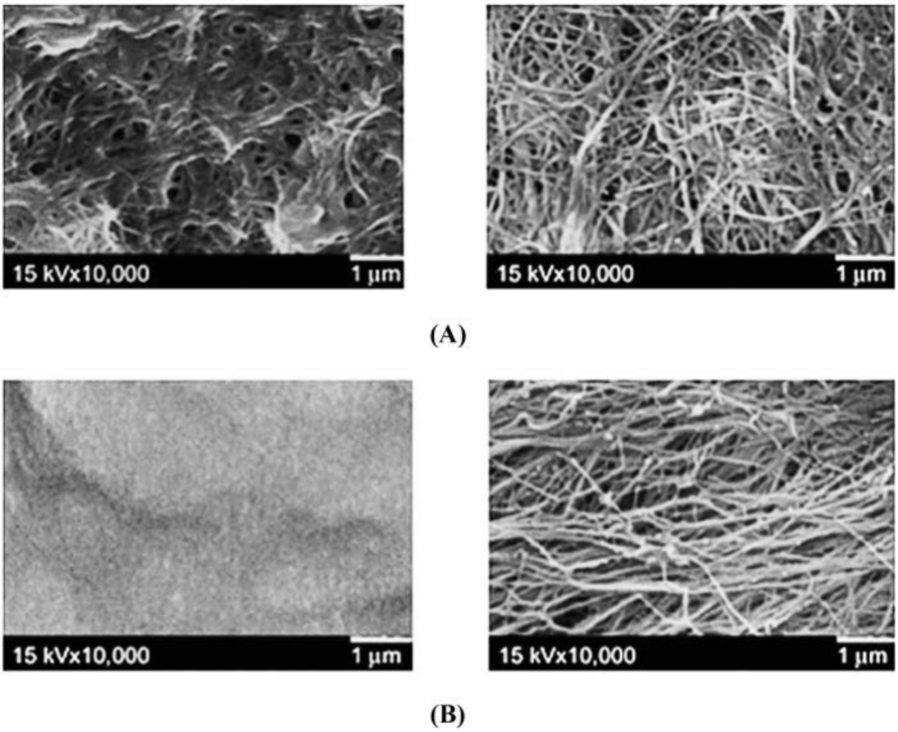


Figure 13. SEM images of the surface morphology of (A) RBC, and (B) 80/20 BC/Al blend membranes before (left) and after (right) reswelling in water and supercritical drying.[34] © John Wiley and Sons. Reproduced by permission of John Wiley and Sons. Permission to reuse must be obtained from the rightsholder.

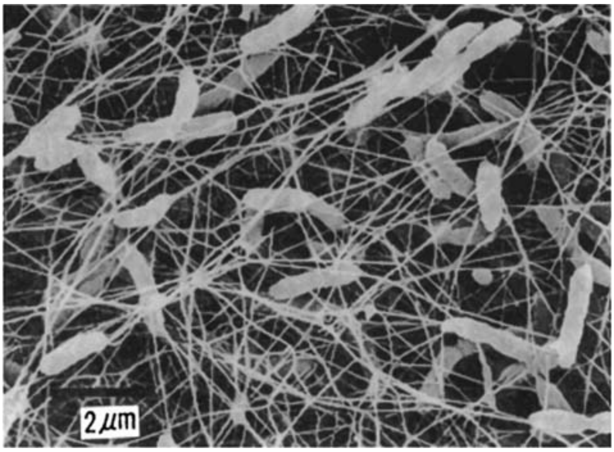


Figure 14. SEM of freeze-dried surface of bacterial cellulose gel.[30] © Springer. Reproduced by permission of Springer. Permission to reuse must be obtained from the rightsholder.

and 31.60%, respectively. The water absorption for the RBC membrane was 49.67%, compared to 52.25% for the blend, which is pretty close. This shows that blending polysaccharides with cellulose does have significant effects. The tensile strength of these membranes is much lower than the bacterial cellulose, which was about 200–300 MPa;[21] however, higher elongation at break was obtained, namely 1.5–2.0% vs. 31.6–35.2%.

An excellent review by Iguchi et al.[30] was published in 2000. It presented an exhaustive review of some of the papers included here and as well as others, and is a good resource if the reader desires more information.

This SEM photograph (Fig. 14) shows the fibrous nature of the surface of a freeze-dried gel. There are fibrous regions and then crystallite regions of collapsed fibers. This clearly shows a porous structure that can hold a lot of water in the never dried state. Another interesting picture in their review is shown below in Fig. 15.

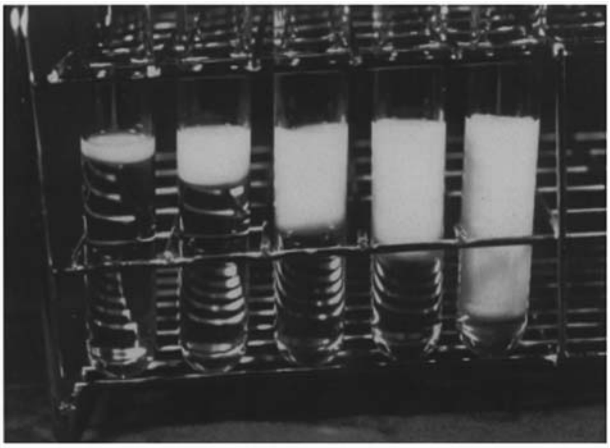


Figure 15. Bacterial cellulose layers grown with different culture time (max 4 weeks).[30] © Springer. Reproduced by permission of Springer. Permission to reuse must be obtained from the rightsholder.

The cylinder on the far right is the longest culture time of 4 weeks, and it is clear the cellulose forms on the surface of the culture, floating above the nutrient substrate.

Wanichapichart et al.[5] characterized four types of cellulose membranes manufactured by a known density of *Acetobacter xylinum* in two different culture mediums. It was found that bacteria grown in coconut juice produced cellulose membranes faster than in the standard Schramm and Hestrin's medium. The cell density and time are two important parameters to control the hydraulic permeability coefficient of the resulted cellulose membranes. The approximate pore size of membranes which were produced in coconut juice was 0.08 μm and with porosity from 1.4% to 2.4%. The filtration of feed solutions (about 100 kPa) containing a mixture of Chlorella sp. and bovine serum albumin (BSA) were also determined by using two-day formed membranes in sucrose supplemented coconut juice. The results showed that Chlorella and BSA rejection of the membranes were about 99.8% and 98.4%, respectively, by using higher cell density of 2×10^8 cfu.ml^{-1}. The membranes were asymmetric-hydrophilic type in which the skin layer of the membrane was the air-facing surface and the sub-layer was the medium-facing with the whole thickness less than 6.0 μm. In addition, they did not observe a significant difference between the membrane thicknesses when the cell density of *A. xylinum* between 1×10^8 and 2×10^8 cfu.ml^{-1} were used. It might be explained as the increasing of producing cellulose threads caused to spread over the entire medium surface which probably only reduced the number of large pores. However, it reduced the water flux and hydraulic permeability coefficient from 3.6×10^{-10} to 0.5×10^{-10} m^{3}N^{-1}s^{-1}.

Recent studies on permeability of BC by Professor Kaplan's group[35] revealed 94.1% porosity and unique morphology indicating that cylindrical pores do not exist, but instead micro-channels of varying sizes are present through which solute (Vitamin B12, lysozyme, and bovine serum albumin) diffusion occurs. The open fiber network is evident from this study; thus immobilizing various compounds is possible for BC. The authors suggest novel

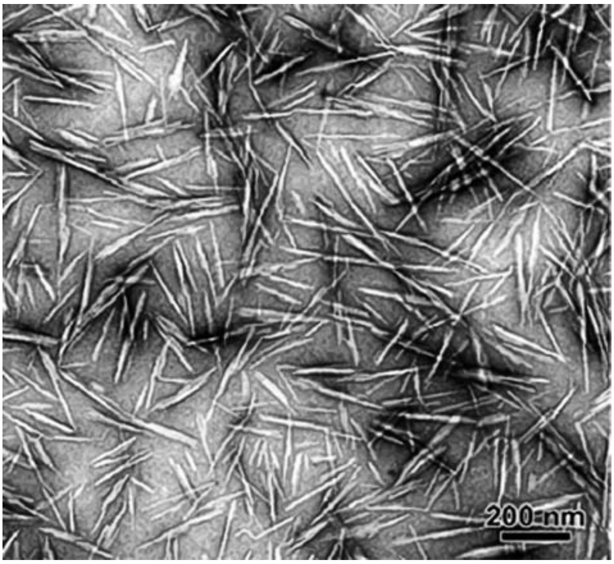


Figure 16. TEM images of dried dispersion of cellulose nanocrystals derived from ramie.[8] © The Royal Society of Chemistry. Reproduced by permission of The Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.

end uses such as tissue growth, cell-based therapies, and drug delivery for bacterial cellulose membrane systems.

In fact, bacterial cellulose is quite different than cellulose of plant origin in terms of molecular formula, purity, water content, and crystalline structure. These unique properties for bacterial cellulose caused an increased interest in its biomedical application commercially over the past few years and it is still an open field for new applications. On the other hand, it has been essential to increase the current knowledge of understanding the biosynthetic process itself to optimize the fermentation process to obtain more cells with more cellulose biosynthesis. It yields commercial scale up and probably the resulted cellulose forming by bacteria could be satisfied entirely for the required applications. The current studies showed that interdisciplinary interactions between biology, physics, pharmacy, medicine, and so on are necessary to optimize biosynthesis.

2.2 Cellulose nanocrystals (CNCs) and nanofibrillar cellulose (NFC) for nanostructured thin films

Highly crystalline native cellulose can undergo acid hydrolytic degradation offering an exciting polymer product for chemical modification. It is generally accepted that amorphous domains and less orders crystals undergo hydrolysis whereas crystalline regions remains intact resulting in microcrystals. This reasoning led to the development of microcrystalline cellulose (MCC) (Fig. 17) in the 1960s. Physiologically inert MCC micron size particles are

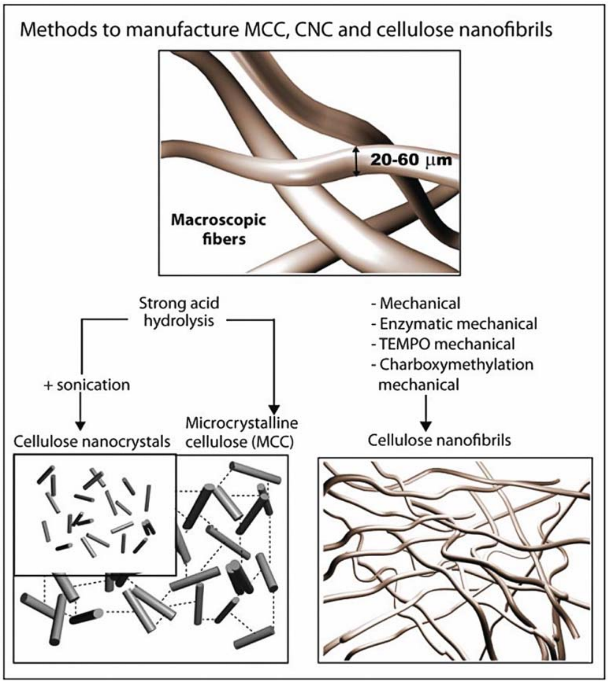


Figure 17. Preparation routes for MCC, CNC and cellulose nanofibrils (NFC/MFC).[36] © Aalto University publication series doctoral dissertations 114/2013. Reproduced by permission of Aalto University publication series doctoral dissertations 114/2013. Permission to reuse must be obtained from the rightsholder.

mainly used now in the pharmaceutical industry as a tablet binder or as additives in paper and composite applications;[14] however, little use of MCC for membrane production was found in the literature by the authors. Interestingly, if the hydrolysis process of native cellulose or cellulosic fibers including cotton, ramie flax, sisal or softwood or hardwood pulp is optimized by sonification,[14,36] a colloidal suspension of rod-like cellulose nanocrystals (CNCs) can be achieved (Figs. 16 and 17). The crystal width is approximately a few nanometers, but the length of CNCs varies from tens of nanometers to several micrometers.[14] CNCs resembling liquid crystals can be assembled with a variable degree of order in super strong thin films or membranes.[37]

For example, CNC thin films obtained by the Langmuir-Schaeffer technique did not exhibit any particular alignment, (Figs. 18a and 18c) but the ones with ca. three layers obtained by using the convective-shear assembly showed distinctive alignment of CNCs.[38]

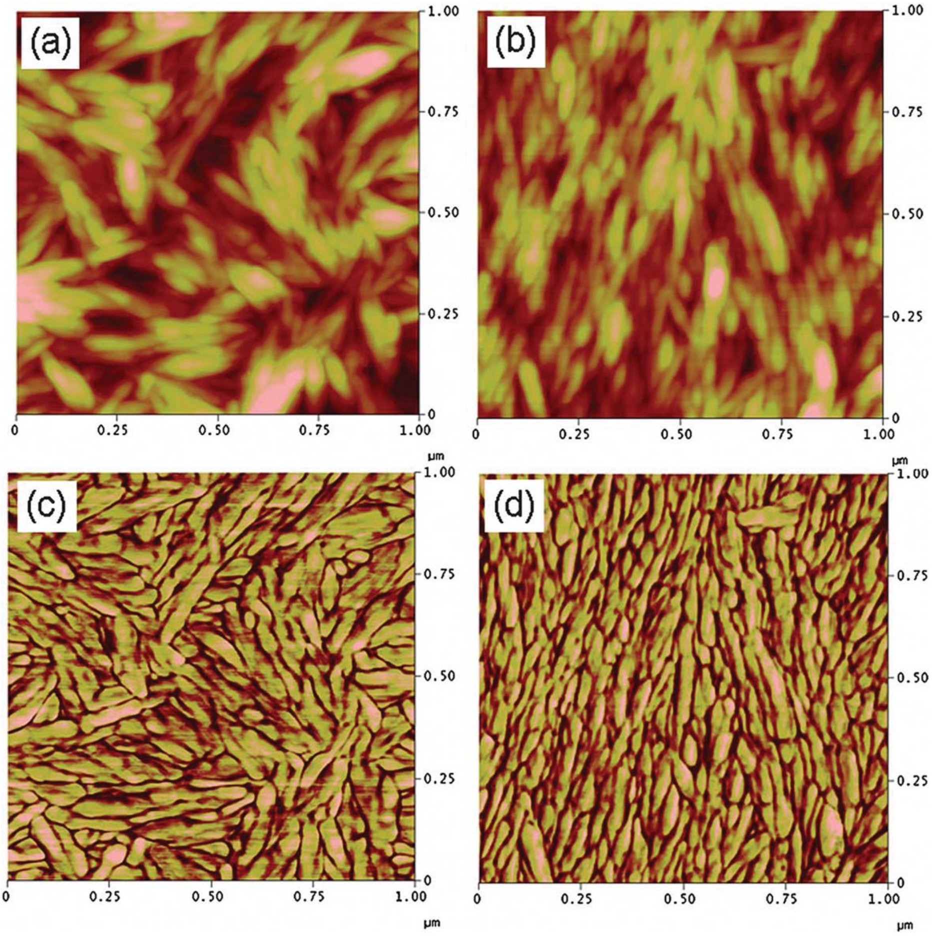


Figure 18. 1 μm × 1 μm AFM height (a and b) and respective phase images (c and d) of CNC films produced with the Langmuir–Schaeffer technique (a and c) and the convective-shear assembly setup using silica substrates with pre-adsorbed PEI (b and d). Images b and d are placed in such a way that the vertical direction was parallel to the withdrawal direction. A withdrawal speed of 8.4 cm h^{-1} and 2.5% CNC concentration were used.[38] © The Royal Society of Chemistry. Reproduced by permission of The Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.

