



Cellulose Regeneration and Chemical Recycling: Closing the “Cellulose Gap” Using Environmentally Benign Solvents

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Strategies to mitigate the expected “cellulose gap” include increased use of wood cellulose, fabric reuse, and recycling. Ionic liquids (ILs) are employed for cellulose physical dissolution and shaping in different forms. This review focuses on the regeneration of dissolved cellulose as nanoparticles, membranes, nonwoven materials, and fibers. The solvents employed in these applications include ILs and alkali solutions without and with additives. Cellulose fibers obtained via the carbonate and carbamate processes are included. Chemical recycling (CR) of polycotton (cellulose plus poly(ethylene terephthalate)) is addressed because depending on the recycling approach employed, this process is akin to regeneration. The strategies investigated in CR include preferential dissolution or depolymerization of one component of the blend, and separation of both components using ILs. It is hoped that this review focuses the attention on the potential applications of regenerated cellulose from its solutions and contributes to the important environmental issue of recycling of used materials.

matched by synthetic fibers. Therefore, the demand on natural and fabricated cellulosic fibers is expected to continue and rise. The production of cotton, however, is not expected to meet this demand because of restrictions on farmland use and availability of irrigation water.^[3] Anticipating the so-called “the cellulosic fiber gap,”^[1] the textile industry currently leads several initiatives for developing fibers that can complement cotton.^[3] Consequently, there is incitement and opportunities for an increase in use of cellulose from other sources, in particular wood, and increased interest in physical (i.e., mechanical) and chemical recycling (CR) of biopolymers.^[4]

Production of fibers and other artifacts from cellulose extracted from wood involves chemical or physical dissolution of the biopolymer, followed by its regeneration in the desired physical

1. Introduction

A consequence of world population growth is that the demand on textile fibers is expected to rise at an annual rate of $\approx 3\%$ until 2030.^[1] For 2018, the textile industry worldwide used 100 million tons of virgin fibers, of which $\approx 60\%$ was petroleum based.^[2] In addition to being a renewable feedstock, cellulosic fibers have favorable properties—in particular breathability and water-retention (sweat, humidity) capacity that are not

form in an appropriate bath. The most important example of cellulose chemical dissolution (i.e., via covalent bond formation) is the viscose rayon fiber, produced by regeneration of cellulose from its xanthate in acid bath. The Lyocell fiber process involves, however, physical dissolution of cellulose in *N*-methylmorpholine-*N*-oxide (NMMO) hydrate, followed by regeneration in an aqueous bath.^[5] Cellulose regeneration is not restricted to formation of fibers. The biopolymer and its derivatives, in particular esters, can be “shaped” into other physical forms including spheres of different diameters (down to the nanoscale), films produced by casting and spin coating, and nonwoven mats produced by electrospinning or solution blowing. This review covers some recent advances of the regeneration of cellulose from alkali solutions and ionic solvents, in particular those based on imidazole, quaternary ammonium electrolytes (QAEs), and salts of heterocyclic super-bases. We refer to these ionic solvents collectively as ionic liquids (ILs). Representative examples of the ILs employed for cellulose dissolution are shown in **Figure 1**. These solvents dissolve cellulose samples of a wide range of degrees of polymerization (DPs) and indices of crystallinity (Ics). For practical reasons, binary mixtures of ILs with molecular solvents (MSs) are used alongside pure ILs. This use is advantageous because of the concomitant decrease in solution viscosity; there are many examples where the binary solvent mixture dissolves more cellulose than the parent pure IL.^[5]

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DOI: 10.1002/mame.201900832



The mechanism of cellulose dissolution in ILs and ILs-MSs was discussed in detail elsewhere,^[7–12] and will be covered here only briefly. **Figure 2** shows a schematic representation of the hydrogen bonding (H-bonding) in native cellulose. As shown in **Figure 2**, the anhydroglucose units (AGUs) are bonded by intermolecular H-bonds, in particular between the OH of C6 and the oxygen of C3 of an adjacent chain along the (002) plane of cellulose I.^[13] Consequently, the cellulose molecules are linked in a layer, and the layers are held together by hydrophobic interactions and weak C–H.....O bonds (see **Figure 3**), as confirmed by synchrotron X-ray and neutron diffraction data.^[14] The relevance of hydrophobic interactions to cellulose crystal structure, dissolution, and regeneration was reviewed elsewhere.^[10]

Consequently, the requirements for physical dissolution of cellulose become apparent: disruption of the inter- and intramolecular H-bonds between the hydroxyl groups of the AGUs, as well as the van der Waals interactions present.^[5] Concentrating on cellulose dissolution in ILs (pure or as mixtures with MSs), the anions of the electrolytes form H-bonds with the hydroxyl groups of the same, as well as adjacent AGU units, as shown by molecular dynamics (MD) simulations.^[17–20] Due to electrostatic repulsion, the negatively charged cellulose-anion complexes start to separate. This separation is enhanced by “condensation” of the (usually voluminous) cations in order to maintain electric charge neutrality. This leads to increased steric repulsion between the chains of the biopolymer-IL complex, with concomitant disruption of the van der Waals interactions between the AGUs, due to interactions of the latter with the IL-cation. A simplified picture of cellulose dissolution due to its interactions with the components of the IL is shown in **Figure 4**. In summary, the charge density, that is, hardness and volume of the anion, the volume, rigidity, Lewis acidity, and hydrophobic character of the cation are determinant to cellulose dissolution.^[8] The importance of the basicity and hardness of the anion is shown by the facts that for the same cation, for example, 1,3-disubstituted imidazolium, the carboxylates (acetate, propionate) and fluorides are better cellulose solvents than the chlorides; most bromides do not dissolve cellulose. One example of the importance of anion volume is that 1-(1-butyl)-3-methylimidazolium pivalate (BuMeIm(CH₃)₃CO₂) dissolves less cellulose than the corresponding acetate (BuMeImAcO),^[21] although the pivalate anion is more basic and much more hydrophobic than the acetate; pK_a of the acids in water are 5.03, 4.76; log P (log (partition coefficient between mutually saturated *n*-octanol and water) = 1.84 and –0.17, for pivalic and acetic acid, respectively. Cation Lewis acidity, hydrophobicity, and rigidity are also important to the efficiency of ILs as cellulose solvents. For example, whereas benzylidiallylmethyl ammonium acetate/dimethyl sulfoxide (DMSO) mixture easily dissolves 10 wt% microcrystalline cellulose (MCC), the corresponding (more rigid) tribenzylmethyl ammonium acetate requires 24 h to dissolve only 3 wt% biopolymer.^[22]

The dissolved cellulose is either regenerated in different “shapes,” or derivatized under homogeneous conditions, for example, into carboxylic esters. We dwell here on regeneration of dissolved cellulose as nanoparticles, films, and nonwovens (mats). We end the regeneration part by discussing the industrially important regeneration strategies to form fibers, with



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aqueous media, nanostructured materials using ILs, hydrogels, stimuli-responsive materials, cellulose dissolution through ILs, and structure property relationships of ILs with conventional solvents.

emphasis on the conditions of the process and the properties of the produced material.

Finally, we briefly discuss chemical recycling (CR) of cellulose-poly(ethylene terephthalate) (PET), collectively referred to as “polycotton.” The reason is that these blends are widely

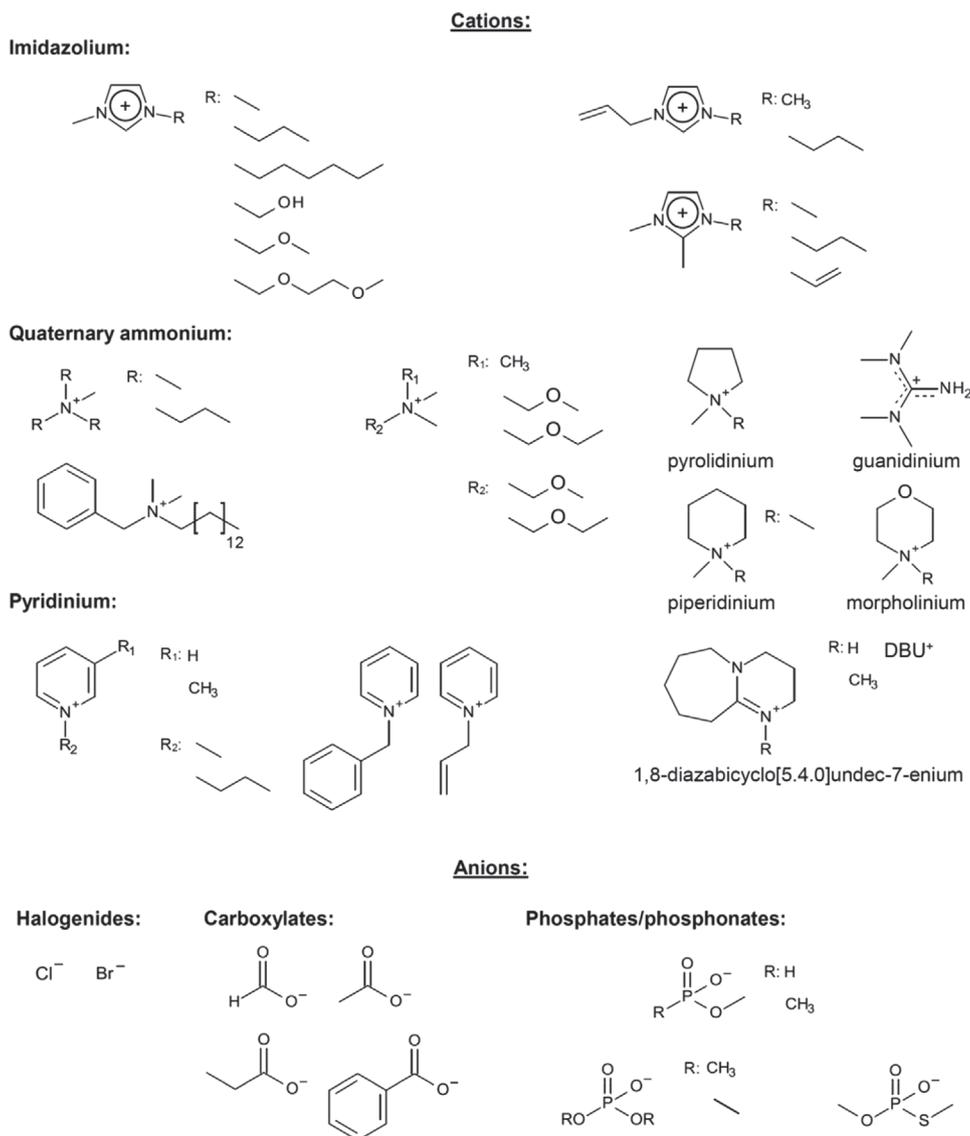


Figure 1. Molecular structures of anions and cations of typical ionic liquids employed as cellulose solvents and discussed in the present review. Reproduced with permission.^[6] Copyright 2012, MDPI.