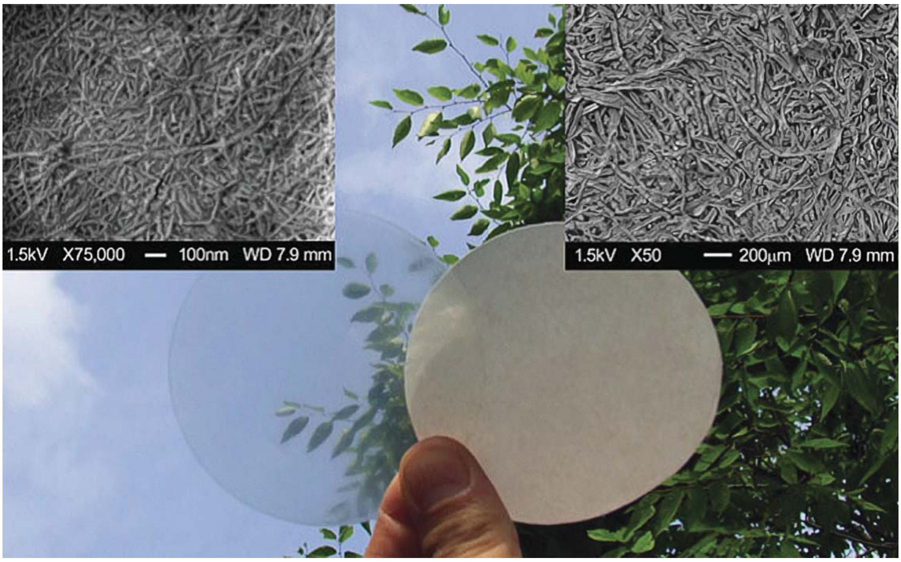


Figure 19. Optically transparent nanofiber paper (left) composed of 15 nm cellulose nanofibers (upper left, scale bar in inset: 100 nm) and conventional cellulose paper (right) composed of 30 μm pulp fibers (upper right, scale bar in inset: 200 μm).[9] © John Wiley & Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

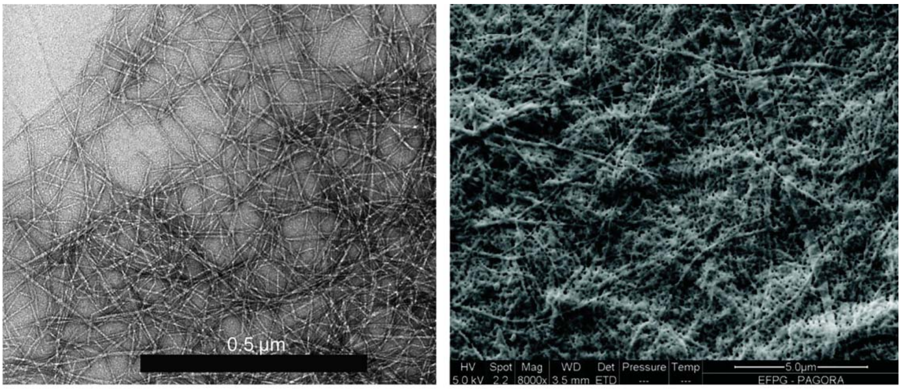
The authors reported a transverse Young's modulus, hardness, and coefficient of friction of 8.3±0.9 GPa, 0.38 ±0.03 GPa and 0.51 ±0.23 GPa, respectively.

Another significant property is the ability of CNCs to self-organize into cholesteric liquid crystal phase, and this has attracted significant interest resulting in formation of multifunctional thin films.[39]

A remarkable property of nanofibers and especially cellulose CNCs is that light scattering can be suppressed (Fig. 19). This fascinating phenomenon was recently demonstrated by Nogi et al.[9] by developing optically transparent cellulose nanofiber (55 μm in thickness) paper that possibly could be a glass substitute in some applications. The utilization of cellulose nanocrystals is expected to expand in the years to come.

On the other hand, during the last decade, bio-based nanofibrillar cellulose has been investigated and essentially used in nanocomposites because of its good reinforcement abilities.[40–41] Nanofibrillar cellulose or nanofibrillated cellulose (NFC), which was first named as microfillated cellulose or microfibrillar cellulose (MFC), is a nanomaterial obtained from different cellulose sources (Fig. 20). It is well known for its surface area which is highly expanded in volume formed by a web-like structure and composed of interconnected fibrils.[42]

NFC that initially derived from wood pulp through a process of high-pressure mechanical homogenization was developed by Turbak et al.[43] Cellulose fibers were pressurized to disintegrate the structural subunits and microfibrils which are 10–100 nm in thickness and several tens of microns in length depending on the nature of source. This process results in an aqueous solution of suspended NFC with gel-like behavior exhibiting pseudoplastic and thixotropic characteristics.[44]



(a) (b)

Figure 20. (a) TEM;[46] (b) SEM.[47] Images of NFC extracted from wood pulp by mechanical processing. © The American Chemical Society. Reproduced by permission of The American Chemical Society. Permission to reuse must be obtained from the rightsholder.

The major issue for industrial scale production has been the very high energy needed to fabricate NFC with high yielding in multiple cycles from the mechanical homogenizer. Therefore, alternative methods including chemical and enzymatic pretreatment or a combination of both were recently put forward in order to assist defibrillation and mechanical shearing. An enzymatic hydrolysis, targeting non-crystalline cellulose in wood pulp, before feeding into the homogenizer greatly contributed to the eco-friendly production of NFC. A relatively inexpensive method, chemical pretreatment, was also combined with mechanical shearing. Such pretreatment includes carboxymethylation and the oxidation of cellulose fibers; both methods provide charged groups into the fiber facilitating homogenization.[7,44]

Some proposed applications for NFC are food packaging and paper and board applications, including nanocomposites for films showing enhanced barrier characteristics. Nutritional, biomedical, and pharmaceutical applications and also cosmetic and hygiene/absorbent products are anticipated uses of NFC.[7,45]

3. Natural cellulose for conventional membranes: An overview

3.1 History of solution processes used to make cellulose membranes

People have been trying for thousands of years to use cellulose products for practical purposes; from the ancient Egyptians making papyrus to the use of straw and stubble as reinforcing fiber for bricks and other building materials. Cellulose is a polysaccharide with a particularly highly crystalline structure due to strong hydrogen bonding between hydroxyl groups, which makes it very difficult to dissolve with traditional solvents and also makes the polymer degrade before melting. Therefore, casting by traditional methods is not possible and the relatively low degradation temperature prevents melt processing.[2,48] Hudson and Cuculo provide an excellent review of the history of the process of dissolving cellulose materials for use in varied purposes.[4]

Following Turbak's[49] suggestion Hudson and Cuculo[4] summarize the dissolving of cellulose into four main categories:

1. Cellulose as a base
2. Cellulose as an acid
3. Cellulose complexes
4. Cellulose derivatives

These categories will be useful for this portion of this review, as it is useful to categorize the solutions of cellulose and then discuss their resulting membranes in later sections.

3.1.1 Cellulose as a base

Cellulose reacts as a base and forms a solution because the hydroxyl groups on the glucoside units are relatively easily ionized by strong acids or Lewis acids under various conditions. Sulfuric acid will dissolve cellulose at acid concentrations above 75%, phosphoric acid dissolves cellulose at concentrations of 81–85% and 92–97%, nitric acid dissolves cellulose at 75.9% with nitration occurring at the same time making another useful material nitrocellulose. Hydrochloric acid dissolves cellulose at 40–42%. Trifluoroacetic acid can also readily dissolve cellulose, but with significant hydrolysis. Each of the above acids will hydrolyze cellulose to one extent or another. The issue is a balancing of conditions to minimize significant hydrolysis.

The use of Lewis acids (large cations) also has been investigated using water as the carrier and primary solvent, following the lyotropic series Zn>Li>Ca>Mg>Mn>Ba>Na>NH_4>K. The most favorable counterions are those of low charge or large size such as I^-, CNS^-, HgI_4^-, and ZnO_2^-. These negative ions provide a steric opening effect, holding the cellulose chains apart. Later work by Hudson and Cuculo[50] used these Lewis acids combined with a liquid amine to provide another mechanism for solvation.

3.1.2 Cellulose as an acid

The hydroxyls of cellulose are deprotonated with a strong base to form a salt that is then soluble in water. Other concentrations of the base are sufficient to swell the cellulose to allow dissolution by other solvents without the formation of a salt compound. Thus 8–10% NaOH causes the maximum swelling of cellulose, whereas about 18% will form sodium cellulosate compounds. Other inorganic bases, potassium and lithium hydroxide, have also been used. Temperature is important as well; colder conditions give more swelling and dissolution. Urea or thiourea has been used to enhance the solubility of cellulose with 8–10% NaOH solutions. Hydrazine has been used at high temperatures and pressures to dissolve cellulose as well.

Using organic bases alone as a solvent for cellulose also have been studied. Quaternary ammonium hydroxides are very effective for unlimited swelling of the cellulose structure leading to complete dissolution. Other studied Lewis bases have been aliphatic and cycloaliphatic amine oxides, leading to the most effective commercially used material N-methylmorpholine N-oxide (NMMO), to give commercial solutions of cellulose. Solvation is accomplished by the rupture of hydrogen bonds between the cellulose chains, and then reformed within individual chains. Methylamine in dimethyl sulfoxide also has been used to dissolve cellulose of low molecular weight or low crystallinity.

3.1.3 Cellulose complexes

The use of various metal complexes to dissolve cellulose is well known. They have been extensively reviewed in the past by various authors including Jayme et al.[51] Turbak[49] discusses problems with using these systems, particularly recovering toxic metals, overall economics, and film/fiber properties that are inferior to the viscose process.

Jayme[51] groups the metal complexes under the headings of

a) metal-amine complexes
b) metal-alkali complexes with tartaric acid, and
c) metal-alkali complexes.

Of these, the metal-amine complexes are most prominent. Cuprammonium hydroxide is one of the most important. Ammoniacal solutions of copper hydroxide have been used since the 1800s to dissolve fibers such as cotton, linen, and silk. Cupriethylenediamine (Cuen) is another important solvent for cellulose, formed by dissolving copper hydroxide in ethylenediamine. However, these solutions oxidize easily and are degraded in the presence of air. Other metals have been used to dissolve cellulose with ethylene diamine: cadmium, cobalt, zinc, and nickel are examples. Metal tartrate complexes, including iron tartrate in sodium hydroxide, and lastly, metal-alkali complexes, including sodium zincate solutions have been attempted.

Turbak[49] states that the possible use of organic complexes is extremely limited. Examples are 16.5% solution of methylamine in dimethylsulfoxide, and bis(hydroxypropyl) disulfide.

Dawsey et al.[52] wrote an important literature review describing how LiCl in N, N-dimethylacetamide can dissolve cellulose; it is discussed in a similar way to the Hudson and Cuculo[4] review, and then concentrates on the unique aspects of the LiCl/DMA process.

This process gives little to no degradation and can also dissolve proteins, polyamides, and chitin. A laboratory procedure was developed to dissolve cellulose in solutions at levels up to 17%. The dissolution mechanism is discussed, along with solvent specificity (LiCl is the only metal salt that led to dissolution as of the date of their review). Other solvent systems using LiCl that are effective are N,N-dimethylacetamide, and N-methyl-2-pyrrolidinone (NMP). Solution properties including viscosity variation over time, blends of cellulose with other polymers using this solvent system, and using this solvent system as a reaction medium for derivatization of cellulose were also discussed.

3.1.4 Cellulose derivatives

Solubilizing cellulose can be done by reacting the cellulose with another substrate and then dissolving the reacted cellulose in a common solvent. Turbak[49] discusses esters and ethers that have numerous commercial uses, but only the acetate and nitrate esters have been used to produce regenerated cellulose products. These derivatives can be either stable or unstable; the unstable ones are used as an *in situ* intermediate as part of the process to regenerate a cellulose material. These will be discussed further later in this review.

3.2 Types of solution processes used to make cellulose membranes

3.2.1 Aqueous base

Kamide et al.[53] and Kamide[54] succeeded in dissolving and characterizing cellulose samples completely using 8–10% wt.% aqueous solutions of sodium hydroxide at low temperatures. Cao and Tan[55] have continued the study of this type of cellulose solution to prepare nicrocellulose membranes from these cellulose solutions and study their physical properties. Various kinds of natural cellulose were treated with enzymes, and then dissolved in about 9% NaOH solutions. The key aspect is the enzyme treatment before the solution process, because it degrades the cellulose to lower molecular weight species.

The aim of the Cao study[55] was to prepare regenerated cellulose membranes from cellulose in aqueous NaOH, using an aqueous sulfuric acid solution as coagulant, and then to investigate the morphology, structure, and physical properties of the regenerated membranes.

The preparation of the membranes consisted of enzyme treatment to prepare first a cellulose sample that is alkali soluble and then dissolving the cellulose in the aqueous sodium hydroxide solution, casting onto glass plates, and immersion in the coagulant solution. Clearly the NaOH reacts with the cellulose to form a soluble "salt," where the cellulose is acting as an "acid." The addition of sulfuric acid then regenerates the cellulose from solution.

The membrane characterizations involved acid hydrolysis, and HPLC to check for carbohydrate composition, degrees of polymerization were determined using viscometry of a copper ethylenediamine solution, scanning electron microscopy, X-ray analysis to find crystalline forms, Fourier transform infrared spectroscopy, tensile testing of the porous membranes, and water flux and permeability. Some of the most interesting results were in the X-ray analysis (Fig. 21) and the SEM pictures.

The X-ray analysis shows a transformation of structure from the cellulose I crystalline structure[56] to a cellulose II crystalline form.[56,57] This transformation is typical for a cellulose solution that is coagulated, transforming the cellulose from the naturally occurring I form, to the II form.[51,58]

The SEM pictures (Fig. 22) show the micro-porous structure of the resulting membranes, both at the surface of the coagulant and at the glass fracture surface. The pore size is larger at the free surface (left), than that on the glass contacting surface (right). The preparation conditions of the membrane greatly affect the resulting porous nature of the membrane. In their method, only one side of the membrane is touching the coagulant solution, so the coagulant must therefore move through the porous film to coagulate the material contacting the glass.

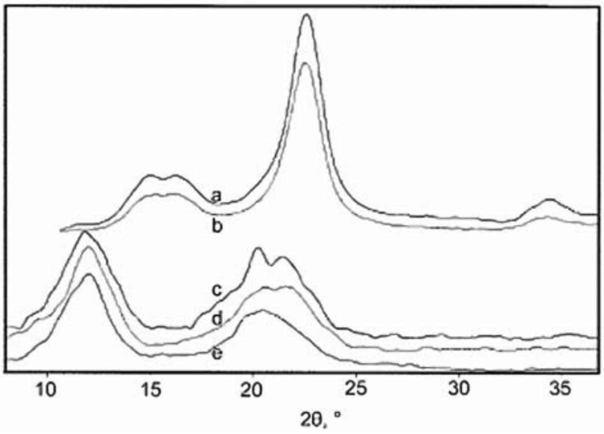


Figure 21. X-ray diffraction patterns of (a) alkali soluble cellulose, (b) the softwood pulp, (c–e) the membranes coagulated with 20, 5, and 2% H_2SO_4 concentration of coagulant solution.[55] © John Wiley and Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

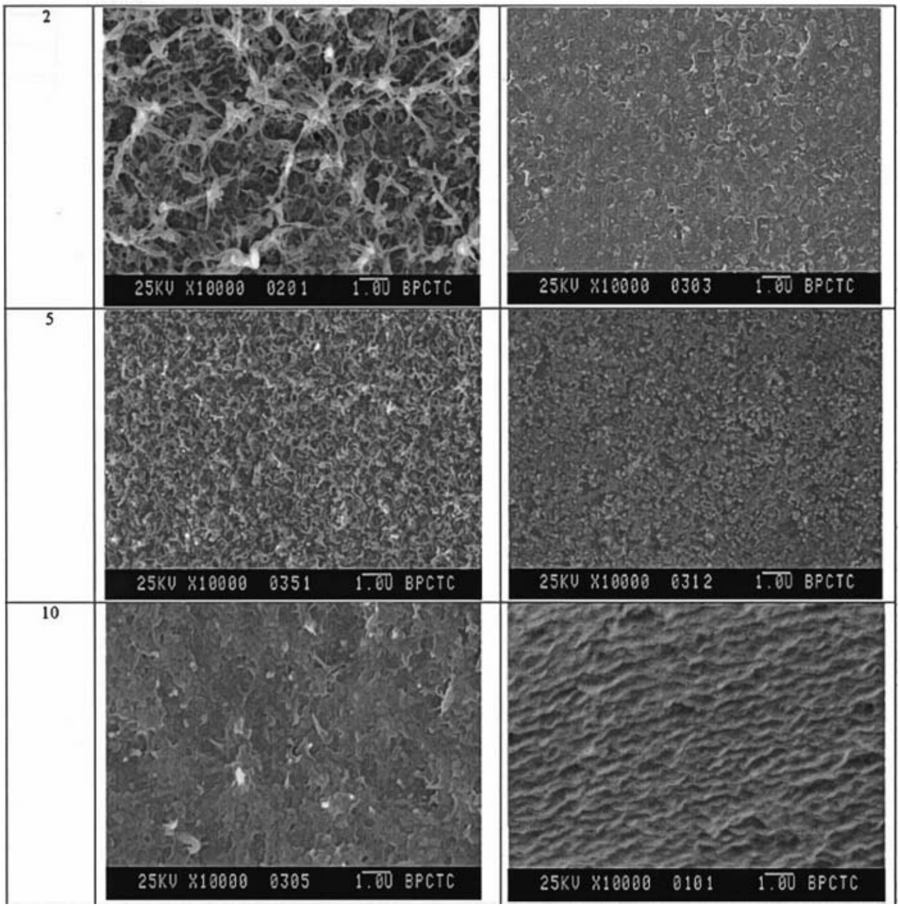


Figure 22. SEM photographs of the membranes with various sulfuric acid levels in the coagulant.[55] © John Wiley and Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

This porous structure is obtained from the regeneration method—the ions holding open the structure while the coagulation and washing removes the ions from the cellulose. Unfortunately, the article does not say how they dehydrate the membranes to take the SEM pictures.