employed in service clothing and healthcare-related items (e.g., hospital clothing, towels, pillowcases, bed sheets, and coats). Depending on the strategy employed, CR is akin to regeneration because the dissolved cellulose can be reprocessed

into fibers, *vide infra*. We stress, however, that the concept of CR as applied to polycotton should not be confused with the above-mentioned chemical dissolution of cellulose. The former means using a solvent to dissolve one component, or a catalyst

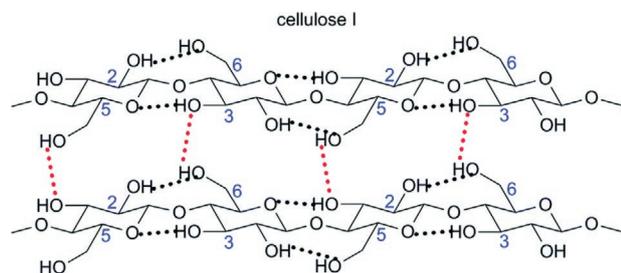


Figure 2. A schematic representation of the structure of cellulose showing the atoms involved in hydrogen bonding. Reproduced with permission.^[15] Copyright 2014, RSC.

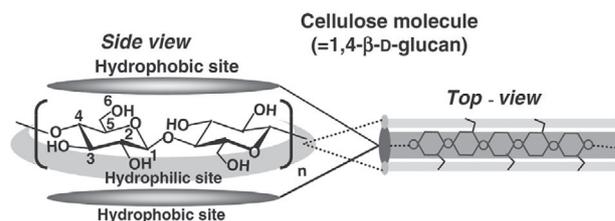


Figure 3. Hydrophilic and hydrophobic domains of cellulose. Reproduced with permission.^[16] Copyright 2007, Springer Nature.

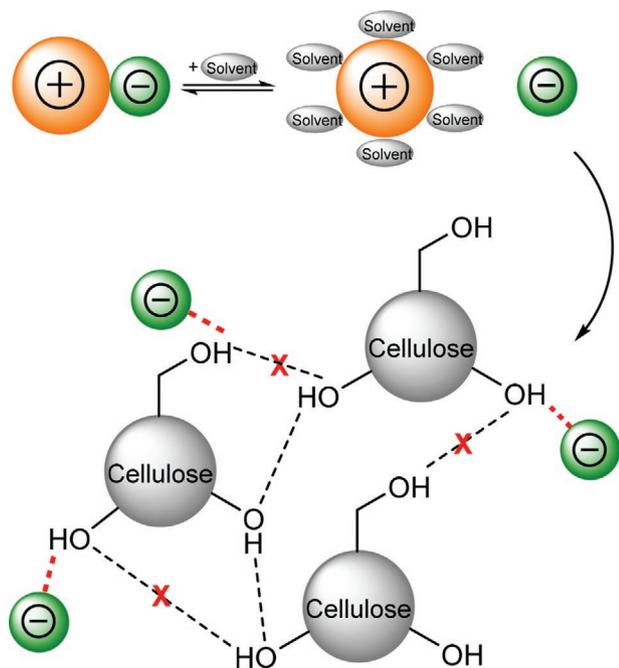


Figure 4. Schematic representation of the interactions of IL ions with cellulose. The anion forms H-bonds to the hydroxyl groups of the AGU at the expense of the inter- and intramolecular H-bonds (red crosses). Biopolymer dissolution is due to a combination of electrostatic repulsion between the negatively charged anion-cellulose complexes, steric, and solvophobic interactions due to “condensation” of the IL cation around these complexes. Adapted with permission.^[23] Copyright 2016, Springer Nature.

to depolymerize one of the two polymers of polycotton; in both cases the second component is recovered. Unlike chemical dissolution of cellulose, the formation of covalent bonds is not required for CR.

Re-use, mechanical recycling, and CR of polycotton are being actively investigated in response to the recently introduced legislations in several countries that ban their disposal in landfills.^[24] We dwell on the strategies employed for CR of polycotton, including preferential dissolution, or depolymerization of one component, for example, PET by basic hydrolysis, and cellulose by acid hydrolysis, as well as regeneration of both components, for example, by dissolving the cellulose of polycotton in ILs, and isolation of PET. We limit our discussion of CR to undyed polycotton as the dye type (e.g., vat or reactive) affects cellulose dissolution and the effect of CR on the color of the regenerated fiber is another issue to address.^[25]

2. Regeneration of Cellulose in Different Physical Forms

2.1. Micro- and Nanoparticles

Cellulose particles are spherical-shaped beads with a diameter in the range of nano- to millimeters. Usually, the diameter depends on the preparation method. Microparticle refers to systems larger than 1 mm whereas nanoparticle designates



Figure 5. Cellulose particles of different sizes. Reproduced with permission.^[26] Copyright 2013, American Chemical Society.

submicron particles (**Figure 5**). Both are used in a variety of application fields such as chromatography, metal ion exchange, water treatment, protein immobilization, or drug loading and release.^[26] For the latter application, the diameter is fundamental because it renders them more biologically available; direction toward target tissues requires particles with less than 500 nm diameter.^[27] Moreover, nano-sized particles are the building blocks for nanotechnology. Thus, design, characterization, and application of structures by controlling shape and size distribution at small scale is the driving force of this continuously fast developing field.^[28]

The simplest and fastest way to obtain spherical-shaped cellulose particles is by dropping the cellulose or cellulose derivative solution into a coagulation medium.^[29] Alternatively, pure cellulose particles are obtained from cellulose derivatives, for example, by hydrolysis during the coagulation process (viscose, cellulose carbamate), or in a separate step after particle formation and separation (cellulose acetate, CA). The size of the particle is determined by the type and size of the syringe or nozzle used; the minimum achievable diameter is rather large, $\approx 250\text{--}500\ \mu\text{m}$.^[26] Smaller particles can be obtained by employing dispersive treatments. Here, the cellulose solution is subjected to high dispersive forces with an immiscible solvent of opposite polarity. The diameters of the regenerated biopolymer beads are generally between 10 and 1000 μm . Particles of submicron diameters are achieved by nanoprecipitation.^[30] Upon slow addition of water to solutions of cellulose^[31] or its derivative,^[32] for example, through a dialysis membrane (**Figure 6**), self-assembly of the polymer molecules into regular nanostructures occurs. Also the slow drop-wise addition of cellulose solution into water is employed.^[33] These methods are relatively straightforward, consume little energy, and use simple equipment. A rather new approach is the fabrication of cellulose microspheres via electrospraying from NaOH/urea or *N,N*-dimethylacetamide (DMAc)/LiCl solutions. Depending on the conditions (cellulose DP, cellulose solution concentration, electric field, etc.) spheres from 170 to 2500 μm can be obtained.^[34] Other physical properties of regenerated cellulose, for example, density, specific area, and pore size and structure, are controlled by the coagulation conditions as well.^[35] Thus, particles

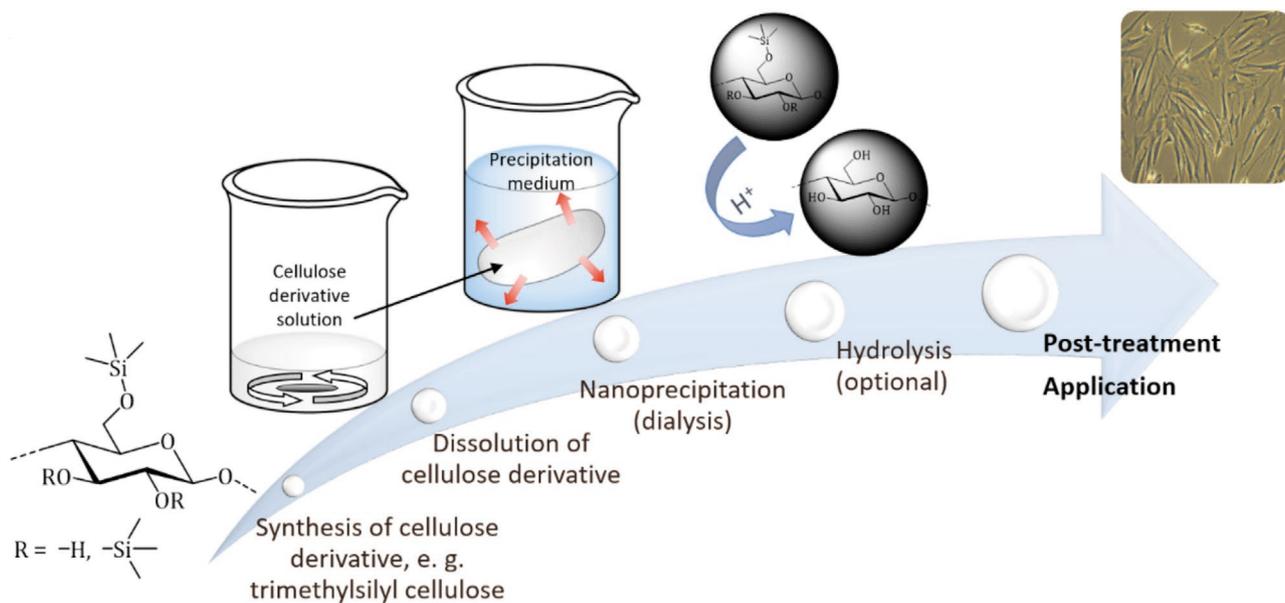


Figure 6. Schematic representation of the steps involved in cellulose nanoparticle preparation starting from cellulose derivative synthesis until application of the particles.

prepared from cellulose solutions of higher concentrations are less porous, whereas the temperature and composition of the coagulation medium affect morphology, internal surface area, and pore size distribution.^[26,36] Consequently, the particles can be specifically designed for their intended application.

Using organic and inorganic additives, the properties of cellulose particles can be modified to increase the spectrum of possible applications, as shown by the following selected examples: i) nanoparticle density can be increased by incorporating TiO₂,^[37] tungsten carbide,^[38,39] nickel,^[40] or stainless-steel powder^[41] into cellulose or cellulose derivative solution prior to the regeneration step; ii) magnetic properties are inferred by including iron, or iron oxide particles^[42–44]; iii) pore size of cellulose nanoparticles can be tailored by incorporating CaCO₃,^[45] or starch^[46]; followed by washing or enzymatic treatment (amylase in case of starch); iv) dye-labeled cellulose acetate nanoparticles for immunoassays were obtained by incorporating hydrophobic dyes into the particle matrix^[47]; v) excellent arsenate absorbers for waste water treatment were obtained using carboxymethyl cellulose nanoparticles coated with ferric oxide.^[48] More information on waste water treatment with cellulose nanomaterials is available in recent reviews.^[49,50]

Further property tuning or functionalization is accomplished by chemical modification of the cellulose particles. This includes reactions such as etherification, esterification, oxidation, and polymer grafting.^[26] For example, light and temperature switchable coating nanoparticles, based on the stearate ester of hydroxypropyl cellulose, can be applied for diagnostic applications.^[51] Chemical modification of particle properties is laborious and may pose potential difficulties (synthesis and purification) compared to the above-mentioned strategies. Under heterogeneous reaction conditions it is difficult to control the degree of substitution of the OH group of the AGUs, hence the concomitant distribution of the substituent along the

polymer backbone. Consequently, these (heterogeneous) products are not employed for medical applications; the products synthesized under homogeneous reaction conditions are usually used.

A multifunctional cellulose II gel (TENCEL gel) was obtained from the Lyocell process. Unlike common cellulose II nanoparticle synthesis, the amorphous regions were preserved.^[52] The gel possesses homogeneous morphology and is composed of individual cellulose particles with a size of less than 1 μm. Its rheological behavior is similar to cellulose nanofibrils.^[53] Aqueous dispersions of the particles exhibit a concentration dependent sol/gel behavior (**Figure 7**): at solid contents <2 wt% they behave as a low viscous liquid (sol). At higher concentrations, however, they form hydrogel.^[54] The synthesis of this new class of cellulose nanoparticles is organic solvent-free, simple, and cost-effective as it can be produced directly from the Lyocell process applying only one homogenization cycle (vs 20 cycles for cellulose nanofibril fabrication).

Sponge-like cellulose particles of ≈80 μm diameter were prepared from droplets of cellulose solution in 1-butyl-3-methylimidazolium chloride (BuMeImCl) and *N,N*-dimethylformamide (DMF) to efficiently encapsulate hydrophilic or hydrophobic substances such as dyes or drugs (encapsulation efficiency >80%).^[55] Upon drying, the particles shrink to a denser structure as can be seen in **Figure 8**. The porosity of the particles is controlled by the surrounding medium. By solvent exchange from 1-butanol to *n*-pentane particles collapse was prevented due to the lower surface tension of the hydrocarbon solvent.^[56] This led to softer particles with higher specific surface area and consequently contributes to the design and property control of the cellulose particles.

Ethylcellulose nanoparticles are the key component of the so-called “Pickering emulsions.”^[57] Compared with traditional emulsions they exhibit ultra-high stability, low toxicity, and

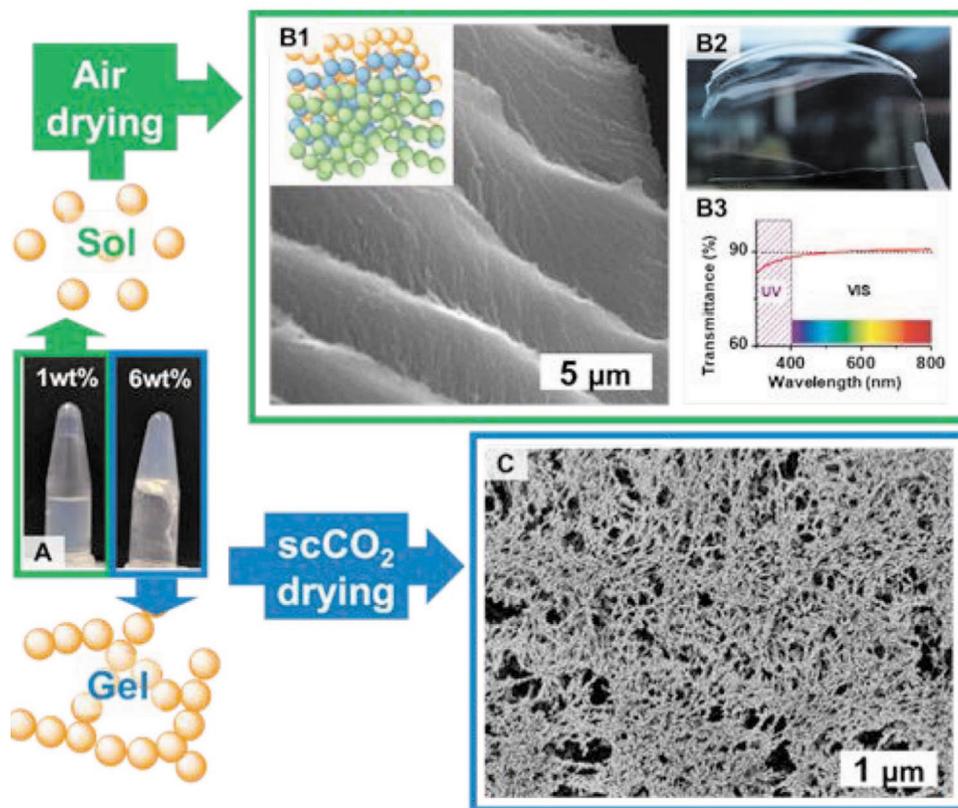


Figure 7. Nanoparticle dispersions in sol and gel states, A) air drying of the sol causes alignment into an anisotropic sheet structure (SEM in (B1), top view of fracture) in form of B2,B3) a transparent film, C) supercritical drying of the gel yields a porous, isotropic aerogel. Reproduced with permission.^[54] Copyright 2019, American Chemical Society.

environmental responsive character, which makes them suitable candidates for food, medical, or pharmaceutical applications such as drug delivery systems. They are obtained through

simple dispersion of ethylcellulose/ethanol and xanthan gum/water mixtures, followed by evaporation of the alcohol. Note that biomaterials based on ethylcellulose are commercially

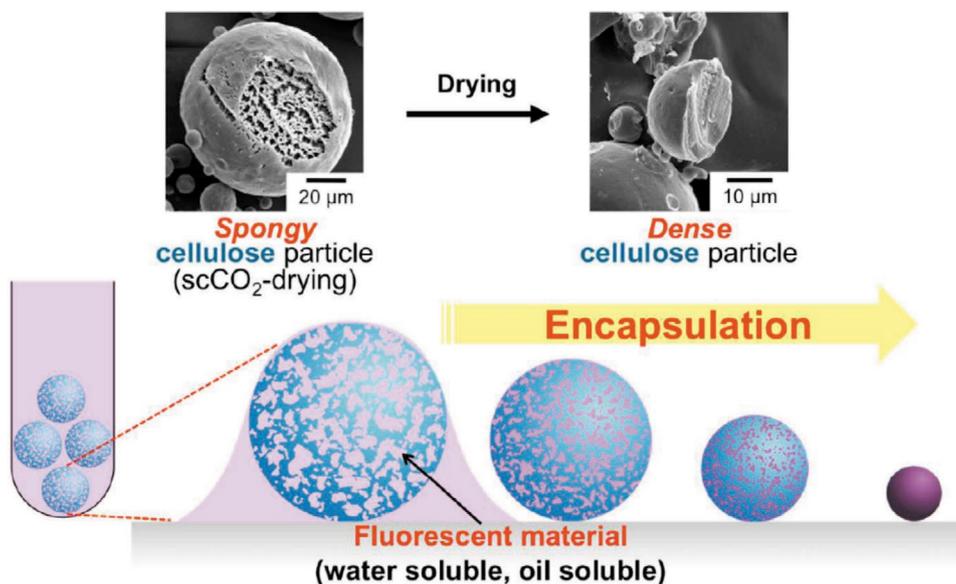


Figure 8. Spongy cellulose particles obtained after precipitation from cellulose/BuMeImCl/ DMF solutions for encapsulation of hydrophilic or hydrophobic compounds. Reproduced with permission.^[55] Copyright 2017, American Chemical Society.