The tensile tests in Fig. 23 show an increase in the properties, with an increase in sulfuric acid concentrations of the coagulation solution up to a maximum at 10%, with a modulus of 46.62 MPa, and 14.32% elongation at break. These results show that a strong membrane results, with a cellulose II crystalline structure and a micro-porous structure.

Cuissinat and Navard published a series of useful papers studying the dissolution of cellulose, in NMMO and water mixtures,[59] NaOH/water and minor additives,[60] various plant fibers in NMMO/water and NaOH/water compared,[61] and lastly, cellulose materials in ionic liquids.[62–63] First, the modes of dissolution were discussed as a foundation. There are 5 modes in their model:

1. Mode 1: Fast dissolution by disintegration into rod-like fragments.
2. Mode 2: Large swelling by ballooning, and then dissolution of the whole fiber.

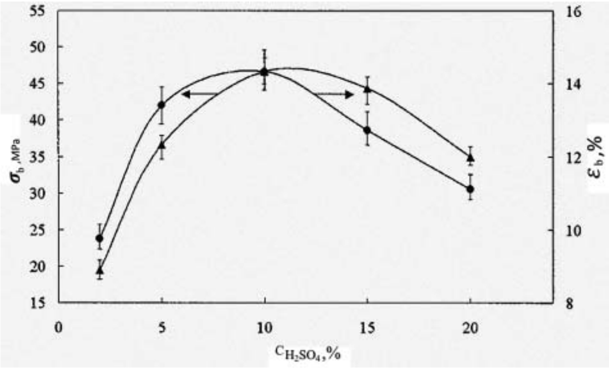


Figure 23. Tensile strength (MPa) and elongation at break (%).[55] © John Wiley and Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

3. Mode 3: Large swelling by ballooning, and partial dissolution of the fiber, still keeping its fiber shape.
4. Mode 4: Homogeneous swelling and no dissolution.
5. Mode 5: No swelling or dissolution.

Part 2 of the series[60] is useful to help understand the nature of the dissolution with NaOH (7–9%) in water. It is shown by their work that NaOH-water mixtures with or without additives are not very good solvents for cellulose. Using these solvents systems does not completely dissolve the cellulose fiber. Because of this problem, using NaOH will not be very useful for manufacturing membranes unless they are pretreated by enzymes in the procedure used by Cao[55] discussed earlier in this review.

A micrograph of some swollen fibers illustrates the ballooning of cellulose and the areas that do not swell or later dissolve. The swollen fiber is observed easily, as are unswollen sections. A Borregaard fir tree pulp was used for this picture (Fig. 24), and it is clear that the 7.6% NaOH solution at −5°C does not give uniform swelling nor dissolution. Clearly this solvent system is inadequate for membrane preparation. The best they could do was mode 4 which is homogeneous swelling with no dissolution.

3.2.2 NMMO – Lyocell process

N-methylmorpholine N-oxide (NMMO) is currently the most commercially used solvent cellulose. However, the manufacturing process is rather dangerous due to the instability of NMMO, and the process is relatively expensive. A relatively recent review by Fink et al.[64] describes the use of NMMO to dissolve cellulose to manufacture fibers and blown films (membranes), currently called the Lyocell process. This process is characterized by the following steps:

1. Preparation of a homogeneous concentrated solution of the starting cellulose in a NMMO- water mixture.
2. Extrusion of the highly viscous spinning dope at elevated temperatures through an air gap into a coagulation bath.
3. Coagulation of the cellulose fiber in the precipitation bath.
4. Washing, drying, and post treatment of the cellulose fiber.
5. Recovery of the NMMO from the precipitation and washing baths.[64]

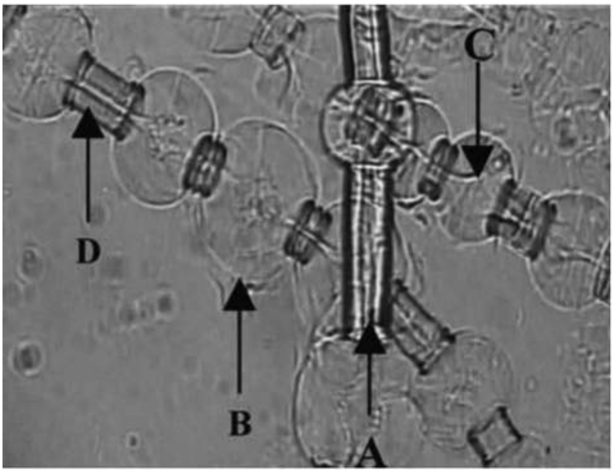


Figure 24. Swelling by ballooning in aqueous NaOH solutions (optical microscopy, transmitted light): (A) nonswollen fiber, (B) balloon, (C) surrounded by membrane, and (D) a section.[60] © John Wiley and Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

These steps are modified to blow a film into a coagulation bath to manufacture films and membranes for various uses. This review goes into the details of the solvation process, and the structure of the cellulose/NMMO solutions. The process for making fibers is summarized in the following schematic (Fig. 25).

This process involves temperatures between 90–120°C, raw material amounts of 8–20% cellulose, 75–80% NMMO, and 5–12% water along with various additives required for the system. The pulps used for this process have a lower DP than those utilized for the viscose process.

As shown in Fig. 26 SEM pictures of the fracture surface of each of the fibers are even more interesting.

Clearly the fiber made with the NMMO process is more uniform and has clearer fibrils within the fiber structure. Likewise the authors discuss modifying the process to make blown films. The process is essentially extruding the dope of cellulose in the

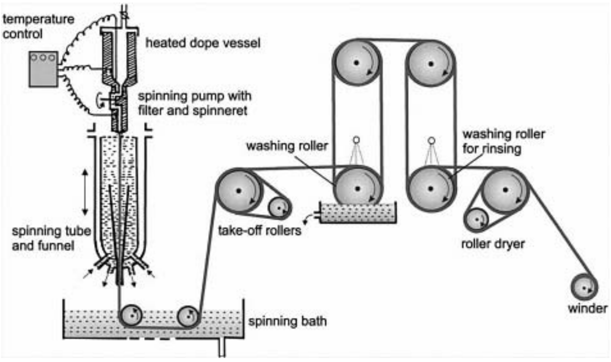


Figure 25. Scheme of the dry jet–wet fiber spinning process for cellulose-NMMO solution.[64] © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

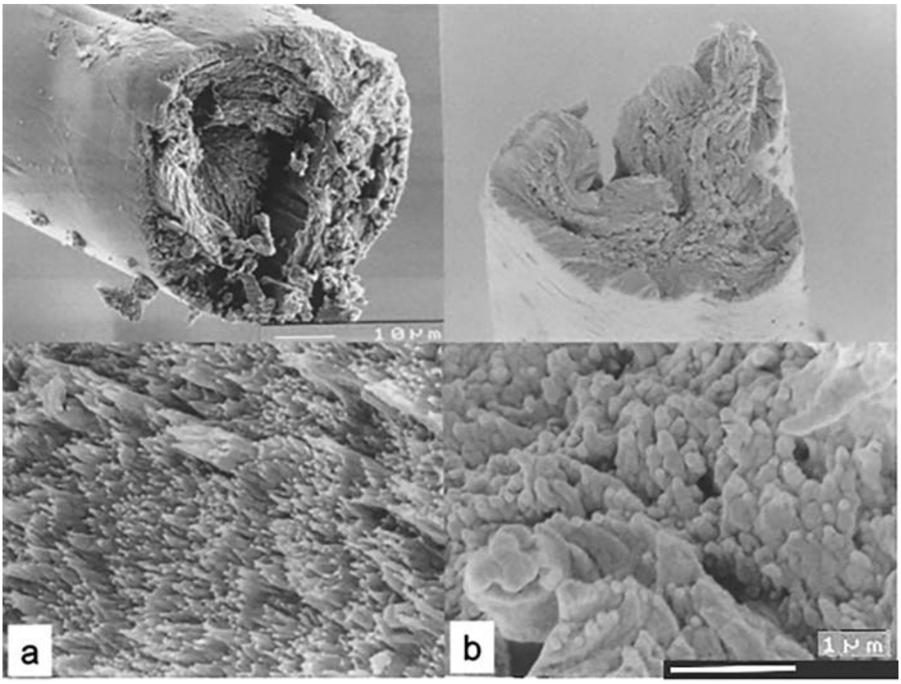


Figure 26. SEM Micrographs of fracture surfaces: (a) NMMO; (b) viscose.[64] © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

NMMO solution through an extruder at 80–100°C to a circular blow nozzle directed downward into an air gap, where the tube can be drawn in the machine direction and blown up transversely, and then into a coagulation bath containing water which contacts both the inner and outer sides of the blown film, as seen below in the schematic of this process (Fig. 27).

Several studies have been done to explore the dissolution process of individual fibers in NMMO and water at various concentrations. An earlier paper by Cuissinat and Navard[59] dealt with the study of the dissolution of cellulose using NMMO and water. In this paper, three native fibers are studied—one bleached cotton, and two wood fibers, Buckeye VFC (refined pine pulp), and Borregaard VHF (treated fir pulp). The NMMO was blended with water and 13% water was shown to be the ideal concentration for the best dissolution of cellulose.

This study revealed the mechanism of the dissolution of cellulose materials in NMMO: essentially the fibers swell, and then disintegrate into soluble pieces, and they call it mode 1. The most effective range for solubilization was between 13 and 17% water to form the spindles (Fig. 28). For 19–23.5%, swelling by ballooning takes place before dissolution. Above 25% water, swelling does occur into ballooning, but the process stops there, with no dissolution.

The disintegration of the fiber into pieces is clearly visible in the above micrograph. No visible swelling occurs before the break up takes place. The micrograph in Fig. 29 shows a swelling process that takes place with water at 23.5%. While at 17% water Mode 1 is the mechanism for dissolution, at 23.5% it is mode 2.

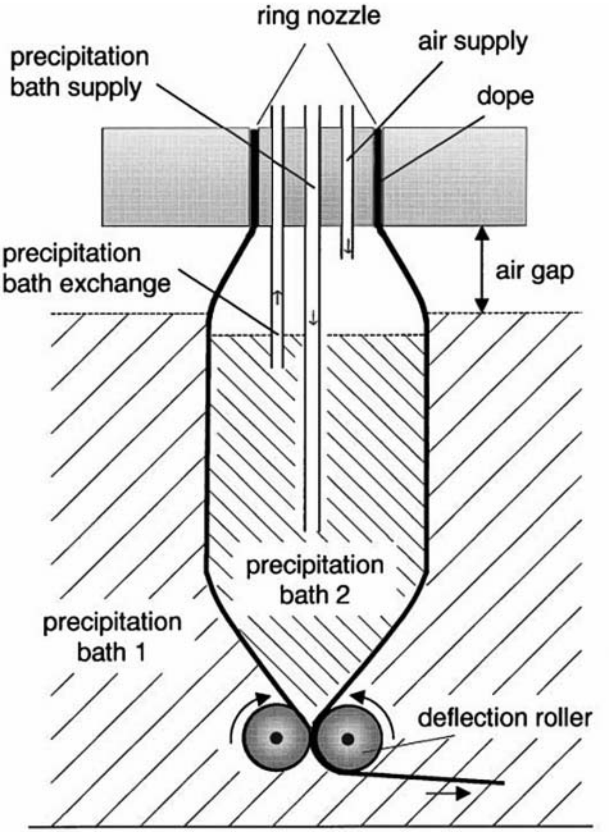


Figure 27. Scheme of the blow extrusion process for cellulose film formation.[64] © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

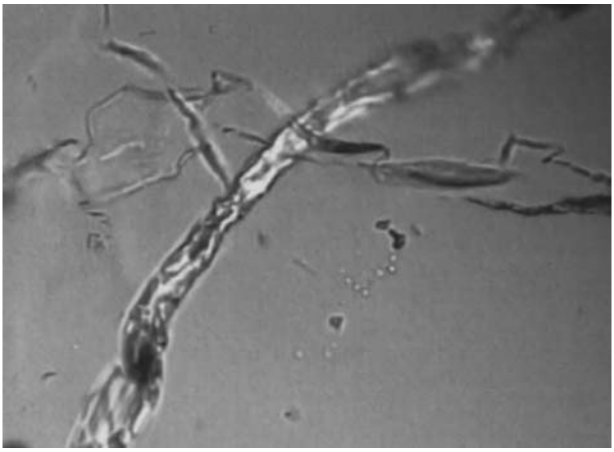


Figure 28. Borregaard fiber swollen in 17% water/NMMO (transmitted light, optical microscopy).[59] © John Wiley and Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

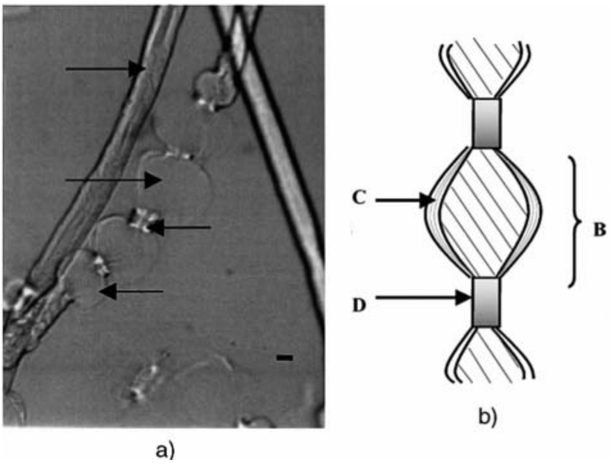


Figure 29. (a) Native cellulose swollen fibers (Borregaard fiber in NMMO – water at 23.5%, optical microscopy in transmitted light). (A) non-swollen fiber; (B) balloon; (C) membrane; (D) non-swollen section between two balloons. (b) Schematic drawing of a swollen fiber of native cellulose. (B) Balloon; (C) membrane; (D) non-swollen section between two balloons.[59] © John Wiley and Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

Understanding this mechanism of swelling and then dissolution is important to understand the reverse process that would occur with casting and coagulation of membranes. For membranes to form properly, a film forming mechanism that enables the polymer chains to begin sticking together by intra- and intermolecular forces upon the removal of solvents or dehydration is needed.

Table 2 (below) shows a good summary of this phenomenon with various water concentrations. Water levels below 24% lead to dissolution. At levels above 24%, swelling does occur but no dissolution occurs, and the process essentially stops.

A further study by the same authors,[61] examined 5 different plant fibers, to see which dissolve well in NMMO/water solutions and at what concentrations of water, compared to NaOH solutions. Table 3 (below) summarizes their results.