available and widely employed for over half a century as biocompatible templates for the design of novel drug delivery systems. They are classified as “Generally-Recognized-As-Safe” chemical substances. This topic was covered in a recent review article.^[58]

Aminodeoxy cellulose derivatives, also referred to as “amino cellulose,” are known for their biocompatibility.^[59,60] Thus, various biocompatible amino cellulose nanoparticles were fabricated with interesting potential applications because the primary amino groups on the nanoparticle surface can be further functionalized. For example, spherical, stable nanoparticles were obtained by self-assembly of functionalized 6-deoxy-6-(ω -aminoalkyl) amino cellulose carbamates. These were incorporated in human foreskin fibroblasts BJ-1-hTERT and breast carcinoma MCF-7 cells without use of transfection reagents; an important prerequisite for various biomedical applications.^[60] Tosyl cellulose, an easily synthesized cellulose derivative (from cellulose and tosyl chloride/triethylamine) was reacted with ethylenediamine and 4-chlorobenzylamine to produce 6-deoxy-6-(4-chlorobenzyl-2-aminoethyl) amino tosyl cellulose. The physico-chemical properties of these cellulose derivatives, for example, their hydrophobicity, are controlled by the partial DS of the groups present (tosylate, carbamate, and amino group). The biopolymer derivatives are soluble in organic solvents (DMF, DMAc, DMSO); this solubility is advantageous because it facilitates processing/shaping. Upon dialysis against water, they produce small, positively charged particles that were labeled with fluorescent dyes (potential use in bioassays) and showed antimicrobial activity.^[61–63]

2.2. Films and Membranes

The first regenerated cellulose film or membrane was called cellophane and was obtained directly from the viscose process. To produce a transparent cellophane film instead of a fiber, the

viscose solution is extruded through a slit into a bath of dilute sulfuric acid. Cellulosic films are the most applied cellulosic materials after fibers. Various cellulose and cellulose derivative films are commercially available and have widespread use as packaging material and in separation processes such as filtration. The generally applied preparation method is coagulation of solutions of cellulose or its derivative in a suitable nonsolvent. The coagulation conditions, cellulose type, and concentration control the film properties.^[64] Additives, for example, metal and metal oxides,^[65–70] activated carbon,^[71] dyes,^[72] or polymeric nanoparticles,^[73] were employed to tailor, modify, or enhance film properties. Blending with additives is not always necessary to achieve better mechanical properties. As shown in **Figure 9**, simple dual cross-linking is very efficient for the preparation of ultra-tough, clear, and highly anisotropic regenerated cellulose films from LiOH/urea solutions.^[74]

Direct processing such as extrusion of the cellulose derivative is only possible when it exhibits thermoplastic properties. As packaging material, for example, for food, the cellulose films are required to possess high mechanical strength and low gas/moisture permeability.^[75] To improve these properties as well as processability, fatty acid esters are widely employed.^[76] The hydrophobically modified surface led to significantly decreased water vapor, oxygen, nitrogen, and carbon dioxide permeability.^[77] Surprisingly, cellulose films prepared from NaOH/urea or LiOH/urea solutions have even lower oxygen permeabilities than commercial oxygen barrier films such as poly(vinylidene chloride) and poly(vinyl alcohol).^[78] Drying conditions of the regenerated films influence the mechanical and oxygen barrier properties as well.^[79] Further discussion on moisture and oxygen barrier properties of cellulose films was published elsewhere.^[80]

For food and medical applications, films with antibacterial characteristics are required. Thus, membranes containing *N*-halamine modified nanocrystalline cellulose particles showed excellent biocidal activity against Gram-positive bacteria

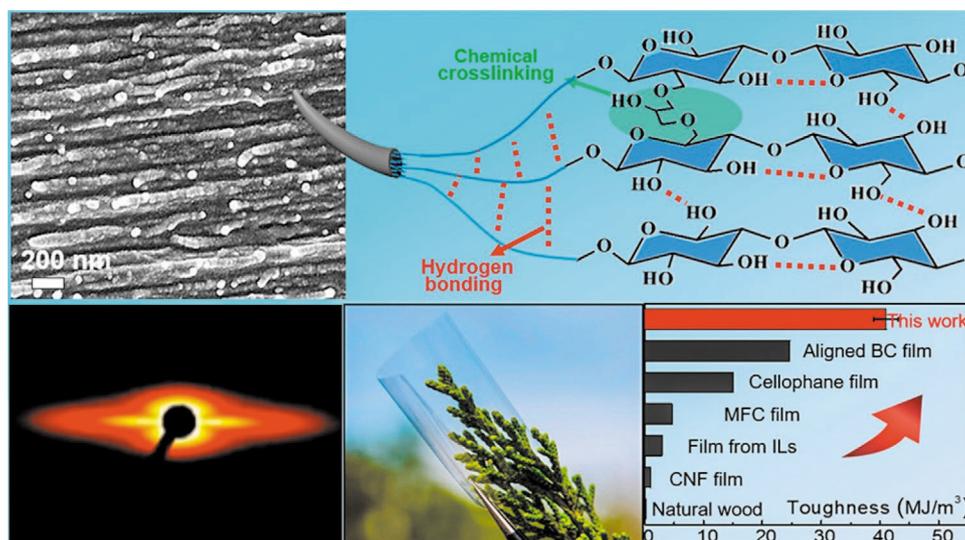


Figure 9. High mechanical strength, transparent, regenerated cellulose film with tightly stacked and long-range aligned cellulose nanofibers self-assembled from cellulose solution in LiOH/urea aqueous system. Reproduced with permission.^[74] Copyright 2019, American Chemical Society.

Staphylococcus aureus and Gram-negative bacteria *Escherichia coli*. Good cytocompatibility, an important prerequisite for such applications, was found for the membranes as well.^[81] Generally, cellulose nanocrystals have favorable properties for medical and healthcare applications. They have been reviewed elsewhere^[82–84] but are not within the scope of this review. The facile preparation of carboxymethylcellulose films incorporating silver, zinc oxide, and copper oxide nanoparticles showed comparable results.^[68] Both, cellulose nanocrystals and carboxymethyl cellulose, are commercially available at reasonable cost which significantly favors their accessibility and application.

Among purification technologies such as distillation, sedimentation, and filtration, the latter one using (cellulosic) membranes is favorable because of its low energy consumption. Activated carbon particles improve the mechanical properties of membranes and enhance their adsorption capacity when incorporated into the matrix, as shown for cellulose acetate. This enhancement is useful for uranium and arsenic removal from water.^[71,85] Zeolitic imidazolate framework reinforced cellulose acetate membranes exhibited water/ion selectivity and enhanced alginate fouling resistance in osmotic driven membrane processes.^[70] Anti-fouling properties are important to keep the membranes functioning properly over longer periods of time, leading to enhanced process economy. A freestanding cellulose membrane as thin as 10 nm was prepared through regeneration of trimethylsilyl cellulose. According to the filtration experiments, the membrane exhibits precise size-sieving performances with an estimated pore size between 1.5 and 3.5 nm depending on the regeneration period and initial cellulose derivative concentration. Thus, selective separation of small molecules is feasible on the basis of a renewable biomaterial via simple filtration.^[86] Membranes were also obtained from NMMO/cellulose solutions. The porosity and pore size of cellulose membranes decreased with lower cellulose DP, higher cellulose concentration, and addition of NMMO in the coagulation bath. Pore sizes of 13.4–20.2 nm were found.^[87] In biotechnology, such regenerated cellulose membranes for centrifugal filters with a pore size of 10 kDa are optimal to concentrate extracellular vesicles without significant loss. The more frequently used filters with larger pore size (100 kDa) lead to 50–80% vesicle loss.^[88] Moreover, the regenerated cellulose membranes were superior to all synthetic polymer filters used for this application, which emphasizes the advantages of using of biocompatible renewable materials.

The development of green, biodegradable, and low-cost flexible films for use in electronic devices is motivated by the global trend of finding sustainable solutions based on renewable resources. Cellulose-based films are the perfect candidates for this application. Ethylcellulose was employed to embed silver nanowires. The resultant transparent, flexible, and conductive film has superior optoelectronic performance, and can sustain various mechanical deformations, environmental exposure, and severe washing. These properties makes it feasible for large-scale manufacturing (Figure 10).^[67] Similarly, to prepare flexible cellulose-based solar cells, cotton was dissolved in NaOH/urea and regenerated as thin transparent film followed by coating with a poly(3,4-ethylenedioxythiophene)/polystyrene sulfonate as anode and current collector, respectively.^[69]

Utilizing cellulose films for material applications and in food industry is an expanding subject. Regarding the first theme, literature shows where some of the business-related interests lie. For example, (biodegradable, renewable) cellulose-based photoresist overcome several drawbacks of conventional photoresists.^[89] On the other hand, the potential for using polysaccharides, for example, cellulose, chitosan, starch, pectin, and alginate is enormous because these biomaterials form films and coatings with good barrier properties against the transport of gases such as oxygen and carbon dioxide. The mechanical properties of the films can be improved by several strategies, for example, cross-linking, addition of plasticizers, and use of composite films.^[90,91]

2.3. Nonwoven Materials (Mats)

Cellulosic nonwovens are sheet or web-like structures consisting of entangled cellulose fibers or filaments of small diameters in the range of nano- to micrometers. These interact with each other via hydrophilic and hydrophobic interactions. After chemical modification or treatment, for example, with cross-linking agents, these interactions can be enhanced, which allows nonwovens to have tailored characteristics, such as absorbency or liquid repellence. Therefore, nonwovens are generally used in medical applications (wound dressing), hygiene products, filters and membranes, packaging materials, or textiles. Unlike the production of cellulose fibers, spinning into yarns is not required to attain nonwovens.^[92]

The most commonly applied methods to form nonwovens is electrospinning,^[93] and solution blowing^[94,95]; the potential industrial application of the latter is larger.^[96–99] Cellulose solutions in ILs, NMMO, and DMAc/LiCl were successfully electrospun.^[98–101] The diameter of these small fibers are mainly dependent on cellulose concentration and solution viscosity.^[94] For example, higher cellulose concentration results in thicker fibers and blocky structures (or beads) start to appear, which decrease fiber quality. Cellulose functionalization or blending increase solubility in volatile organic solvents and facilitates electrospinning. Thus, antibacterial (*S. aureus* and *Klebsiella pneumoniae*) aminocellulose nonwovens were obtained.^[102] Hydroxyethyl cellulose (HEC) scaffolds support cellular attachment and proliferation of osteosarcoma cells to be applied in bone tissue engineering.^[103] However, the main obstacle with electrospinning is the low cellulose concentrations employed and the use of single jets. Thus, upscaling of this process for nonwoven production of sufficient quantities to meet industrial demands remains challenging. Solution blowing (Figure 11) is an efficient technique to circumvent this limitation.^[98,104] Analysis of the mechanical properties revealed higher effective stress and a lower strain compared to commercial spun bond polypropylene. Another strategy is combination of electrospinning and solution/air blowing. Flow rates between 5 and 12 mL h⁻¹ are reported, which is much higher than conventional coaxial electrospinning and results in increased fiber diameters. Interestingly, this technique can be applied to produce core/sheath and hollow fibers.^[105] In view of continuously increasing efforts toward more sustainability, reuse and recycling of cellulosic nonwoven materials are discussed as well.^[106,107]

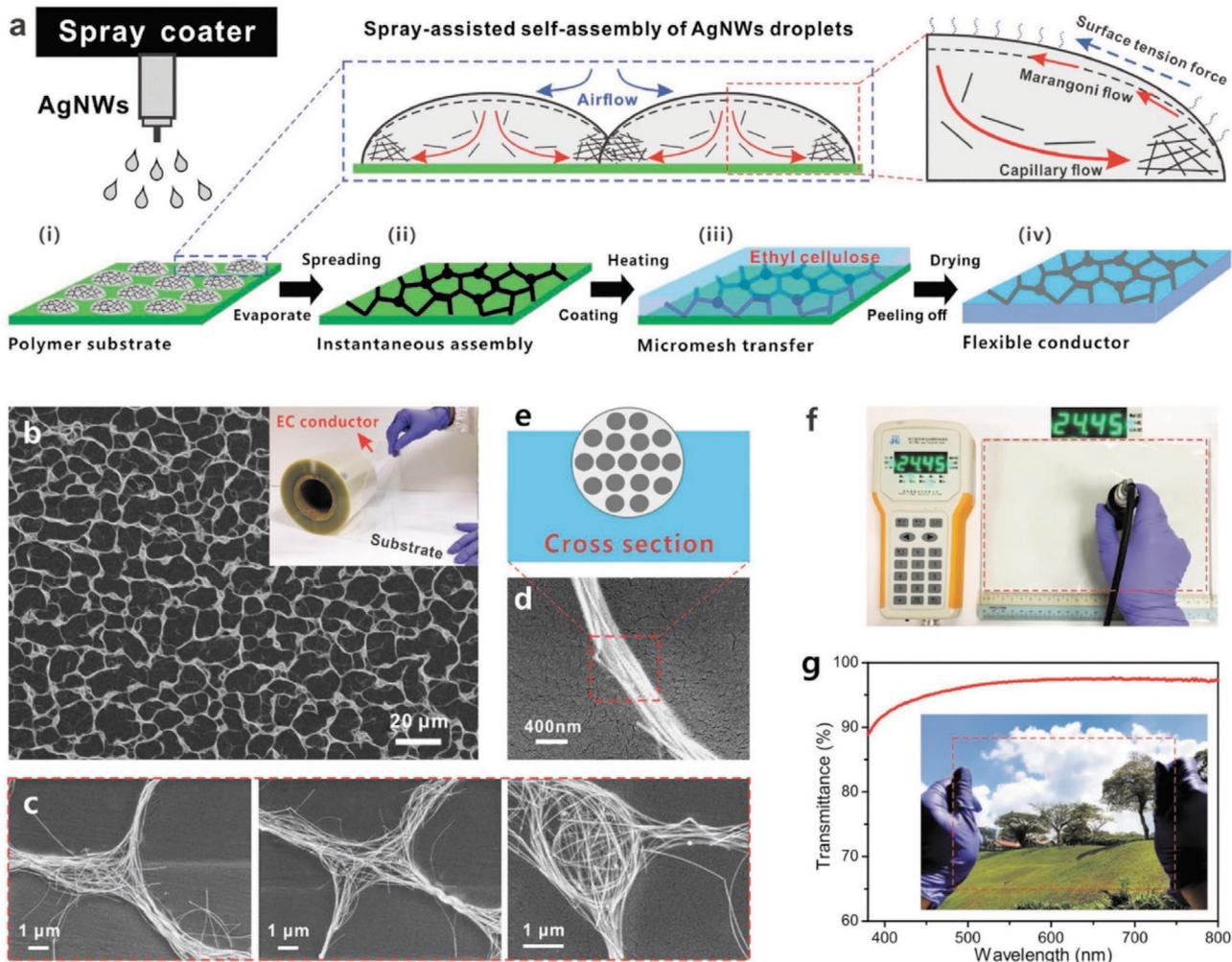


Figure 10. a) Schematic illustration of the fabrication process of ethyl cellulose (EC) conductor with embedded silver nanowires (AgNWs) micromesh. Inset is the schematic of spray-assisted self-assembly of AgNWs bundles from droplets of AgNWs. b) SEM planar top view of the AgNWs micromesh with EC substrate. Inset is a photo of EC conductor with PET roll indicating the scalable process. c) SEM images of three representative knots of AgNWs bundles. d) SEM image of an AgNWs bundle with embedded structure. e) Cross-section schematic depicting the embedded AgNWs bundle. f) Real time R_s measurement photo of an EC conductor with dimension of $15\text{ cm} \times 25\text{ cm}$. g) Transmittance spectra of the corresponding AgNWs micromesh conductor in the visible light range. Inset is the photo of this EC conductor ($15 \times 25\text{ cm}^2$) with high transparency and low haze. R_s of the sample is given in (f). Reproduced with permission.^[67] Copyright 2018, Wiley-VCH.

2.4. Cellulose Regeneration as Fibers

There are two commercial processes for forming regenerated cellulose fibers; the viscose process (derivatizing) and the Lyocell process (non-derivatizing). The viscose process is based on formation of cellulose xanthogenate which is dissolved in NaOH and wet spun into an acidic coagulation bath to form high-performance fibers. The Lyocell process, on the other hand, is based on physical dissolution of cellulose in NMMO and formation of fibers via dry-jet wet spinning into an aqueous precipitation bath. More information on these commercial processes and their respective advantages and limitations can be found elsewhere.^[108,109]

The present account on regeneration of cellulose fibers will focus on solvent systems that are potentially important for industrial processes, for example, certain ILs including salts of super-bases. Noncommercial processes based on cellulose dissolution in alkaline systems, with or without preceding

derivatization, will be discussed. Because the reader may not be familiar with some of the terms employed in the textile industry, we included in Supporting Information definitions and explanations of these terms.

2.4.1. Regeneration of Cellulose from ILs

IL technology for cellulose processing is a promising field with good potential for reaching industrialization. The chemical and thermal stability of many ILs as well as their miscibility with other solvents makes them interesting for production of cellulose-based fibers and materials. ILs based on imidazolium cations are most explored for cellulose dissolution and regeneration. Solubility of cellulose in imidazolium-based ILs has been covered in review articles and book chapters.^[7,110,111] As discussed above, the choice of cation and anion affects cellulose dissolution and bears