One variety of Ramie dissolves well up to 23.5% water in NMMO, but not in a NaOH solution. Two varieties of Flax dissolve at levels up to 19%, but not in a NaOH solution. Sisal,

Table 2. Different swelling and dissolution mechanisms for cotton and wood fibers in NMMO – water mixtures at various water contents.[61]

Cellulose	NMMO/water 17%, 90°C	NMMO/water 19% 90°C	NMMO/water 20% 90°C	NMMO/water 23.5% 90°C	NaOH/water 7.6% −5°C
Ramie (INRA)	Mode 1	Mode 1	Mode 1	Mode 1	Mode 4
Ramie (Innsbruck)	Mode 4	Mode 4	Mode 4	Mode 4	Mode 4
Flax (Innsbruck)	Mode 1	Mode 4	Mode 4	Mode 4	Mode 4
Flax (A&F Innovations)	Mode 4	Mode 4	Mode 4	Mode 4	Mode 4
Flax (Frauhofer IAP)	Mode 1	Mode 1	Mode 4	Mode 4	Mode 4
Sisel (A&F Innovations)	Mode 4	Mode 4	Mode 4	Mode 4	Mode 4
Abaca (A&F Innovations)	Mode 4	Mode 4	Mode 4	Mode 4	Mode 4
Hemp (A&F Innovations)	Mode 4	Mode 4	Mode 4	Mode 4	Mode 4

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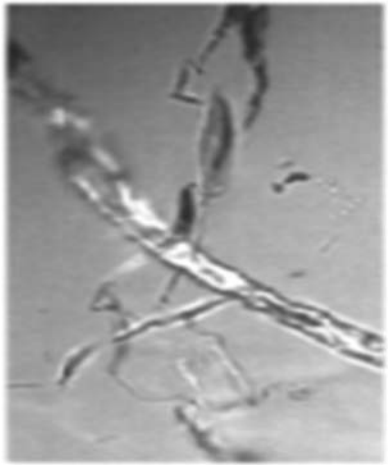
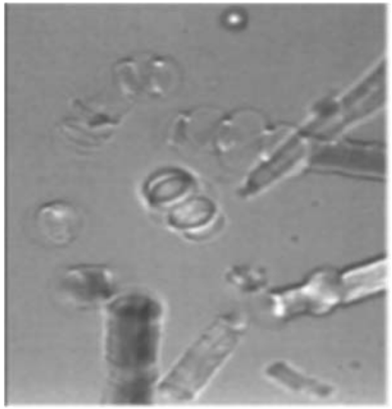
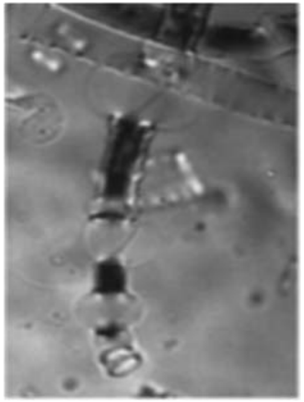
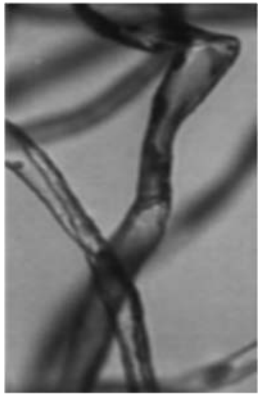
Table 3. Swelling, dissolution modes for raw plant fibers in aqueous solvents.[59]

Content of water	<17%	19 – 24%	25 – 35%	>35%
Swelling and Dissolution Mechanism	Dissolution by disintegration in spindle (Mode 1)	Swelling by ballooning, dissolution (Mode 2)	Swelling by ballooning, no dissolution (Mode 3)	Homogeneous swelling, no dissolution (Mode 4)
10 μm •–• SEM Picture	Wood fiber 	Wood fiber 	Wood fiber 	Wood fiber 

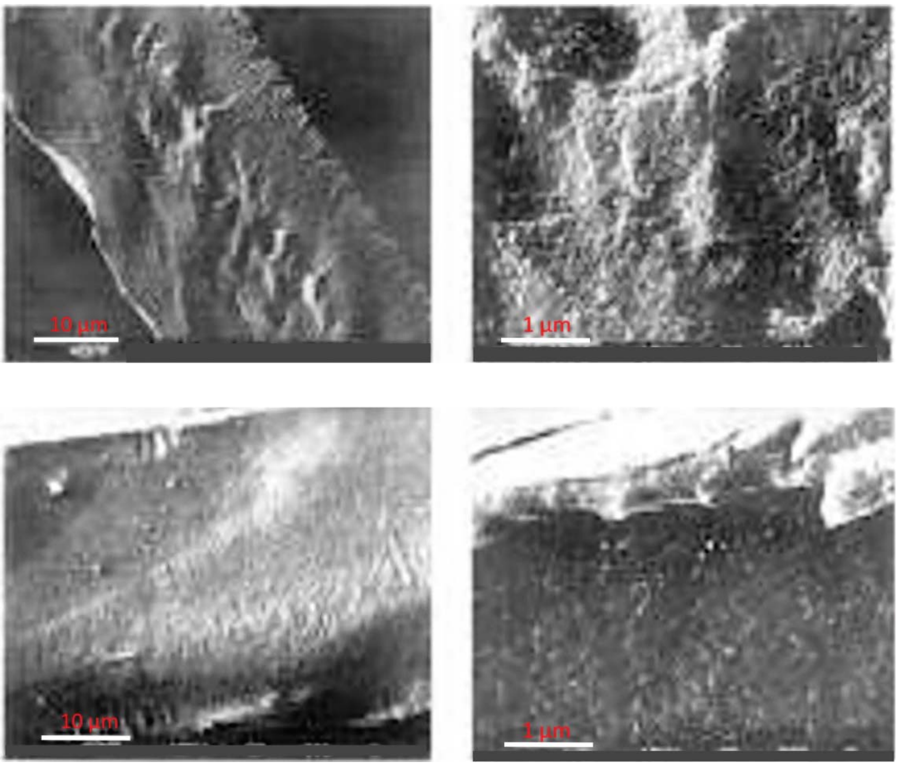


Figure 30. SEM photographs of cellulose membranes with different pulps and conditions.[65] © John Wiley and Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

Abaca, and Hemp do not dissolve in either solution (NMMO or NaOH at any level) despite swelling of the fibers. When the fibers are refined Abaca and Sisal do dissolve in Mode 1 at 17% water, and then mode 2 up to 23.5%. Obviously, the refining process breaks up some of the bonds holding the fiber body together through either chemical or mechanical means, and yet the mode of refining is not mentioned in this article.

Khare et al.[2] studied the preparation and characterization of dense and porous cellulose films (membranes) from a NMMO solvent system. In the introduction, referrals are made to various papers discussing the study of cellulose films made from NMMO solution. Wu and Yuan[48] measured the gas permeability of dry and water swollen cellulose films. Zhang et al.[65] studied the permeation of proteins (BVA) through these kind of cellulose membranes. Zhang presented (Fig. 30) some interesting SEM pictures showing these membranes.

Zhang et al. concluded that not only the DP, but the type of cellulose pulp has a great effect on the membrane morphology and permeation properties.[65] Each of these studies involved the production of dense cellulose films, with no concern for the porosity of the resulting films. Khare et al.[2] documented their attempts to make porous cellulosic films and then compared the properties with nonporous cellulose films coagulated with water alone.

The previous articles referenced by Khare, some of which are described above,[48,65,66] did not report the resulting morphological structure of the films. Their experience showed their casting protocols generated dense (nonporous or nanoporous) films when they were dried.

The purpose of this investigation was to make porous cellulose films with morphologies suitable for ultra or micro filtration applications.

Their procedure for making the cellulose solutions was to dissolve 4–12 wt.% cellulose in a NMMO and water solution with DMSO as a cosolvent. To stabilize the solution at the bath temperature of 135°C, a small amount of propyl gallate was added. To cast the solutions, the solution was poured onto a glass plate and spread with a casting knife.

A typical process to make dense films consisted of the following steps:

a) The glass plate was immersed in a water bath to coagulate the films, and the film peeled off within five minutes.
b) The films were then washed twice in successive water baths for 30 minutes, and then overnight.
c) The resulting films were then very swollen with water, and when dried underwent significant shrinkage and deformation.

To minimize deformation they used two different drying methods:

1) After cutting off the ragged edges the wet films were placed on glass plates and allowed to dry in ambient conditions. Since the films adhered to the glass, they retained their flat shape upon drying. When the corners started peeling due to stresses, the glass plates were then placed in a water bath and the films quickly peeled off. Then the mostly dried (surface wet) films were dried further on paper towels, kept in a vacuum oven for 24 hours at room temperature, and then placed in a vacuum oven at 110°C for 24 hours.
2) The swollen films were transferred and stored in an isopropanol bath for 24 hours. Slow drying was then conducted by placing the films between two glass plates with a 1 mm gap into a vacuum oven for 48 hours at ambient temperature; the films were then placed in a vacuum oven at 110°C for 24 hours. Figure 31 presents SEM micrographs of these cellulose films.

To make the porous films the glass plate was placed in an acetone bath to coagulate the cellulose, then immersed in an acetone bath for 20 minutes, then an isopropanol bath for 20 minutes, and finally in a heptane bath for 24 hours. The films were then dried by placing

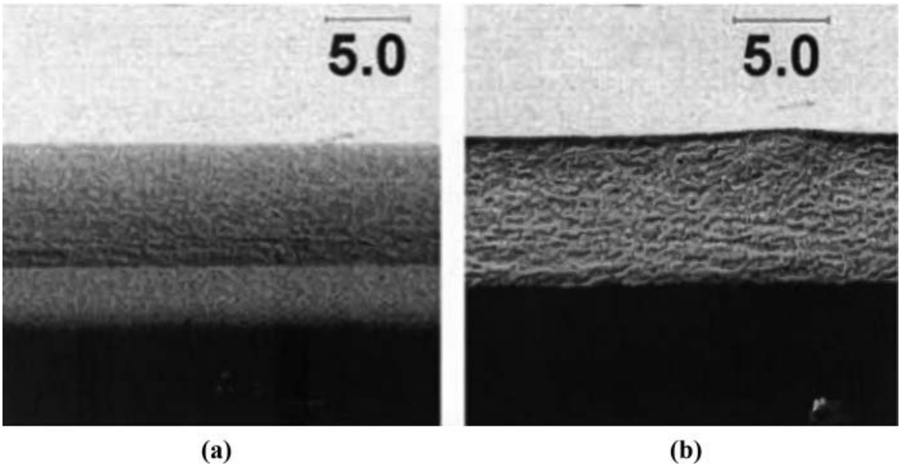


Figure 31. SEM micrographs of two identical dense films 4 wt% cellulose: (a) drying protocol (1); (b) drying protocol (2). No pores are observable in the cross sections.[2] © John Wiley and Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

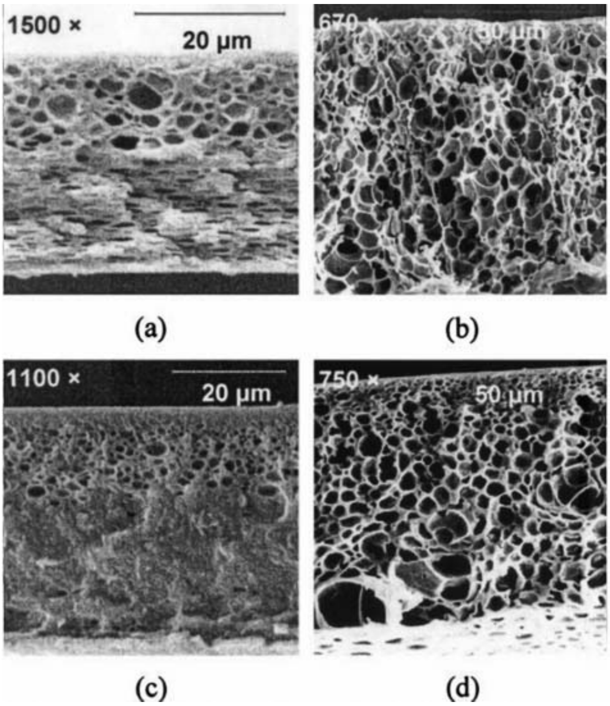


Figure 32. SEM micrographs of four identical dense films (a, b) 7wt% cellulose; (c, d) 10wt% cellulose. (a, c) with water recycle; (b, d) without water recycle during dissolution.[2] © John Wiley and Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

them on glass plates, first exposing them to dry ambient conditions, and then, placed in a vacuum oven at 80°C.

SEM pictures were taken with and without water recycle as part of the coagulation process, and the morphologies seen in Fig. 32 show the pore collapse due to water evaporation during drying.

Generating a porous membrane was successful using their protocol. These membranes were then investigated to see how the initial concentration of cellulose in solution affected the amount and size of pores in the membranes.

t is clear from Fig. 33 that the greater the starting cellulose concentration, the smaller the average pore diameter. This makes sense because when less solvent is available for swelling of the initial casting solution, a tighter mesh of cellulose chains results in the coagulated membranes, and the solvent exchange is efficient. The pores are smaller because the size is locked into place upon coagulation.

3.2.3 Metal–amine complexes

As discussed in the review by Hudson and Cuculo,[4] in these cases the cellulose acts as an acid, and the amine solvent combined with the metal complexing agent solubilizes the material. Jayme et al.[51] describe the use of these different materials to dissolve cellulose, mainly for fiber applications. Cuprammonium hydroxide is one of the most important, and

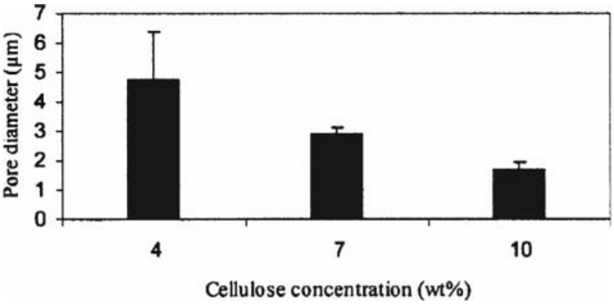


Figure 33. Influence of the cellulose concentration in the solution on the mean pore diameter.[2] © John Wiley and Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

ammoniacal solutions of copper hydroxide have been used since the 1800s to dissolve fibers such as cotton, linen, and silk.

3.2.3.1 Cuoxam (tetraaminediaquacopper dihydroxide) process. A process was developed for dissolving cellulose in a Cuoxam solvent, and making a useful membrane from these materials that had micro-porous properties. (A patent was applied for in Great Britain by Dunweg[67] with Akzo Nobel.) The virtue of this process is that there is a high compatibility of the regenerated cellulose made from Cuoxam with blood, and the market has been demanding membranes for purposes that contact with blood. This patent application describes a process to make micro-porous membranes in the form of flat films, tubular films, or hollow filaments that can be spun from Cuoxam solution. A polyether glycol is added to act as a lubricant/cosolvent to enable better flow in solution and better coagulation conditions, where the PEG is removed in the washing steps. The coagulant for one process was an aqueous acid solution, where sulfuric acid gave the best properties. In another process, dilute NaOH was used as coagulant. In their first example a 9.2% cellulose solution was used; then the PEG and water were added to make a final spinning solution of 5.1% cellulose. The spinning solution was then extruded through the annular slot of a hollow filament spinneret into an aqueous NaOH bath at 25°C. The characteristics of the hollow-filament fiber that resulted were:

External diameter: 260 μm
Internal diameter: 220 μm
Tensile strength: 18.1×10^3 cN/mm^2
Breaking elongation: 27.5%
Ultrafiltration capacity: 271 mL/m^{2}h.mmHg

In another example, the solution was coagulated into a dilute sulfuric acid solution at 30°C under similar conditions resulting in a hollow-filament membrane with the following properties:

External diameter: 329 μm
Internal diameter: 227 μm
Tensile strength: 13.3×10^3 cN/mm^2
Breaking elongation: 31.7%
Ultrafiltration capacity: 580 mL/m^{2}h.mmHg

Screening coefficient for albumin
Mw of 68000 100%
Transmembrane flow 1% of albumin
At 0.1 bar 580 mL/min.m^2

These results show the efficacy of using both types of coagulation baths; the dilute acid coagulation bath gave the best properties for the resulting hollow-filament membranes. These membranes can be effectively used for various medical applications, including plasmaphoresis and microfiltration.

3.2.3.2 Cuen (cupriethylenediamine) process. Cupriethylenediamine (Cuen) is another important solvent for cellulose, formed by dissolving copper hydroxide in ethylenediamine. However, these solutions oxidize easily and are degraded in the presence of air. Therefore, using these materials to cast membranes is not often studied. Similar to using copper to dissolve cellulose with ethylene diamine, other metals have also been used; cadmium, cobalt, zinc, and nickel are examples. Metal tartrate complexes include iron tartrate in sodium hydroxide. Lastly, metal-alkali complexes including sodium zincate solutions have been attempted.

However, studies of membranes formed with Cuen and other metal complexes with ethylene diamine have not been attempted often, since other more promising technologies have been used due to concerns for the toxicity of the heavy metals in this process.

3.2.4 LiCl / N,N-dimethylacetamide process

Matsuda and co-workers[68] used this process to make cellulose membranes and studied their physical properties. The coagulation solvents were THF or ethyl acetate. The properties of the membranes were compared with a Cuprophan membrane for hemodialysis, and the characteristics of the membranes were described based on the fabrication process and the membrane structure while swollen in water. Unfortunately, these articles are in Japanese, so a summary is all that is generally available. These authors then went on to study the solvation of cellulose in NMMO, which was discussed in an earlier section. Kim et al.[69] did a study using this system to make fibers using electro-spinning. They studied the effect of the temperature of the collector, the nature of the collector, and the post spinning treatment of the fibers such as coagulation conditions.

Other articles that utilized this process to make membranes were found. The authors used cellulose as a blend with another polymer to make a functional membrane. Blends will be discussed in the final section of this review.

3.2.5 Paraformaldehyde / dimethyl sulfoxide process

Johnson and Nicholson[70] developed a patent that describes the solvation of cellulose to make membranes using dimethyl sulfoxide (DMSO) and paraformaldehyde (PF). The examples given in the patent essentially involve solvation properties, the resulting solutions, and production conditions. It was determined that blends of polysaccharides also could be used when dissolved with the cellulose. The patent is essentially about the processing of this solvent system to dissolve cellulose and other polysaccharides.

In the work that led to this patent, Johnson et al.[71] describe more specifically their process and the results they achieved. Cotton linters and Kraft softwood pulp (57.5% yield, 12.6% Klason lignin) and neutral sulfite semi-chemical poplar pulp were dissolved in this system. Regeneration of dissolved cellulose (I) was accomplished by dilution with water or methanol.

Hydroxymethyl cellulose was isolated from solution I and characterized by its solubility, laser Raman spectroscopy, and formaldehyde analysis. The NMR spectra showed that this system contained several oxymethylene chains. This indicates this process forms cellulose derivatives to enable solubilization, so a membrane formed from this is probably a mixture of cellulose and hydroxymethyl cellulose. A later article by Swenson[72] uses the same process to dissolve cellulose, but it is clear from both Johnson's and Swenson's papers that the paraformaldehyde decomposes to form formaldehyde which then reacts with the cellulose to enable DMSO to dissolve it. Therefore, it derivativizes the cellulose to dissolve it, which is known because derivatives of cellulose have been solubilized in common solvents for over a century, for example, with cellulose forming nitrocellulose, that is easily dissolved, or forming cellulose xanthate in the viscose process.

He and Wang[73] used this process to dissolve cotton linters to form a cellulose membrane and then to study the membrane for physical properties. The solution was prepared by blending with PF and DMSO at 60°C for 30 minutes, 80–90°C for 1 hour, and at 115–125°C for another hour. The solution was then put under vacuum for 15 minutes and filtered to obtain a homogeneous solution. The membranes were cast with a lab caster through the phase inversion process and then washed with distilled water until free of solvents and then kept in distilled water for use. These membranes were tested WET, by measuring water flux using an ultrafiltration device. Measurement of ability to retain Glucosan T40 was then measured. Both were compared to the cellulose concentration of the casting solution to get the graph in Fig. 34.

From this figure it is clear that the water flux decreases sharply as the cellulose concentration increases to 4.5% and then remains relatively constant. The retention of Glucosan T40 increases with cellulose concentration. It is suggested that this is because the cellulose chains in solution exist in two states:

1) a macromolecular network formed by intermolecular interaction and macromolecular entanglement, and
2) a micelle aggregate formed by macromolecular entanglement and aggregation.

The evidence for these specific conclusions is not compelling in this paper, as it is clear only that when the water flux (flow through of water) decreases to a stable level, the

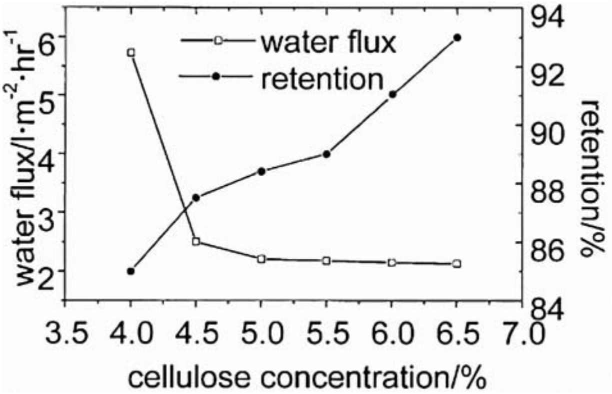


Figure 34. Dependence of water flux and retention on cellulose concentration.[73] © John Wiley and Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

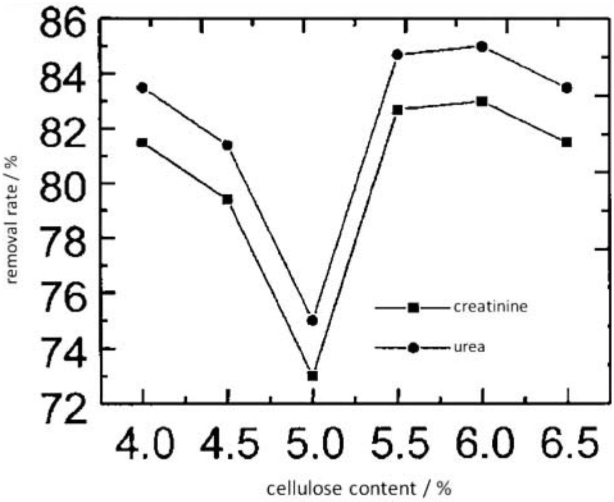


Figure 35. Dependence of removal rate of creatinine and urea based on cellulose concentration.[73] © John Wiley and Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

retention of Glucosan increases as the cellulose concentration increases. More relationships are developed comparing water flux and retention based on pre-evaporation time (which is not explained), and temperature of the bath. This relates to the evaporation of the solvent from the system, which does not relate much to reality because the membranes are washed thoroughly to remove solvents before testing. Figure 35 shows that the cellulose membrane has a high ability to remove creatinine and urea at the same level compared to a commercial polyacrylonitrile membrane during dialysis.

Based on these results it is suggested that this membrane may be useful to develop an artificial kidney.

3.2.6 Amines and metal thiocyanates process

Wertz et al.[74] in their recent book on cellulose describe that ethylene diamine and other amines effectively swell cellulose, without dissolving the cellulose.

Comparison of the structure of native cellulose with this complex in Fig. 36 shows the extent of rearrangement that occurs due to the interaction with ethylene diamine. Ions also interact with cellulose to cause swelling. The decreasing order of swelling for various cations and anions is displayed in Fig. 37.

Alkylamines effectively swell cellulose but not as well as ethylenediamine.[74,77] Cellulose also swells in ammonia, hydrazine, and tetramethylenediamine. Quaternary ammonium hydroxides form swelling compounds at intermediate concentrations, for example, trimethylbenzylammonium hydroxide at around 30% by weight.

Table 4 illustrates the effect of amine swelling agents on the (101) interplanar spacing (primary spacing of cellulose chains) of cellulose.

The most useful quantities from the above table are those of liquid ammonia, hydrazine, and ethylenediamine which have all been used as an ingredient to dissolve cellulose using an appropriate salt as shown in Fig. 36.

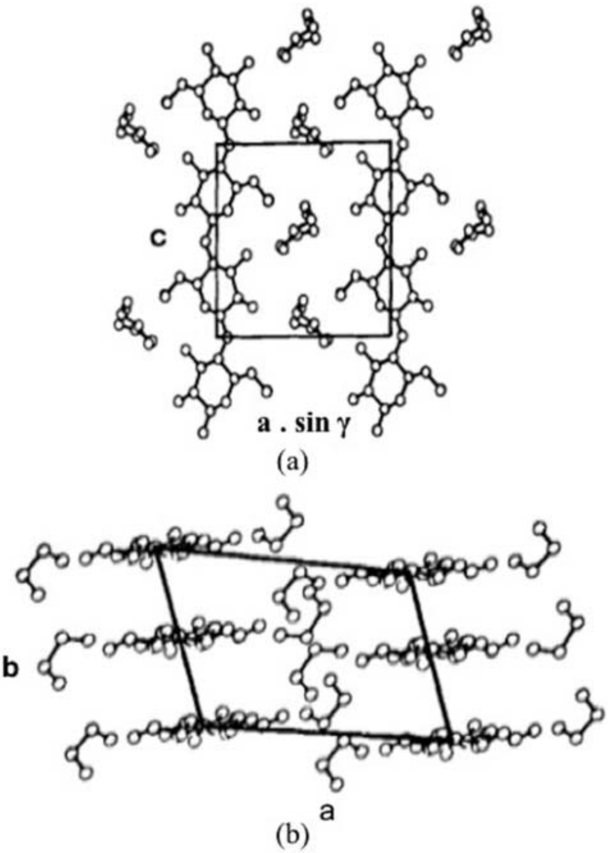


Figure 36. Structure of ramie cellulose I – ethylenediamine complex (a) ac sin γ projection; (b) ab projection.[75] © John Wiley and Sons. Reproduced by permission of John Wiley & Sons. Permission to reuse must be obtained from the rightsholder.

Hudson and Cuculo[4] used these amines and thiocyanate salts to dissolve cellulose. The first study of ammonia and ammonium thiocyanate was addressed by Hudson[50] in his doctoral dissertation, where ammonia and ammonium thiocyanate were used to make fibers, and a patent resulted from their work by Cuculo et al.[79] A blend of ammonium thiocyanate at 72.1 wt.% was made with ammonia at 26.5 wt.% and a small amount of water at 1.4 wt.%. The solutions were prepared at −12°C for about 6 hours followed by mechanical stirring of the mixture while it reached ambient conditions. Viscosity measurements were then done on the solutions to determine optimum levels of cellulose in solution. The optimum level

$$Zn^{2+} > Li^{+} > Ca^{++} > Mg^{2+} > Mn^{2+} > Ba^{2+} > Na^{+} > NH_4^{+} > K^{+}$$

$$SCN^{-} > I^{-} > CrO_4^{3-} > Br^{-} > Cl^{-} > NO_3^{-} > SO_4^{2-} > ClO_3^{-}$$

Figure 37. Order of decreasing swelling of cellulose.[76] © American Chemical Society. Reproduced by permission of American Chemical Society. Permission to reuse must be obtained from the rightsholder.

Table 4. Amine swelling agents and the interplanar spacing (d_{110}).[77–78]

Swelling Agent	d_{110} (Å)
Liquid ammonia	10.3–10.6
Methyl amine	14.67
Ethylamine	15.72
n-Propylamine	18.48
n-Butylamine	19.73
n-Amylamine	21.92
n-Hexylamine	24.85
n-Heptylamine	28.74
Hydrazine	10.3
Ethylenediamine	12.26
Tetramethylenediamine	14.65
Tetramethylammonium hydroxide	13.0
Ethyltrimethylammonium hydroxide	13.0
Benzyltrimethylammonium hydroxide	16.5
Dibenzyldimethylammonium hydroxide	16.5

was at 6% by weight cellulose in this solution, as it was desired to have good viscosities for fiber spinning. However, it was found that above 40°C ammonia would bubble out of the solution leading to loss of one of the components of this system. X-ray results indicated the crystal form of the cellulose after dissolving and spinning was cellulose II, after starting with cellulose I. It is not clear from the patent which experiments they did with films or membranes.

Later work by Liu (under the guidance of Cuculo),[10] involved a coagulation study of the ammonia / ammonium thiocyanate solvent system. This was to determine the best coagulant for spinning fibers from the solution. Gelled rods were made which were then brought in contact with a coagulating liquid. The movement of the coagulating liquid into the gel was then measured with a stereomicroscope and a calibrated scale to measure the depth of penetration. Methanol was determined to be the most effective coagulant for this system and gives the best fiber properties and also ease of dissolving (to remove) the ammonia and the ammonium thiocyanate. Their study essentially investigated gels in rods, and determined what gave the best throughput to thoroughly coagulate the system. Some of the solvents were too slow, resulting in small pores, as in the cases of 1-butanol, and 2-methyl-1-propanol and also resulted in hollow cored fiber.

Hattori (with the guidance of Hudson and Cuculo)[12] studied the dissolution of cellulose in hydrazine and thiocyanate salts, and compared them to the results of the ammonia/thiocyanate solutions mentioned earlier. The salts used were lithium, sodium and potassium thiocyanates. It was discovered that the dissolving power of the hydrazine system was less than that of the ammonia system. It was believed that this difference was because of the chemical reaction of hydrazine with ammonium thiocyanate that was used to liberate ammonia. It was discovered that the sodium thiocyanate dissolved the most cellulose in the hydrazine series. Lithium and potassium thiocyanates formed gels at room temperature, whereas the sodium salt remained a liquid. It was discovered that lithium thiocyanate in the ammonia system did not dissolve cellulose I at all, whereas it was effective to dissolve cellulose in hydrazine. This dissolution was effective even at room temperature. The maximum cellulose solubility of cellulose DP210 reached 18% (w/w) in hydrazine/sodium thiocyanate (76/24 w/w).

A follow up study was done by Hattori et al.[11] on dissolving cellulose in ethylene diamine/thiocyanate systems. Calcium thiocyanate was used, along with the previous salts (Na, Li, and K) used in the Hydrazine system. Solution viscosity measurements were performed on each system to determine ideal cellulose levels. It was discovered that calcium and lithium thiocyanates with ethylene diamine did not dissolve cellulose at all. Both sodium and potassium salts were effective in ethylenediamine at dissolving cellulose up to a level of 16%, and resulted in liquid crystal forms of the cellulose solution. It was determined that water was the coagulant giving the best quality cellulose. The making of fibers and films per se were not attempted in this study, as the material was coagulated in water, washed, dried, and X-ray analysis performed to see the resulting crystal structures. Cellulose II resulted from this procedure, again consistent with the use of other solution systems. Other coagulants, methanol, 2-propanol, and acetone resulted in primarily amorphous cellulose. A follow-up study was conducted by Frey et al.,[80] who further studied the dissolution mechanism of the ED/KSCN system. FTIR, DSC, and rheological measurements were used to document the changes in morphology on dissolution. Frey et al.[81–83] also did other studies to further characterize the ED/KSCN system for dissolution, and other physical properties of the dissolved cellulose.

Hyun Jik Lee[84] followed up the work with a study to optimize the amounts of KSCN in an ethylene diamine system to make usable fibers with good physical properties. It was discovered that the optimum percentage of each component was 65% ethylenediamine and 35% potassium thiocyanate. Furthermore, Onori and Kotek[85] discovered that fast cellulose dissolution in this solvent occurs upon heating above 80°C. Consequently, the freeze thaw-time consuming process was abandoned. Cellulose fibers produced by Hyun Jeek Lee had excellent mechanical properties as compared to commercialized cellulose fibers such as Lyocell and Rayon. Some membranes were also produced but only to check coagulation properties. Frey et al.[82] did dissolution studies, rheological testing of the solutions, and then filament formation studies with the solutions. Ethanol as a coagulant resulted in a swollen fiber that required further washing with ethanol to remove residual solvent. Methanol as coagulant resulted in solid filaments which broke easily during handling. In comparing Hyun Lee's results with Frey's it is likely that the latter's dissolution process (a freeze thaw process in a plastic bag) and spinning conditions may have affected the film's physical properties. The method used by Frey et al.[82] to make the films was clearly deficient as described. "Films were formed by spreading solutions on glass plates. Two layers of scotch tape at the plate edges were used to control the film thickness at 0.11 mm. Plates were immersed in coagulant for 30 min followed by 5 min of drying in ambient conditions before removing the film from the plate. Films were washed by reimmersing in coagulant up to two additional times." This method does not follow any standard protocol for film casting, and is not specific enough.

3.2.7 Ionic liquid solution process

Ionic liquids have found some success in dissolving cellulose to form useful materials. Ionic liquids have certain advantages that suggest their use:

a) a wide temperature range
b) excellent dissolution abilities
c) no real vapor pressure issues, and d) ease of recycling.

Swatloski et al.[86–87] did early studies of the dissolution of cellulose with ionic liquids. Ionic liquids containing 1-butyl-3-methylimidazolium cations ([C_4mim]+) were screened with a

Table 5. Solubility - Cellulose in ionic liquids.[87]

Ionic liquid	Method	Solubility (wt.%)
$[C_4mim]Cl$	Heat 100°C, 70°C	10
		3
$[C_4mim]Cl$	Heat 80°C, Sonication	5
$[C_4mim]Cl$	Microwave 3–5 sec pulses	25
$[C_4mim]Br$	Microwave	5–7
$[C_4mim]SCN$	Microwave	5–7
$[C_4mim][BF_4]$	Microwave	Insoluble
$[C_4mim][PF_6]$	Microwave	Insoluble
$[C_6mim]Cl$	Heat 100°C	5
$[C_8mim]Cl$	Heat 100°C	Slightly soluble

range of anions, from small Cl- to large noncoordinating ions ($[PF_6]$-) and also including Br-, SCN- and BF_4- anions. Table 5 summarizes their results.