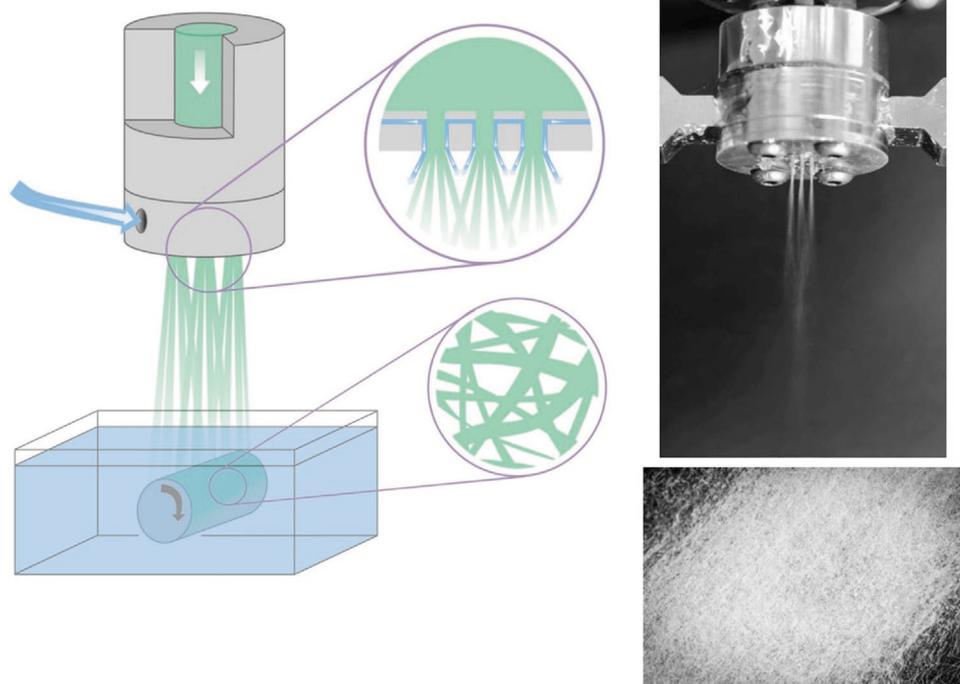


Figure 11. Solution blowing of $C_2MelmAcO$ /cellulose solutions to produce cellulosic nonwovens. Reproduced with permission under the terms of the Creative Commons Attribution License.^[104] Copyright 2019, the Authors. Published by Wiley Periodical Inc.

on environmental aspects and sustainability of the process.^[112] Common imidazolium-based ILs, such as BuMeImCl, 1-ethyl-3-methylimidazolium chloride and 1-ethyl-3-methylimidazolium acetate were compared with NMMO as spin dopes for shaping cellulose into fibers.^[113] Cellulose was dissolved in concentrations between 13 and 16 wt% depending on the molar mass of the solvent (as all solutions had similar molar ratio of cellulose to IL) and was shaped by a dry-jet wet spinning process. The spinning conditions, especially the temperature and condition at the air gap was adjusted for each solution but all were analogous to spinning with NMMO. Cellulose solutions in ILs had comparably higher viscosities and were shaped into fibers with tenacities higher than those spun from NMMO monohydrate. Due to cellulose degradation and the corrosive nature of 1,3-dialkylimidazolium halides, other anions, for example, $[(EtO)_2PO_2]$ and $[AcO]$ are generally preferred.^[114,115] The efficiency of imidazolium-based ILs as cellulose solvents, and their molecular structural flexibility promotes continued research efforts in this area.^[115,116] As an example of more recent results, a paper by Zhu et al. described dry-jet wet spinning of MCC dissolved in $[EtMeIm][(EtO)_2PO_2]$ combined with DMSO, which made it possible to dissolve a high concentration of cellulose (23.6 wt%) and obtaining highly aligned fibers with an E modulus of 41 GPa.^[117]

Other ILs, such as QAEs, were recently explored as solvents for regeneration of cellulose into fibers.^[7] For fiber spinning, solvents based on mixtures of tetra(*n*-butyl)ammonium acetate (Bu4AOAc) in combination with DMSO have shown some promise. Thus, 5 wt% bamboo pulp dissolved in Bu4AOAc/DMSO (1:4 mass ratio) was regenerated as fibers via wet spinning, using ethanol as coagulation medium. The resulting fibers had good mechanical properties with a dry tenacity of 38.5 cN per tex and elongation of 11.9%.^[118] Similar results were also

presented for cellulose softwood pulp solutions with concentrations between 4 and 10 wt%, where the regenerated fibers had somewhat lower tensile strengths (21.5–30.7 cN per tex) and elongation between 9.7 and 11.8%.^[119] Dissolution of cellulose (8 wt% cellulose powder) in Bu4AOAc/DMSO/crown ether (18-crown-6), weight ratio 2:7:1, at mild conditions (40 °C) was achieved within only 5 min; the cellulose was regenerated to fibers by coagulation in ethanol.^[120] These results illustrates the potential of utilizing the swelling power of DMSO as well as other additives that positively affect and facilitate solubilization of cellulose.

Finnish research groups made important contributions for the production of new cellulose textile fibers using ILs via, for example, the Ioncell-F process.^[121–124] This process is based on using the salt of super-base electrolyte, namely, 1,5-diazabicyclo[4.3.0]non-5-enium acetate (DBNAcO) as cellulose solvent. Strong fibers (tenacities above 50 cN per tex) were produced using dry-jet wet spinning of these solutions (15–17 wt% cellulose; coagulation in cold aqueous baths).^[114,122,125] Spinning conditions depends on the composition of the solution, however spinning temperatures were generally in the range of 65–80 °C and draw ratios up to 17.7 were applied.^[122,124,126] The same solvent and process was applied to co-spinning cellulose with lignin as precursors for carbon fiber production,^[127,128] as well as to produce man-made cellulose fibers from recycled material (newsprint).^[129] Direct dissolution of the cellulose and coagulation in water makes this process interesting for up-scaling and commercialization, however there are still challenges concerning the efficiency of IL recovery.

There are several review articles covering shaping of cellulose using different ILs and comparing them with fibers from other processes, including both relevant commercial fibers (e.g., viscose, modal, cupro, and Tencel [Lyocell] fibers) and alternative

experimental fibers (e.g., Fiber B and BioCelSol fibers).^[92,114,130] As there are many factors affecting the final mechanical properties of regenerated cellulose fibers, for example, the type of pulp, its initial DP, the concentration of cellulose in the spinning solution, and process parameters such as draw ratio, spinning temperature, and spinneret design, as well as drying conditions and post-treatments; a straightforward comparison is not feasible. Nevertheless, we summarized data in **Table 1** to provide a perspicuous overview of the mechanical properties reported for different types of regenerated man-made cellulose fibers.

The collected data illustrate the great variety of fiber properties that were obtained, based on the selection of solvent/derivatization system, spinning conditions, and after-treatment.

Fiber B or Bocell are fibers produced via dissolution of cellulose in anhydrous phosphoric acid, followed by dry-jet wet spinning into a coagulation bath consisting of acetone and then washed with water and neutralized with Na₂CO₃.^[144,145] These fibers show the highest tenacity values reaching almost 90 cN per tex, that is, more than twice as high as commercial Lyocell fibers, most likely due to the presence of liquid crystalline structures. Despite this impressive mechanical property, there is no commercial production of cellulose fibers from (corrosive) phosphoric acid. Liquid crystalline structures were observed in cellulose-IL solutions too. However, all lyotropic cellulose-IL systems have a clearing temperature (at which the solutions turn isotropic) lower than their process temperature.^[114]

Table 1. Mechanical properties of regenerated cellulose fibers produced via different processes.

Process	Tenacity, dry [cN per tex]	Tenacity, wet [cN per tex]	E modulus [GPa]	Elongation, dry [%]	References
Viscose ^{a)}	22–26 ^[109] 23 ^[114]	10–15 ^[109]	5.4–11 ^[131]	17–25 ^[109] 22.5 ^[114]	Zhang et al. 2018 Hummel et al. 2015 Budtova & Navard 2016
Modal ^{b)}	31 ^[125]	15 ^[125]		16.5 ^[125]	Kreze et al. 2003 ^[132]
Lyocell (NMMO) ^{c)}	40–42 ^[109] 40.2 ^[133]	34–38 ^[109] 37.5 ^[133]	13.2–30 ^[131]	11–16 ^[109] 13 ^[133]	Zhang et al. 2018 Röder et al. 2009 Budtova & Navard 2016
Cupro ^{d)}	22.3 ^[126]	17.6 ^[126]		24.3 ^[126]	Röder et al. 2009 ^[133]
Fortisan ^{e)}	23.9 ^[126]	27.7 ^[126]		3.2 ^[126]	Röder et al. 2009 ^[133]
Phosphoric acid ^{f)}	89.4 ^[126]	75.8 ^[126]		6.8 ^[126]	Röder et al. 2009 ^[133]
[BuMelm]Cl	53.4 ^[113] 50.1 ^[133]	39.4 ^[133]		13.1 ^[113] 9.3 ^[133]	Kosan et al. 2008 Röder et al. 2009
[EtMelm]Cl	53 ^[113] 43 ^[133]	35.9 ^[133]		13 ^[113] 9.6 ^[133]	Kosan et al. 2008 Röder et al. 2009
[AlMelm]Cl ^{g)}	45 ^[116] 27–37 ^[134]			17 ^[135] 8–11 ^[134]	Luo et al. 2014 Zhang et al. 2017 Laus et al. 2005
[BuMelm][OAc]	44 ^[106]			15.5 ^[106]	Kosan et al. 2008 ^[113]
[EtMelm][AcO]	46 ^[113] 44.7 ^[133]	38.1 ^[133]		11 ^[113] 10.4 ^[133]	Kosan et al. 2008 Röder et al. 2009
[EtMelm][(EtO)2PO2] ^{g)}	26 ^[136]		22–41 ^{[117]h)}	6 ^[136] 4.6–6.5 ^{[117]h)}	Ingildeev et al. 2013 Zhu C et al. 2018 ^{h)}
[DBN][AcO] (Ioncell-F)	37.5–50.5 ^[114] 33.6–50.7 ^[124]	24.9–47.6 ^[114] 25.7–47.5 ^[124]	13.9–23.6 ^[124]	8.5–10.0 ^[114] 7.4–9.8 ^[124]	Hummel et al. 2015 Stepan et al. 2016
TBAOAc/DMSO	38.5 ^[118] 30.7 ^[119]			11.9 ^[118] 10.9 ^[119]	Jiang et al. 2016 Sun et al. 2015
CarbaCell	13–26 ^[137] 17 ^[138]		4–9 ^[137]	8–27 ^[137] 16 ^[138]	Fink et al. 2014 Harlin 2019
Cellulose carbonate	12.0–19.7 ^{[131]i)}	10.4–22.8 ^{[131]i)}		8.8–11.3 ^[131]	Oh et al. 2005 ^[139]
NaOH (aq.)	16.8 ^{[132]j)}			15 ^[132]	Okajima & Yamane 1997 ^[140]
NaOH-ZnO (BioCelSol)	17 ^[133] 15–16 ^[141]	7.2 ^[133]		7.8 ^[133] 15–16 ^[141]	Röder et al. 2009 Struszczuk et al. 2002
NaOH-urea	10–20 ^[134]			9–21 ^[134]	Cai et al (2004) ^[142]
NaOH-urea + LiOH	20–35 ^[135]	14–25 ^[135]		8–24 ^[135]	Zhu K et al. (2018) ^[143]