In a typical procedure to prepare a 10 wt.% solution, 0.5–1.0 g of fibrous cellulose was placed in a glass vial and $[C_4mim]Cl$ ionic liquid (10 g) was added as a liquid at 70°C (i. e., above the melting point). The vial was then loosely capped, placed in a microwave oven, and heated with 3–5 s pulses at full power. Between pulses, the vial was removed, shaken, or vortexed, and replaced in the oven. A clear, colorless, viscous solution was obtained. ILs are heated with exceptional efficiency by microwaves, and care must be taken to avoid excessive heating which induces cellulose pyrolysis. Decomposition appears to be more rapid when in contact with the ILs than for isolated cellulose under equivalent conditions. Solutions containing up to 25 wt.% cellulose can be formed as viscous pastes in the chloride-containing ILs, although compositions between 5 and 10 wt.% cellulose are more readily prepared. The greatest solubility was obtained using $[C_4mim]Cl$ as the solvent. When high concentrations of cellulose ($>$10 wt.%) were dissolved in $[C_4mim]Cl$, the viscous solutions obtained were optically anisotropic between crossed polarizing filters and displayed birefringence."[87] Some basic analysis of the resulting materials was done including these SEM pictures (Fig. 38).

They clearly show the solvation ability of cellulose in these solvents, and the nature of the regenerated cellulose material. It is not clear from the article how the samples were prepared

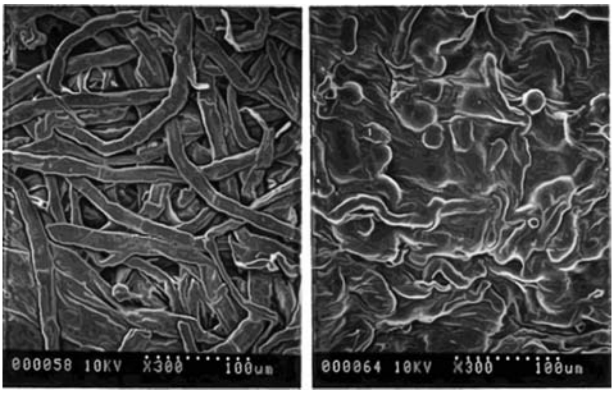


Figure 38. SEM micrographs of initial dissolving pulp (left) and cellulose regenerated into water (right).[87] © The American Chemical Society. Reproduced by permission of The American Chemical Society. Permission to reuse must be obtained from the rightsholder.

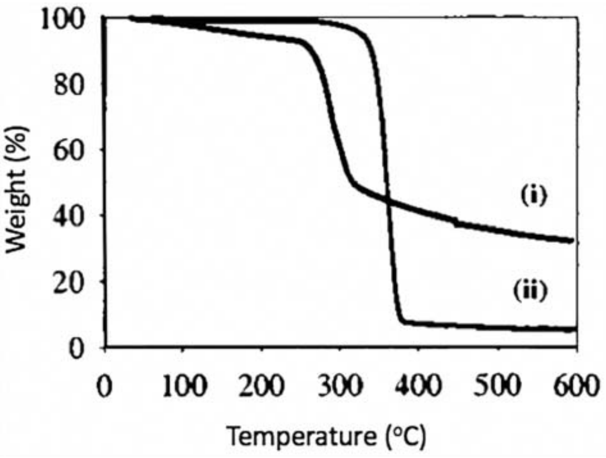


Figure 39. Thermal decomposition profiles of (i) regenerated cellulose and (ii) original dissolving pulp.[87] © The American Chemical Society. Reproduced by permission of The American Chemical Society. Permission to reuse must be obtained from the rightsholder.

for the SEM micrographs. The TGA results (Fig. 39) are quite interesting, as it shows a typical decomposition curve for cellulose pulp, and then a curve shifted downward in temperature, and a greater residue left behind on the heating of the regenerated material.

This indicates that the process has made the cellulose more difficult to decompose. This could be due to more crystalline regions on regeneration compared to the original, or some chemical crosslinks have formed within the system, or some other unknown factor.

Zhang and coworkers[88] found an ionic liquid material that could be used as a solvent for cellulose, and upon coagulation with water, gave a material with good mechanical properties. 1-allyl-3-methylimidazolium chloride (AMIMCI) was used at room temperature to dissolve various forms of cellulose. Microcrystalline cellulose, wood pulp, and cotton linters were used in this study. A known weight of cellulose sample was dispersed into 20 mL of the AMIMCI in a flask and the mixture was heated and stirred until fully dissolved. The solution was cast onto a glass plate, and coagulated with water to obtain a transparent regenerated cellulose gel. The cellulose gel was washed with running, distilled water and then dried at 60°C in a vacuum oven. The recovery of the ionic liquid was then accomplished by evaporating the water from the recovered coagulation liquid. The regenerated cellulose films were then cut into small pieces and dried at 70°C in a vacuum oven before use. SEM, FTIR, X-ray, and tensile testing were then performed on the dried film samples.

Figure 40 shows the differences in the X-ray diffraction pattern between the raw material pulp and the materials regenerated from this solvent system:

It is clear that the polymorph structure changes from crystalline cellulose I to a more amorphous one. This is consistent with results that come from studies with different solvents, which indicates that if one finds a good solvent for the cellulose, these solvents dissolve the materials in a similar fashion. The SEM pictures do not show any obvious structure, but they are consistent with other solvents that dissolve cellulose, and are then coagulated with water or other liquids and then washed to remove any residual solvents. The SEM pictures were done on the dried films, and no porous structures resulted. The main advantage of this process is that recycling the ionic liquid is an elementary process. The process is simply to

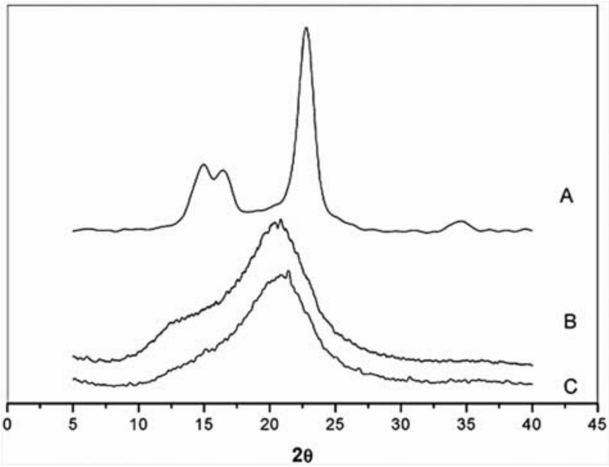


Figure 40. WAXD patterns of original and regenerated pulps. (A) Original cellulose (pulp); (B) regenerated cellulose from AmimCl/pulp cellulose solution (RC-P100); (C) regenerated cellulose from recovered AmimCl/pulp cellulose solution (ReRC-P).[88] © The American Chemical Society. Reproduced by permission of The American Chemical Society. Permission to reuse must be obtained from the rightsholder.

reduce the atmospheric pressure and distilling under vacuum to remove the water, leaving the ionic liquid behind. However, there was an issue of decrease in DP over dissolution time, showing that the ionic liquids do provide a venue for hydrolysis to occur.

There have been many recent investigations of the use of ionic liquids to dissolve cellulose. Cheng et al.[89] studied the solubility and dissolution rate of cellulose in two ionic liquids, [AMIM]Cl and {BMIM]Cl. A decrease of DP also occurred in this study. They showed the transformation of cellulose I to cellulose II structure, using X-ray analysis, consistent with Fig. 37.

Cuissinat et al.[90] used three different ionic liquids to study the differences and similarities between swelling and dissolution mechanisms of aqueous and nonaqueous systems. “Native and enzymically treated cellulose fibers (cotton and wood fibers) were dipped into three ionic liquids. (1-N-butyl-3-methylimidazolium chloride ([C_4mim]+Cl—)/DMSO, allylmethylimidazolium bromide ([Amim]+Br-), and butenylmethylimidazolium bromide ([Bmim]+Br-). ([C_4mim]+Cl)/DMSO showed swelling of cellulose by ballooning and then dissolution of the fiber. ([Amim]+Br-) and ([Bmim]+Br-) showed homogeneous swelling but no dissolution. The swelling and dissolution mechanisms of cellulose in ionic liquids were similar to those observed in aqueous solvents. This indicates that the swelling and dissolution mechanisms are entirely due to the way cellulose fibers are structured, (and do (sic)) not depending on the type of solvent.”

Egorov et al.[91] studied the use of ionic liquids to make functional films for metal ion detection. “Cellulose films containing entrapped analytical reagents suitable for metal-ion detection were produced by joint dissolution of cellulose and the reagents in ionic liquids and then coagulation with water. The conditions of coagulation of these test materials were optimized and their properties were studied. The film obtained using the ionic liquids 1-butyl-3-methylimidazolium chloride and 1-(2-pyridylazo)-2-naphthol was used for colorimetric determination of divalent zinc, manganese, and nickel with detection limits at the 10–6 mol L-1 level.”

Erdmenger et al.,[92] Kadokawa et al.,[93] Kosan et al.,[94] Li and Chen,[95] and Turner et al.,[96] all have done studies on the dissolution of cellulose using a variety of ionic liquids, characterizing the solubilization parameters and the resulting solutions. Zhu et al.[97] wrote a mini-review of the work that had been done up to the year of publication (2006) using ionic liquids to dissolve cellulose. In this paper, the dissolution of cellulose with ionic liquids and its application were reviewed. Cellulose can be dissolved, without derivation, in some hydrophilic ionic liquids, such as 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-allyl-3-methylimidazolium chloride (AmimCl). Microwave heating significantly accelerates the dissolution process. Cellulose can be easily regenerated from its ionic liquid solutions by addition of water, ethanol, or acetone. After its regeneration, the ionic liquids can be recovered and reused. Fractionation of lignocellulosic materials and precipitation of cellulose derivatives and composites are two of its typical applications. Although some basic studies, such as economical syntheses of ionic liquids and studies of ionic liquid toxicology are still much needed, commercialization of these processes has made great progress in recent years."

Sui et al.[98] developed cellulose nanomaterials (100–500 nm diameter) including fibers and particles that were produced from ionic solvents by electrospray spinning. The fundamental role of concentration was studied. Structural, morphological, and crystalline phase features were also studied using SEM, TGA, and X-ray diffraction.

Novoselov et al.[99] did a study of the dissolution of cellulose in ionic liquids using computer modeling. It was discovered that computer modeling of the geometry and electronic structure of the solvent and its complexes with water and cellobiose resulted in an explanation for the decrease in the dissolving power of an ionic liquid in the presence of water. Using data on the electronic structure of the molecules, the overall mechanism of solvation of cellulose by ionic liquids and other organic solvents was determined by calculating the favorable change in the energy during formation of a solvate complex of the elementary cellulose unit with 1-butyl-3-methylimidazolium chloride, which was −20.64 kcal/mol.

Zhang et al.[100] used an ionic liquid 1-butyl-3methylimidazolium chloride to dissolve cellulose, and then regenerated the cellulose with water coagulation. They used TGA, DSC, XRDS, and SEM to characterize their materials. They then studied the cellulose by pyrolysis to investigate how pyrolysis products were affected by the different crystalline status for the original and regenerated cellulose, particularly comparing cellulose I with cellulose II. They believe that performing pyrolysis on regenerated cellulose II leads to more CO_2 removal and a high value added material 5-(hydroxymethyl)-2-furancarboxy-aldehyde can be produced by the pyrolysis of cellulose II.

Liu et al.[101] made a whole series of cellulose films from cotton pulp, using various ionic liquids, and thoroughly characterized the resulting films using SEM, XRD, FTIR, DSC, and TGA. They also studied the rheological properties of the solutions that were used to make the cast films. They were successful at making solutions of cellulose in these ionic liquids of up to 16 wt.% cellulose. Their results showed that some ionic liquids can lower the DP of the cellulose, because of a degradation process initiated in the ionic liquid. This is an interesting study of the dissolution of cellulose in various ionic liquids.

3.3 Regenerated cellulose membranes

Films and membranes made from cellulose derivatives have been made for over a century, including cellophane, nitrocellulose, cellulose acetate, and other derivatives. The use of cellulose derivatives for fibers and particularly membranes of all types, from plastic wrap, moving picture and other photographic films, to various varnishes was investigated in the past.[77] Turbak[102] updated the use of cellulose and cellulose derivatives for membranes in another book. All involve dissolving the cellulose derivative in a common solvent, and then extruding, casting, or applying the solution for some practical use. Because of the established art of using cellulose derivatives as membrane raw materials, membranes made with cellulose derivatives are not part of this review.

However, there are some important membranes that have been studied over the last 40 years; these are regenerated cellulose membranes made by the *in situ* hydrolyzing of cellulose derivative membranes. A membrane is formed by casting a cellulose derivative by traditional (such as extrusion, coating, or blade casting) or modern means (such as electrospinning[103]), and then it is hydrolyzed with a dilute base solution and washed leaving a regenerated cellulose material behind.

Some patents by Gregor[104–105] present examples of this process. Cellulose acetate is dissolved in an acetone/N,N-dimethylformamide mixture, forming a membrane on a glass plate with a conventional doctor blade, allowing the film to dry for 2 minutes, and then keeping it in a closed container for 2 hours, and allowing the membrane to be exposed to water vapor for 30 minutes at 30°C. The membrane is then immersed in ice water and washed free of solvent. The result is a swollen cellulose acetate membrane which is then placed in a 9.9 pH buffer for 24 hours at 65°C. This resulted in a film having a wet thickness of 25 microns. The water content of this membrane was 88%, and a hydraulic permeability of 3.5 liters per hour at a pressure of 50 psig for a 11.3 cm^2 area of film. This membrane was effective at separating soy bean and pancreatic trypsin inhibitors from the suspension in water.[105] The purification of the protein antibody to human serum albumin was then achieved using a similar process. The membranes in all cases were prepared wet and then kept wet for the testing.

Hafez et al.[106] developed a process for preparing thin cellulose membranes using a similar hydrolysis process. Regenerated cellulose (RC) was first prepared by denitrating cellulose nitrate in Patent #264,987, then it was commercialized as described in Patents #2,445,33 and #2,451,768. Regenerated cellulose from cellulose xanthate as described in Patents #981,368, and #991,267, and German Patent #413,511 is called cellophane. Cuprophane is made by a regeneration process cellulose regenerated with the Cuprammonium process as described in patents #2,035,645 and #2,067,522. Klinkman and Kulshrestha[107–108] developed more membranes using the cupriethylenediamine (and variants) process. "Thin membranes and membranes of modified porosity were prepared. The first type of procedure used two novel cellulose solvents, cupriethylenediamine hydroxide and cadmium ethylenediamine hydroxide, for the regeneration of cellulose. Membranes thus formed were called Cuenophane and Cadophane, respectively."[107–108]

The Hafez[106] patent makes some very important points about traditional regenerated membranes:

a. All forms of regenerated cellulose are essentially the same.
b. Cuenophane is claimed to be more permeable by virtue of the fact that it has less crystalline structure.
c. The equivalent average pore radius is about 210 nm.
d. All regenerated membranes, like most other membranes cannot be dried, and must be kept wet at all times for use. This is due to the internal structure collapse due to intrachain hydrogen bonding.

e. Because of its pore size, regenerated cellulose is very useful for and has found use in hemodialysis, and hemofiltration to purify toxins in an artificial kidney apparatus.

The Hafez invention involves these main aspects, particularly to retain porosity:

i. Dissolving a cellulose (or cellulose derivative) raw material to form a solution.
ii. Casting the solution to form a film.
iii. Coagulating the cellulose solution film using an alkali alcoholic solution.
iv. Washing with an alcohol to remove alkali.
v. Regenerating the cellulose using an acidic alcohol solution.
vi. Washing in alcohol to remove the acid.
vii. As a final step the membrane may be dried and as such retains the porosity developed in the earlier steps.

The material resulting from this invention can be in the form of sheets, tubes, and fibers, etc. Sheets are preferred for typical uses, because the end use is to separate organic materials in production streams.

Chen et al.[109] did a characterization study of regenerated cellulose membranes hydrolyzed from cellulose acetate. A unique observation was made that only membranes with a spongy structure can be obtained with this method. Cellulose acetate (CA) membranes were prepared using formamide as an additive, and then hydrolyzed in an alkali solution to obtain regenerated cellulose membranes. The effect of hydrolysis time on the degree of substitution, pore size, pore characteristics, and thermal stability of the membranes were studied. After 8 hours the acetyl groups were almost completely removed by dilute alkali. The most interesting portion of this study is the SEM micrographs showing the porous structure of the initial and final structures of the membranes. The micrographs in the article show a porous structure for both with no visible differences. It would have been more useful to show higher resolution pictures of the same samples. The thermal properties of the raw CA membranes and the RC membranes were studied using DSC, and the results are somewhat baffling because from TGA results from our lab, the cellulose decomposes, and has no real melting point. The fact that CA melts is interesting, but the conclusions they draw based on the RC results are questionable. The solvent resistance of the membranes showed the obvious, that CA is easily dissolved in acetone, DMSO, and pyridine, whereas the RC does not dissolve in any of those solvents. Neither material dissolves in water or alcohol; again that is not a surprise. Drawing these obvious conclusions from subjective results and calling them “new” seems a stretch.

Regenerated cellulose membranes can be easily made from other cellulose derivatives, but CA as a starting material is less expensive than other materials and it is easier to hydrolyze than other derivatives, so most of the work done in the last 50 years has been done with cellulose acetate as the starting material.

4. Cellulose or cellulose derivatives blend with other biomaterials for making composites

Traditionally cellulose has not been blended with starch and other polysaccharides because the unique characteristics of cellulose make it insoluble in water, unlike most other polysaccharides which are soluble in water (at least to some extent) under various dissolving conditions (such as heating). Cellulose is easily swollen with water, but because of the crystalline regions formed when the cellulose chains lay down next to each other, water does not provide enough energy to break the hydrogen bonds holding the crystalline regions together.

Over the last 20 years cellulose has been blended with polysaccharides under various conditions that will be discussed in this part of the review.

4.1 Composite material blends—cellulose, starch, wood pulp, wood fibers used for composites as fillers with resins as binders

In these materials, cellulose in the form of wood pulp or wood fibers is blended with other polysaccharides to act strictly as a filler material for a composite. Polysaccharides, such as starch, are used in these composites to provide more biodegradability since starch or other polysaccharides can be decomposed by soil life forms, such as plants, bacteria, or fungi naturally occurring in the soil. Alvarez et al.[110–112] used cellulose derivatives, and cellulose fibrous materials combined with starch to make biodegradable biocomposites. The sole purpose of the starch was to provide a medium for animals, plants, and fungi to digest the material enabling the biocomposite to decompose rapidly. Alvarez et al. were able to quantitatively demonstrate a significant reinforcement of sisal fiber content on the creep performance and the flexural modulus. Starch and cellulose derivatives were just an inert filler of the composite that gave it biodegradable characteristics. The physical tests performed were not done to see variability due to the presence or absence of starch or cellulose derivative in a particular blend.

Echte and Feldmann[113] developed a halogen free, fire resistant, thermoplastic molding composition using 10–70% cellulose and starch and/or wood flour. The starch and/or wood flour are added as a char ingredient that would give off water on heating in a fire, resist the flames due to charring, and also for the release of water vapor on decomposition of the thermoplastic polystyrene resin, or styrene-acrylonitrile resin binders due to the fire's heat. A UL-94 flammability rating of V-0 resulted.

Kamite et al.[114] developed a foam material using a mixture of cellulose, starch, and polyvinyl alcohol at 50–70% with thermoplastic resins to make a thermal insulating material. Here the cellulose and starch (and PVA) is used as a filler that provides good heat insulating properties and also provides flammability resistance. This patent basically developed a polymer blend to make insulating foams, and was not a study that showed differences in amounts or cellulose or starch to provide better physical properties. The polysaccharides and PVA were essentially functional additives for the purpose of thermal insulation.

Nabar et al.[115] studied the physicomechanical and hydrophobic properties of starch foams with cellulosic materials used as additives to provide hydrophobicity to the starch foam. Here the cellulosic material (CA specifically) and other biodegradable additives were used to interfere naturally with the hydrophilic nature of the starch foam and provide structural enhancement of the foam itself. The other biodegradable materials had a functional purpose to provide some structural property enhancement for the end product. An increase in dimensional stability resulted from the expected absorption of water under use conditions. Starch foams with CA and methylated pectin in the presence or absence of glyoxal had marginally lower unit densities and slightly higher expansion ratios. Willett and Shogren[116] also studied extruded foams of starch blended with PVA, CA, and/or several biodegradable polyesters like polylactic acid, polyhydroxyester ether (PHEE), or poly(hydroxybutyrate-co-valerate) (PHBV). Significantly lower densities and greater expansion ratios than the control starch resulted.

Takyama and Hatano[117] developed a biodegradable thermosetting resin composition by reacting 100 parts of methylol urea with 20–100 parts of blends of cellulosic materials and starch (from 5–95% of each). This material was then milled with ammonium chloride and zinc stearate and press molded to form a disk with good degradability in soil. Because this is a Japanese patent, it is unclear whether this composition will have any real commercial value, other than the fact the blend was achieved.

Tyukova et al.[118] also developed biodegradable blends of starch and cellulose derivatives. Three systems were studied: methyl cellulose /starch, carboxymethyl cellulose/starch, and hydroxypropyl cellulose/starch. The solvent used for these blends was water. Films and other materials were made with these blends, and the water sorption and biodegradability of each blend was studied. The MC/starch and CMC/starch blends were thermodynamically compatible, whereas the HPC/starch blend was not compatible. After a kinetic CO_2 aspiration study, the results showed biodegradation of these systems was higher with greater concentrations of starch in the blends. These results are understandable because the morphology of the starch chains is inherently easily biodegradable.

Warth et al.[119] made composite materials using cellulose acetate and cellulose acetate compounds, grafting cyclic lactones simultaneously onto polysaccharides, hydroxyfunctional plasticizers, or onto hydroxyfunctional fillers such as cellulose, starch, chitin, and organosolve lignin. These hydroxyfunctional fillers were added to effect reinforcement of the polymer matrix. Such blends use renewable resources and are of interest in waste disposal due to the biodegradability of the systems. The fillers, when added during the reactive extrusion process, had greater compatibility in the melt. This was a simultaneous *in situ* grafting carried out in the melt with no need to add additional solvents.

Yu et al.[120] reviewed recent advances in polymer blends and composites from renewable resources, and introduced some potential applications for this material class. One short section of their review involves cellulose/starch composites, with essentially cellulose microfibrils blended as a filler into starch based materials, decreasing water sensitivity. The presence of cellulose affected the growth of amylose crystallites orienting them in a less embrittling fashion.[121] The study by Dufresne and Vignon[121] made starch films using glycerol as a plasticizer and the cellulose microfibrils added as a filler.

Guan et al.[122] studied the use of acylated starches that were blended with 3, 7.5, and 12% cellulose in ethanol and then twin screw extruded to make a starch-cellulose composite foam. This is a reaction extrusion process where the ethanol has a cross condensation with the hydroxyls on both acylated starch and cellulose to varying degrees. The differences in the degree of substitution of the various acylated starches were studied to learn how they affected the end physical properties. This study also showed that 12% cellulose in the extrudate gave the highest bulk density and the highest compressibility. Higher cellulose content required more specific mechanical energy to extrude a useful product.

Miskiel et al.[123] studied the use of microfibrillated cellulose as an additive to a high amylose starch sizing to improve the tensile strength of a type of paper. This essentially is a blend, with no common dissolution of the materials.

4.2 Blends in suspension and then alkylation to form solution in water

Sauer and Bochow[124] developed another way to blend polysaccharides and form a solution with a common solvent (water). The reaction of powdered cellulose pulp or cotton linters and native starch was accomplished by suspending the ingredients with chloroacetic acid in ethanol in the presence of alkali at 30–70°C which gave mixed ethers that were easily dissolved in water. This patent clearly showed creativity in making the cellulose and starch compatible with each other by forming compatible derivatives.

4.3 Bio-transformed (enzymes) cellulose blend with starch in water

Another method developed by Suominen et al.[125] used to make cellulose compatible with starch in water is to react cellulose and starch first with enzymes, which will make them both equally soluble in water. Clearly, this involves using hydrolysis by enzymes to degrade both the cellulose and starch to low enough degrees of polymerization to enable both to be soluble in water, and to be compatible. Since a decrease in DP is not usually desired for physical property retention, this method has limited usefulness. This method was designed to develop a biodegradable polymer composition that could be used in disposable applications.

Wawrom et al.[126] continued this line of research and developed biodegradable films made from cellulose/starch blends that were biotransformed first. Films were prepared using alkaline solutions of biotransformed cellulose and starch. The results revealed that blends of biotransformed cellulose and starch have potential industrial applications in packaging materials due to good mechanical properties and biodegradability.

4.4 Solution blends for making specialty membranes

Solution blends are blends where both the cellulose and cellulose derivative are dissolved to form a common solution of both materials. Cellulose and starch (and other normally water soluble polysaccharides) cannot be normally blended in solution by common solvents, without developing novel procedures to compatibilize either materials or finding novel solvents. Over the last 40 years some scientists have attempted to blend cellulosic materials with polysaccharides (and other polymers) using novel methods. This portion of the review gives an overview of some of the investigations done to make blends of cellulosic materials with other polymers.

4.4.1 Methyl cellulose and starch

Arvanitoyannis and Biliaderis[127] developed aqueous blends of methyl cellulose and water soluble starch to make an edible material. The blends were plasticized with glycerol or sugars, and prepared by casting, extrusion, and hot pressing. Their mechanical (tensile and flexural), thermal, gas, and water permeation properties were studied after conditioning at various relative humidities. It was discovered that the physical properties changed based on the level of plasticizer. These studies did not involve different starches or methyl cellulose to see how those ingredients changed physical properties, as it was clear the results were more concerned with issues of edibility and palatability, based on the amounts of sugars or glycerol used.

Suvorova et al.[128] did a more specific study of two systems for interval sorption and diffusion of water vapor, and swelling characteristics in water. Methyl cellulose and starch, and carboxymethyl cellulose with starch were the two systems. Carboxymethyl cellulose/starch was a more compatible system, than the MC/starch system. Biodegradation studies were performed in a water-soil environment and the biodegradability was increased with higher levels of starch.

Tyukova et al.[118] studied blends using methyl cellulose, carboxymethyl cellulose, and hydroxypropyl cellulose blended with starch in water solution. The HPC/cellulose blend showed clear incompatibilities compared to the MC/starch, and CMC/starch blends.

4.4.2 Carboxymethyl cellulose and starch

Bajpai and Shrivastava[129] did an enzymatic degradation study of blends of carboxymethyl cellulose and cross-linked starch in aqueous solution. Hydrophilic blend matrices of cross-linked starch and CMC were synthesized and their susceptibility to degradation by amylase was studied. The polymeric blends were characterized using FTIR, DSC, and SEM, and then the influence of chemical composition, pH, and temperature profiles of the enzyme treatment were studied. The blends were found to have a mixed type of degradation profile, caused by both diffusion and surface erosion.

A process was developed and patented by Bryk et al.[130] to form porous membranes. Porous cellulose ether was graft polymerized with acrylic monomers in the presence of an iron salt and hydrogen peroxide to give porous membranes. The porous products developed were micro- and ultrafiltration membranes with improved separation properties compared to the original CMC membranes. Starch was a part of these composite membranes, though its benefit or detriment was not studied.

4.4.3 Hydroxyalkyl cellulose and starch

Hydroxyethyl and hydroxypropyl cellulose can easily be blended with starch to form a solution in water. These materials are commonly used in foodstuffs, as raw materials, to provide non-digestible fiber, and as a food product in one blend. One example is a study of edible starch based films by Bertuzzi et al.[131] where water permeability and biodegradability was studied. Most of the other studies of the uses of these solutions or blends were for the manufacture of pill substrates for dispensing medications at a controlled release rate. Bussemer et al.[132] is but one example of many. Another example was a study by Tyukova et al.[118] using hydroxypropyl cellulose blended with starch in water solution. The HPC/cellulose blend showed clear incompatibilities compared to the MC/starch and CMC/starch blends.

4.4.4 Cellulose carbamate and starch

Mikolajczyk et al.[133] developed a blend of cellulose carbamate and starch for use to form biodegradable beads for controlled release of herbicides. These polymers formed the microstructure of the cellulose beads. The bead preparation process included the preparation of the polymer solution, coagulation in an acid bath, washing, drying under vacuum to enhance porosity, and then final drying in a fluidized dryer. The cellulose carbamate/starch beads gave a 97% decomposition in water, and 100% disintegration in soil. Possible applications for these beads are controlled release of bioactive substances.

4.4.5 Cellulose derivatives blended with starch derivatives—ketones as solvents

Two patents illustrate this use of derivatization of cellulose and starch to form compatible materials to form fibers, films, and plastic materials. Hoechst Celanese scientists developed these materials for plastic applications.[134–135] Making acetate derivatives of cellulose and starch make them both soluble in ketone or ketone/water solvent systems. From these solutions, fibers can be drawn, films can be cast or extruded, and parts can be fabricated. The starch acetate is less expensive than the cellulose acetate, and the resulting materials emit less solvent upon fabrication due to more effective drying of the materials.

4.4.6 Cellulose and polyacrylonitrile

He et al.[136] studied the water flux of a cellulose / PAN membrane. The results showed an increase in water flux, and a decrease of Glucosan T40 flux as more PAN was added to the blend. The water flux decrease and retention increased with the whole solid content, and the membranes obtained were effective at removing creatinine and urea. Nishio et al.[137] used the LiCl/DMAC process to obtain these polymer blend membranes. Visual inspection and optical microscopic observation gave no evidence of phase separation in these blends. Detailed characterization of the state of miscibility was studied using wide-angle X-ray scattering, DSC, and dynamic mechanical instruments. The results showed miscibility of the chains of each in the amorphous regions, suggesting the nitrile group interacts well with the hydroxyls of the cellulose. The conclusions that are drawn from the DSC measurements are not clear, as cellulose does not have a glass transition temperature per se since it decomposes easily upon heating by driving off water, effectively lubricating the chains. Adding polyacrylonitrile into this system will merely enable the water to escape more easily upon heating.

4.4.7 Cellulose and polyvinyl alcohol, Nylon 6, and polycaprolactone blends

Nishio et al.[138] also developed membranes using the same LiCl/DMAC process to make a cellulose, polyvinyl alcohol blend. Nishio et al. followed the same process in investigating the cellulose/PVA blend as in the above study of cellulose/PAN blends. The results of both studies were similar. Particularly the miscibility of the hydroxyls of the PVA with those of the cellulose in the amorphous regions was good. The blending of nylon 6 and polycaprolactone with cellulose in the same solvent was also studied by the same investigators[139] with similar results. In each of these investigations DSC results are relied on for some conclusions. However, the only glass transition temperatures that are useful are those that occur with the blended polymer below the decomposition point for cellulose (which starts the driving off of water from the cellulose polymer).

The work summarized above in the cellulose/PAN, cellulose/PVA, cellulose/Nylon 6, and cellulose/polycaprolactam studies by Nishio et al. all use the LiCl/DMAC solvent system to do the dissolving of both polymers at the same time. Each study has relatively low amounts of cellulose and the other polymer 1–2% each for the solutions, and study of the gels and the membranes that result.

4.4.8 Cellulose and starch (nonionic and cationic) – NMMO – Lyocell process

Nishio et al.[137–139] in the above studies, used LiCl/DMAC to dissolve cellulose along with other polymers to make unique cellulose blends for study. Many authors have similarly used NMMO in the Lyocell process to dissolve cellulose along with other polymers and studied the resultant blends.

Nishio et al.[137–139] made biodegradable film nanocomposites with cellulose and starch using the Lyocell process. Nanocomposites were made by dispersing a nonmodified or modified sodium montmorillonite in cellulose or cellulose-starch solutions using NMMO as the solvent. The flow curves, X-ray diffractograms, and the mechanical properties of the obtained composites were studied.

Meister et al.[140] used NMMO to dissolve cellulose and a series of polymers to study mechanical properties, water retention, and humidity-dependent changes of electrical resistance of conductive cellulose fibers. The physical properties of textile fibers derived from several cellulose polyelectrolyte (e.g., carboxymethyl chitin, polyethyleneimine, and chitosan) blends, as well as cellulose/starch blends were investigated. The electrical resistance of the cellulose blended filaments was determined to be dependent on the cellulose/polymer ratio and the relative humidity.

Nechwatal et al.[141–142] did a series of investigations of cationic starch in a cellulose matrix. The new Lyocell process showed interesting possibilities for dissolving and forming cellulose/polymer blends when both are dissolved in NMMO. If cationic starch is used as the second polymer, three main aspects set the resultant fibers apart from conventional cellulose fibers:

1) Improved moisture absorption
2) Drastic increase of dyestuff sorption
3) Fibers are highly biodegradable.

Cellulose/cationic starch blends were dissolved in the Lyocell process, and spun into fibers. The characterization done on these fibers were moisture and dye absorption, and enzymatic hydrolysis. Cellulose/starch blend fibers with up to 30% starch content were found to retain up to three times as much water, take up to five times as much dye, and show much faster degradation by cellulose hydrolysis compared to the control Lyocell fiber. In addition to starch content, the fiber's performance also depended on the amounts of cationic substituents on the starch additive.