^{a)}Also known as Rayon; ^{b)}Modal is a trade name for a special type of viscose produced from beech pulp, with higher tenacity and wet strength compared to ordinary viscose; ^{c)}Trade name: Tencel (Lenzing AG); ^{d)}Cupro fibers are based on regeneration of cotton linters dissolved in ammonia and copper oxide. Produced commercially by Asahi Kasei under trade name Bemberg; ^{e)}Fortisan fibers are produced by spinning of the derivative cellulose acetate (CA) dissolved in acetone. The CA fibers are subsequently converted to pure cellulose fibers by saponification using NaOH; ^{f)}Also known by the names Fibre B or Bocell; ^{g)}The tenacity, dry (MPa) of these fibers are 74,^[135] and 305–556,^[117] respectively; ^{h)}MCC used as cellulose source; ⁱ⁾Values recalculated from g per den to cN per tex. References are given in parentheses.

Applying IL/cellulose solutions, there is a range of possibilities to process cellulose for applications other than continuous filaments or fibers. Such new developments were highlighted in a review by Hermanutz et al.^[146] Interesting technical applications such as all-cellulose composites, spinning of polymer blends (e.g., cellulose plus chitin) and precursors for carbon fibers were described.^[147] For carbon fiber precursors, it was shown that the use of different ILs makes it possible to co-spin lignin (another abundant renewable wood-based macromolecule) with cellulose. This can result in an increased yield of the final carbon fiber as well as reduced processing time during the stabilization step of the conversion to carbon fibers.^[128,148–150] An interesting development is the use of ILs for partial dissolution of natural fibers (e.g., cotton and linen fibers) in a post-processing treatment called natural fiber welding. During this treatment, loose fibers are partially solubilized and consolidated upon removal of the IL, leading to increased interactions between the fibers. This results in an increase of both mechanical and thermal properties of the fibers. Thus, natural fiber welding offers a simple and green approach to further enhance and tailor the properties of biopolymer yarns and composites.^[151]

As previously mentioned, the main issue regarding any application of ILs on commercial scale is solvent recovery and re-use. As known, recovery by evaporating volatiles is energy demanding. Among the alternatives proposed, we mention ion exchange,^[152] using CO₂ for separation of IL and water,^[153] freeze crystallization in combination with evaporation,^[154] and refer the reader to recent comprehensive reviews on this subject.^[155,156]

2.4.2. Regeneration of Cellulose from Alkaline Solutions without and with Additives

A comprehensive critical review covering all aspects of dissolution of cellulose in aqueous NaOH solvents (both pure aqueous NaOH and aqueous NaOH + additive), including mechanisms of swelling and dissolution, influence of additives as well as properties of materials produced from these solutions was reported by Budtova and Navard.^[131] The obvious advantage of this solvent system is its low cost, potential for large-scale applicability, and the relative simplicity of chemicals recycling. Regeneration of cellulose into fibers from solvents based on aqueous NaOH were reported by several groups, and, in general, the properties of the regenerated cellulose fibers are comparable to those of viscose, albeit lower compared to those of Lyocell. The reasons that NaOH-based cellulose solvents have not reached full-scale industrialization include: the need for low cellulose dissolution temperature, the limited stability of the biopolymer solutions, the low cellulose DP and concentrations that can be used, as well as a need for additives, *vide infra*. However, some of these issues may not be as severe as to hinder large-scale production as recent patents describe both a dissolution and spinning process for cellulose in an NaOH-based system, including a system for recovery of chemicals.^[157–159]

Dissolution of cellulose in aqueous systems consisting of NaOH/urea, NaOH/thiourea, or LiOH/urea at low temperature has been investigated extensively.^[160] Regeneration of cellulose

from these systems into, for example, fibers, membranes, films, microspheres, hydrogels, and cellulose derivatives, for example, hydroxypropylcellulose (HPC) and methylcellulose (MC) was summarized.^[161] As an example of recent results from these systems, it was shown that multifilament fibers of cellulose (5–6 wt% conc.) dissolved in NaOH-urea with addition of a small concentration of LiOH (≈0.5 wt%) at –12 °C could be produced. The fibers were prepared using lab-scale equipment and the coagulation bath consisted of 15 wt% phytic acid and 5 wt% sodium sulfate. The coagulation system was proposed to lead to removal of a shell of an alkali-urea complex leading to assembly of desolvated cellulose chains in a parallel geometry which then aligned easily in the spinning direction. Fibers with good mechanical properties; an average diameter of 25 nm and tensile strength (dry state) of 35 cN per tex were produced,^[143] see Table 1 for comparison with other solvents and processes.

Another potential technology for the formation of fibers using an alkaline system is the so-called BioCelSol process, which was developed by Polish and Finnish research teams.^[141] The BioCelSol process is based on enzymatic and mechanical treatments of cellulose prior to dissolution in sodium zincate.^[162] The mechanical properties were similar or slightly inferior compared to commercial viscose. However, the BioCelSol fibers consumes less dye for coloring a fabric compared to viscose or cotton.^[163] It is still questionable whether the greenness of this process can compensate the use of enzymes under large-scale production conditions.

2.4.3. Cellulose Carbonate and Carbamate Processes

Similar to the viscose process, it is also possible to use other types of cellulose derivatives and subsequently dissolve them in dilute alkali to form fibers via wet spinning and precipitation in acidic coagulation baths. There is an obvious environmental advantage for replacing the viscose process, especially avoiding the use of CS₂, and liberation of H₂S (harmful, volatile, and flammable) during viscose manufacturing.^[164]

One potential alkali-soluble cellulose derivative is cellulose carbonate, which can be synthesized under both heterogeneous and homogeneous reaction conditions.^[165] An interesting approach was presented by Oh et al.^[139,166] where cellulose carbonate was synthesized by reaction of soda-cellulose with CO₂ under ≈40–50 bar pressure in the presence of ZnCl₂ and acetone or ethyl acetate. The derivative was subsequently dissolved in NaOH with the addition of zinc oxide (ZnO) and the solution was wet spun into continuous filaments using acid/water or acid/salt/water coagulation baths. The resulting fibers showed mechanical properties comparable to viscose rayon fibers.^[139]

Another promising alternative to the viscose process is the cellulose carbamate process (CarbaCell). It was described already in the late 1930s that a reaction between cellulose and urea results in the formation of cellulose carbamate which easily dissolves in dilute NaOH.^[167–170] Many synthesis routes were presented that can be used to form cellulose carbamate, examples include heterogeneous reaction without solvent using microwave heating of cellulose/urea mixtures, or by using supercritical CO₂ as solvent to introduce urea to the

cellulose.^[165,171] Regarding fiber spinning of cellulose carbamate, experiments were conducted at both pilot scale^[137,172,173] and semi-industrial production scale.^[138,174] Cellulose carbamate was dissolved in aqueous NaOH solution containing ZnO, and was subsequently wet spun into coagulation baths of 8 wt% H₂SO₄ and 20 wt% Na₂SO₄, at 25 °C. The regenerated cellulose fibers obtained have tenacities of ≈17–26 cN per tex and elongation of 12%.^[172] The produced fibers also showed improved dyeing compared to viscose rayon.^[173] In addition, improvements were made to reduce the amount of urea required for the cellulose carbamate synthesis.^[175] In addition to elimination of the (CS₂/H₂S) environmental problem, the cellulose carbamate process uses the same equipment employed for the viscose process. Cellulose carbamate is also relatively stable at room temperature; it can be stored for longer periods of time without losing quality.^[137,165] As compared with viscose production, the alkali consumption is higher in the carbamate process. This limitation may be removed by further optimization of the process variables. This could potentially lead to industrialization of the process in a not too far future.^[138] Interesting work was done by combining cellulose carbamate with the Lyocell process. By dissolving cellulose carbamate in NMMO, high polymer concentrations was reached (up to 30%), and regenerated fibers reached a very high tenacity (≈65 cN per tex) and a high modulus (≈50 GPa).^[137]

3. Chemical Recycling of Polycotton

At the outset, we cite a few statistics about textile production, use and recycling. In 2014, ≈90.8 million tons of textile fibers were produced worldwide. The global textile and apparel market is expected to grow at a compound average rate of ≈3% per year and to exceed 100 million tons by 2025.^[1,176] In 2017, the annual textile waste in China, the United Kingdom, and the United States was ≈26.0, 1.0, and 12.4 million tons, respectively.^[176,177] According to one estimate, the world disposes 75% of textiles waste annually due to the absence of viable recycling strategies; 87% of all post-use textiles go to landfill and incineration; only 20% of clothing is collected for reuse or recycling; <1% of the textile materials used to produce clothing is currently recycled into new clothing.^[178] Therefore, the volume of textiles produced, that used by consumers, and the (subsequent) generated waste is huge and will continue to grow because of increased world population. Consequently, developing efficient, economically viable recycling schemes is necessary, and should be actively pursued.