4.4.9 Cellulose and glucomannan

Yang et al.[143–144] performed a couple of investigations making blend membranes from cellulose and konjac glucomannan (KGM) first in a cuprammonium solution, and then in NaOH/thiourea aqueous solution. Cotton linter was used as the cellulose feedstock and a standard 10 wt.% of cellulose was dissolved in cuprammonium following their earlier procedure.[145] Then KGM was dissolved in cuprammonium solution which was then mixed with the cellulose solutions at various ratios to make a ladder of blends. The cellulose concentration for each experiment was kept at 8 wt.%. The mixed solutions were cast onto glass plates and then immediately coagulated with the 10 wt.% NaOH solution, 20°C, and 40°C water, respectively, for 5 minutes. These membranes were then characterized with SEM, XRD, and a viscoelastic spectrometer. They found the physical properties and pore sizes were related to the amount of KGM in the blend, and the coagulation conditions played an important role in the final properties of the membranes.

The later work continued these investigations by studying these membranes using NaOH/thiourea aqueous solutions for the dissolution medium. A similar characterization procedure was used on the different ratio blend membranes. FTIR, XRD, DSC, SEM, Brass membrane osmometer, and a universal testing machine were used to determine tensile properties. The membranes that resulted were of better quality than previous work, and the data they generated was more thorough, particularly the effect on pore size, morphology, and permeability based on the ratios of the cellulose and the glucomannan. It is concluded that the KGM help form through pores leading to higher water permeability. Higher KGM ratios give high tensile strength and breaking elongation compared to cellulose membranes alone. The blend membranes are alloys of cellulose and KGM, and a mesh structure is formed weaved by the two polymers on coagulation.

4.4.10 Cellulose and silk fibroin

Freddi et al.[146] investigated making blend films with cellulose and silk fibroin. Cotton linters were used as the raw material source, and silk fibers were obtained from fresh cocoons by alkaline degumming with an aqueous solution (0.7 vol%) olive oil soap at 98°C for 1 hour. Pure and blend films with different blending ratios were prepared by separating and dissolving the cellulose and silk fibroin in cuprammonium solution. The solutions were spread over glass plates and coagulated with an acetone/acetic acid (4:1) bath. Then they were washed with glycerin/water (7/13), then with water, and then dried at room temperature. The membranes were then characterized using WAXD, density measurements by the floatation method, a tensile testing machine, FTIR, and SEM for surface morphology. They got clear blend films with good physical properties. A blend was significantly stronger than just plain fibroin films, and so they conclude that adding cellulose with this (or another) method would do well to enhance the tensile and elongation strength of fibroin films. Conclusions from this work include: Cellulose can be added to silk fibroin to make useful blends; the chemical structure of both components is not significantly altered by the solvent system used; blend films are transparent and homogeneous; and physical properties depend on the blending ratio. It was noted that adding cellulose significantly improved the elasticity of the films. Evidence was observed of changes in shape and intensity of IR absorption, leading to the conclusion of significant intermolecular interactions between the two polymers, "inter-chain hydrogen bonds."

Yang et al.[147–148] follow up on the above earlier work by studying

1) the effect of Coagulants, and
2) the effect of post treatment by alkali.

These investigators used the same preparation procedures as Freddi et al.[146] and more data was generated using up to date analytical equipment. The first paper seems to just be an updating or redoing of the previous work as done by Freddi et al. The results showed that the coagulant plays an important role in the structure and micro-porous structure of the membrane. Freddi et al. studied only the surface morphology of the resulting membranes. Yang et al. studied the porous structure more extensively. It was also discovered that coagulating with 10 wt.% NaOH solution results in extraction of the silk fibroin from the structure, opening up the pores further. The second journal article discusses the post-treatment of these membranes by 10 wt.% NaOH solution from 2 to 60 minutes of soaking time, followed by washing with water and air drying the samples. With increasing post-treatment time, the crystallinity and mean pore size decreased slightly, and thermal stability was not affected. Alkali is a good solvent for SF; some of the blend membranes were alkali-resistant.

An excellent review paper on progress in research for silk fibroin blend membranes by Xu et al.[149] summarizes the issue and give a series of papers describing the different blend types, and end uses etc. They conclude by saying the blending of silk fibroin with other polymers can be done to enhance physical and mechanical properties of the resulting membranes and so have great promise for use in high-tech and biomedical fields.

4.4.11 Cellulose and casein

Zhang et al.[150] and then later Yang et al.[145] studied making cellulose blend membranes of cellulose and casein (milk protein). Cotton linters were used as the cellulose feedstock, and the casein was purchased commercially. An 8 wt.% cellulose solution was prepared in Cuoxam, and the casein was dissolved in aqueous ammonia to a concentration of 20 wt.%. The solutions were then mixed and spread over glass plates; they were coagulated by clear running water. FTIR, Solid State NMR, SEM, and XRD were used to characterize the membranes. DSC and TGA was done to characterize the samples as well. Finally tensile, tearing, and breaking elongation strengths were investigated. A Bruss membrane osmometer was used to determine permeability and mean pore radii. The results found a miscible blend which developed when the casein level was below 15 wt.%, giving a homogeneous blend. The physical (tensile etc.) properties were enhanced using casein as a blend, and the permeability of materials through the blend was better than a regenerated plain cellulose membrane.

4.4.12 Cellulose and soy protein

Chen et al.[151–152] published a series of articles on cellulose/soy protein blend membranes which was developed following up on earlier work with membranes regenerated from NaOH/thiourea aqueous solutions (discussed earlier in this review). These blends were produced by making two separate solutions of cellulose (cotton linters) in their NaOH/thiourea aqueous solution, and soy protein isolate (SPI) solution in the same NaOH/thiourea solvent, and mixing the two solutions in specific proportions to get 10, 20, 30, 40, and 50 wt.% of SPI. They discovered that the pore structure and physical properties of the blend membranes were improved upon addition of SPI. The increase in tensile strength and thermal stability at SPI levels below 40 wt.% was deemed significant. They concluded that this is due to the strong interactions between SPI and cellulose in the membrane.

In their second investigation, the physical properties of new membranes were measured when the previous membranes were hydrolyzed with 5 wt.% NaOH aqueous solution. This hydrolysis procedure resulted in the extraction of the SPI from the membrane, while retaining a new porous structure of the cellulose. The pore size increased and the tensile strength of the membranes remained high in both the wet and dry states.

Wu et al.[153] developed cellulose / soy protein isolate (SPI) blend films (membranes) using a room temperature method of dissolving the materials in an ionic liquid 1-allyl-3-methylimidazxolium chloride (AmimCl). They used natural cellulose from bamboo pulp with a DP of 650 obtained from a paper company in China. The SPI used had a 90% protein content, and was obtained from a commercial source. The cellulose and SPI were mixed into the ionic liquid in the desired ratios, and then heated to 80°C with continuous stirring until the solution became transparent. The level of the cellulose/SPI was about 6 wt.%. The films were cast onto a glass plate at a wet thickness of around 5 mm, and then coagulated with distilled water resulting in transparent gelatinous films. They were then washed until no Cl- was evident with a Silver Nitrate test. They then characterized the films for physical properties. They were able to make useful films (that could be characterized) from a 1/9 to 9/1 ratio of cellulose to SPI; pure SPI was not a film former.

The most interesting result of their research was a significant decrease in water sensitivity and water absorption of these films. As the amount of cellulose present increased, they found an increase in tensile strength and elongation at break. The films gave excellent barrier properties to oxygen and carbon dioxide transport through the films. They conclude with these observations:

1) From FTIR and XRD analysis, the blend films are amorphous in nature with few crystalline regions
2) co-continuous phase morphology exists in the blend films, they are compatible with each other in the membrane
3) good mechanical properties of the films were found, rising with the cellulose content
4) lower water sensitivity as cellulose content increases, and
5) the films have good oxygen and carbon dioxide barrier properties compared to non-biodegradable films currently used for gas barrier purposes.

Luo et al.[154] investigated the physical properties and biocompatibilities of cellulose / soy protein isolate membranes, coagulated from a NaOH / urea aqueous solvent mixture. Cotton linter was used for the cellulose, with a 7 wt.% NaOH, and 12 wt.% urea solvent to make a 3.5 wt.% solution; then SPI was dispersed in the solvent to form a slurry with an SPI content of 10 wt.%. The two solutions are then mixed in various ratios to obtain a series of solutions with 10, 20, 30, 40, and 50 wt.% SPI content. The solutions were cast onto glass plates to provide a gel sheet with a thickness of about 200 μm, and then the gel was coagulated with either a 5 wt.% acetic acid solution or a 5 wt.% sulfuric acid solution. The resulting membranes were washed for 12 hours in distilled water to remove residual acid and urea. These membranes were then characterized in both the wet and dry state using a variety of methods. Then, of most interest, selected membranes were tested with various cell cultures to test for biocompatibility and biodegradability. An in-vivo implantation study was finally conducted using rats as the substrate.

Their physical property results were consistent with previous work done by them and others using methods described in other journal articles. Most interesting was that all of the rats survived the experiments. After 8 months of implantation, biodegrading was evident in the removed specimens. The SPI composite membranes showed fusing with surrounding tissue indicating good biocompatibility and *in vivo* biodegradability. This also indicated *in situ* nourishment for nearby cells invading the membranes, primarily into the holes and pores put there in the casting and coagulation process. They conclude with "the SPI-modified membranes exhibited an improvement in vivo biocompatibility and biodegradability over pure cellulose membranes and the biodegradation and fusion speed of the membranes increased with an increase of SPI content incorporated." The acetic acid coagulated membrane gave better results, in terms of structure and mechanical properties of the membranes. Cells adhered and grew well on the surface of the membranes, with more present as the level of SPI increased, indicating good cyto-compatibility of the membranes.

Luo et al.[155] then investigated the preparation and characterization of cellulose/soy protein isolate composite sponges using the same NaOH–urea dissolving process as above. This is in contrast to earlier work done with cellulose/SPI membranes using ionic methods or NaOH–thiourea solvents (previous article, above). They found that cell viability was higher in these composite sponges compared to a pure cellulose sponge. The mixed solutions were then placed in a mold and freeze dried to remove the water, and then the composite sponges were washed with a 5 wt.% acetic acid solution to neutralize the NaOH and remove the urea. They were next rinsed with distilled water for 4 hours to produce porous wet cellulose/SPI composite sponges. The researchers then did *in vitro* and *in vivo* evaluations of the sponges to test for biocompatibility, and biodegradability. Their results are summarized. This study is an excellent primer for future work leading to products that can be used in biomedical applications for diseases and injuries. Both features of biocompatibility and biodegradability are very useful in those settings as cell and tissue scaffolds, implantation devices, and for drug delivery.

4.4.13 Cellulose and chitin

Liang et al.[156] successfully made blend membranes of cellulose and chitin using a 9.5 wt.% NaOH/4.5 wt.% thiourea dissolution process, followed by casting on glass plates and coagulation with 5 wt.% ammonium sulfate solution. The morphology and structure of these membranes were then investigated using SEM, FTIR, and WAXRD. What is particularly interesting about this study was that they used a double cell and solution depletion method to determine the permeability and partition coefficient of three model drugs in a phosphate buffer solution. This investigation was done to clarify and understand the diffusion mechanism of these solutes through the membranes. All the membranes had a porous structure, and the addition of chitin to the structure affected greatly the morphology and crystal structure of the membranes. The permeability was very different for the membranes containing chitin, and they suggest a dual mechanism and hindrance by polymer obstruction to explain the different transport of drugs across the membranes. They hope to "develop better cellulose-based biocompatibility materials for drug delivery, encapsulation, bio-separation, and water treatment."

Takegawa et al.[157] used an ionic liquid process to dissolve cellulose (10 wt.%) and chitin (5 wt.%) individually and then mix the solutions to make composite blend membranes and gels. First, chitin and cellulose were dissolved in each appropriate liquid and then the two solutions were mixed in the desired ratios, and stirred at 100°C to give homogeneous mixtures. The gels were made by allowing the mixtures to stand for 4 days, and films were obtained by spreading the mixtures unto glass plates using a casting knife, followed by soaking/washing with water and then drying. They used XRD and TGA to characterize the materials, and the mechanical properties were evaluated using compressive and tensile tests. This study was merely an attempt to make the blend gel and membranes and then complete a basic characterization of the final product. Perhaps one day someone will come up with a useful blend membrane or gel using a similar method.

Ma et al.[158] have built upon previous work done by those above and others to manufacture thin-film nanofibrous composite membranes containing cellulose or chitin for the purification of waste water. They developed a barrier layer high-flux ultrafiltration (UF) thin-film nanofibrous composite (TFNC) membranes for the purification of waste water (from bilge tanks), using cellulose, chitin, and a cellulose–chitin blend regenerated from an ionic liquid. They used a composite PAN and PET electrospun fibrous support, which they then dipped into the blend solution of cellulose and chitin, coagulating the solution with ethanol on to the fibrous framework. They characterized the materials using TGSA and WAXD, and the surface morphology was studied using SEM and molecular weight cut off methods. An oil-water emulsion was used to simulate bilge water, and was fed through the membranes to determine the permeation flux and the rejection ratio, comparing their results to standard TFNC membranes. They got 10x higher permeation flux, and a similar rejection ratio when compared to a commercial product. Therefore, they concluded that these composite membranes may have commercial utility for ultra-filtration applications.

5. Conclusions

Cellulose membranes are produced with a variety of methods, old and new. The old processes have certain disadvantages including toxicity, cost, and inefficiency. The newer ones claim to be "better" for a variety of reasons, usually including recyclability of the solvents or chemicals used in the process or the process may be less toxic for the environment. The new processes can be optimizations of "old" ones, such as mass production of bacterial cellulose for a variety of medical applications with engineered bacterial factories being "fed" simple sugars, or novel solvent systems such as NMMO (Lyocell), which can easily be recycled, but have their own unique set of issues that must be compensated for. Another example is the addition of chemical stabilizers to prevent decomposition of the NMMO. The raw materials used for solution processes can be left-over materials from saw and paper mills, sugar cane or beet bagasse, or the processed stems of tobacco plants.

Bacterial cellulose has particular advantages since it is produced *in situ*, and, after washing, is uniform and predictable for various end uses.

The most effective solvation systems involve treating the cellulose as an acid which is then reacted with a strong base or Lewis base (and perhaps a metal complexing agent that assists in providing a common ion). This disrupts inter- and intramolecular hydrogen bonds in a common solvent. Each of these systems uses distilled water or another common non-solvent of cellulose to coagulate and regenerate the solid cellulose preferably as a mesh that would then be useful as a separation membrane.

Each of these dissolving processes involves dissolution by disintegration of the crystalline regions and swelling of the amorphous regions to allow flow to occur. Some of the dissolution processes involve a reversible derivatization process for the cellulose, which is then fully soluble in the carrier solvent (i.e., water), and when the coagulant is added, the equilibrium is reversed and the cellulose drops out of solution to form a gel or mesh that can be processed further. Because the degree of polymerization of cellulose typically is above 400, the maximum useful amount that can be dissolved is around 15% weight basis. Higher levels of cellulose lead to a gel structure that will not flow appreciably under normal circumstances and as such would be difficult to process.

The Hafez patent[106] makes very important points about the nature of all these cellulose solvation membrane processes:

a. All forms of regenerated cellulose are essentially the same.
b. Cuenophane is claimed to be more permeable by virtue of the fact that it has less crystalline structure.
c. The equivalent average pore radius is about 210 nm.
d. All regenerated membranes, like most other membranes, cannot be dried and must be kept wet at all times for use. This is due to internal structure collapse due to intrachain hydrogen bonding.
e. Because of its pore size, regenerated cellulose is very useful for and has found use in hemodialysis, and hemofiltration to purify toxins in an artificial kidney apparatus.

All of these solvation processes regenerate the cellulose molecules in a structure after coagulation, in contrast to a derivatization process which is then reversed chemically to regenerate the cellulose in another form or structure compared to its original form as wood pulp or waste material. The way Hafez describes regeneration, the term would apply to both types of regeneration.

If the solvation process dissolves cellulose efficiently, it is evident (just by common structural elements) that other polysaccharides can be dissolved in the same solvent system and blends can be produced. Either pure cellulose or cellulose blends with other polysaccharides can be used to make useful materials using novel solvation processes.

The future of developing new solvation techniques for cellulose and blends involves developing systems that are environmentally safe, relatively cheap, and show an improvement in costs compared to current systems that are used industrially. It is expected that scientists will expand their research in directions such as ionic liquid studies, biocompatibility studies, and issues of sustainability of natural resources. Some potential applications of nanofibrillar cellulose (NFC) are also proposed in food packaging and paper and board applications as nanocomposites for films showing enhanced barrier characteristics. The utilization of cellulose nanonocrystals (CNC) for production of highly oriented super strong films or thin films will take place in the next decade.

Funding

We greatly appreciate funding from College of Textiles, North Carolina State University and United Soybean Board Association.

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