Figure 12 shows a typical life cycle of fibrous material where post-industrial waste is produced, for example, during fabric manufacturing. Examples of post-consumer waste are clothes and service items (hospital towels, bed sheets, pillowcases, coats, etc.). See definitions of both types of wastes in Supporting Information. Among employed waste disposal processes, incineration causes secondary air pollution. Mechanical recycling for fiber production is limited to single polymer waste streams,^[179–183] although the chemical recycling strategy was also applied to cotton shirts. In this case, relatively mild acid hydrolysis of cotton was carried out (0.05 wt% aqueous H₂SO₄, 12 min, 120 °C), followed by cellulose washing and

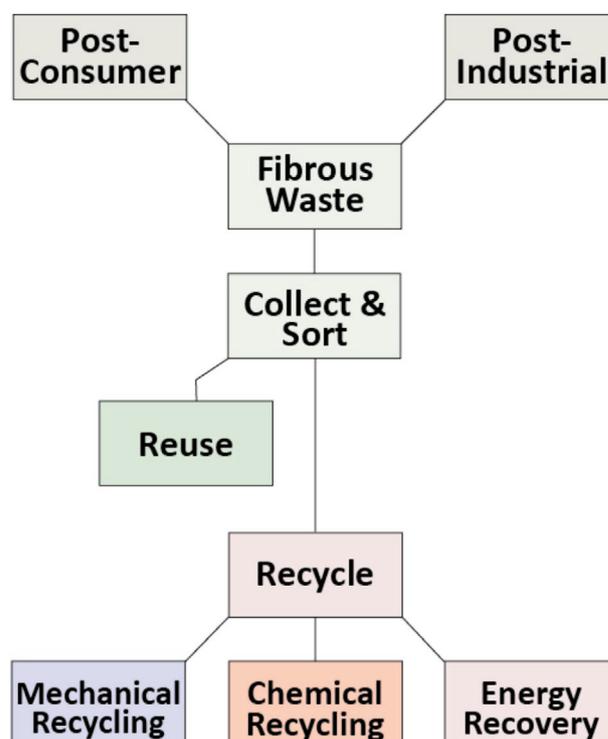


Figure 12. Schematic representation of a typical life cycle of fibrous material after manufacturing (post-industrial) and use by consumers (post-consumers). Waste disposal in landfills is not shown.

drying. The recovered cellulose (DP 660) was dissolved in aqueous alkali (LiOH/Urea and NaOH/urea, −12.5 °C) and regenerated in an acid bath (aqueous H₂SO₄/(NH₄)₂SO₄).^[184] Recycling of post-industrial blended waste is simpler than its post-consumer counterpart because its composition is usually known.

In principle, CR is conceptually simple, cost-effective, and environmentally benign.^[185,186] The most relevant aspect of chemical recycling of polycotton is to separate its components.^[187] The separation strategies are summarized in **Figure 13**, including: i) preferential dissolution of PET using a suitable solvent; ii) depolymerization of one polycotton component using acidic, alkaline, or enzymatic catalysts leaving the other less affected by the treatment^[188]; iii) dissolution of cellulose in a suitable solvent followed by PET/solution separation and regeneration of the dissolved biopolymer using a suitable nonsolvent. Currently, strategy (ii) is attractive because of its lower cost, and economically viable end-use for the depolymerized products. Strategy (iii) is, in principle, superior because both polymers are recovered. Its economic viability requires chemical and thermal stability of the solvent, and efficient, low energy solvent recycling. Relevant to the discussion below is the work aimed at optimizing the conditions for cellulose and PET recycling by acid-, base-, and enzyme-catalyzed hydrolysis, alcoholysis, aminolysis/ammonolysis,^[189–191] and use of quaternary ammonium and quaternary phosphonium phase-transfer catalysts (PTCs).^[179,180] The reason is that the conditions employed to depolymerize the pure polymer can be applied to polycotton recycling after appropriate modifications.

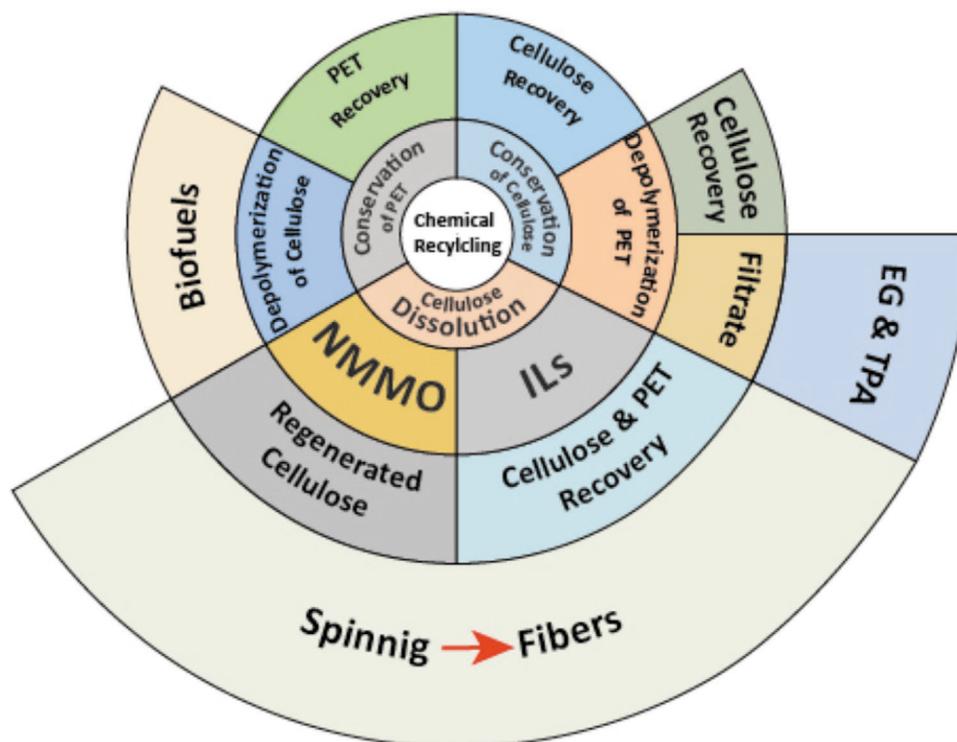


Figure 13. Schematic representation of recycling of polycotton. The strategies depicted include depolymerization of one component (cellulose or PET), preferential dissolution of cellulose, and recovery of both components. Preferential dissolution of PET is not shown.

3.1. Chemical Recycling through Preferential Dissolution of PET

Several examples are known where the PET component is dissolved, for example, in pure hexafluoro-2-propanol, or as its mixture with chlorinated solvents (chloroform and dichloromethane); in phenol and m-cresol^[192]; phenol/tetrachloroethane^[193]; DMSO and sulfolane (Sulf) at elevated temperatures.^[194] This strategy did not gain importance because most of the solvents employed are objectionable due to their environmental impact and corrosive nature.

3.2. Chemical Recycling through Cellulose Depolymerization and Recovery of PET

An example of acid-catalyzed depolymerization of the cellulose component of polycotton is the treatment with 5–10 wt% aqueous sulfuric acid at 80–100 °C for 15–30 min and separation of cellulose powder (DP ≈ 100) from the PET component. The latter can be used in spun yarn manufacture, or in fabrication of nonwoven material.^[195] In another variant of this treatment, polycotton was treated with gaseous HCl for 15–30 min at 49–71 °C. After HCl gas removal by compressed air and washing with water, cellulose was separated as a fine powder whereas PET remained in the treatment vessel.^[196]

The hydrolytic cleavage of the β -1,4-glucopyranose bonds of cellulose was performed using different acids. Ouchi and his co-workers optimized a simple two-step process to separate cellulose powder from various cellulosic fabrics, including mercer-

ized cotton, Tencel, rayon, and polycotton.^[197] The steps include a short-time (\approx 10 min) acid treatment with 10 N aqueous H₂SO₄ or 10 N HCl at 95 °C, followed by mechanical beating (15 min to 4 h) in water at room temperature, and separation of cellulose powder from PET, see **Figure 14**.

To reduce the amount of acid employed, the fabric was padded in the aqueous mineral acid and the hydrolysis was carried out in toluene. The results showed faster hydrolysis of cellulose in the presence of toluene rather than that in the aqueous acid. The DP of cellulose decreased from \approx 2200 to 160–170 for the powder. Hydrolysis with HCl gave similar results, except for lower recovery of cellulose powder. These authors reported complete separation of the mixed fabrics with high recovery of both cellulose powder and polyester cloth.^[197]

Phosphotungstic acid (H₃PW₁₂O₄₀) is a solid (m.p. 89 °C), strong acid (K₁ in water = 10³),^[198] that hydrolyzes cotton to MCC; the catalyst can be recycled by diethyl ether extraction.^[199] The treatment steps are schematically shown in **Figure 15**.^[200]

Waste polycotton fabric (WBF) was treated with aqueous solution of H₃PW₁₂O₄₀ in an autoclave at 120–170 °C for 3–8 h. The obtained solid residues (PET and MCC) were recovered by filtration, and the filtrate was collected for recycling of H₃PW₁₂O₄₀. PET was then separated using a 2 mm sieve and washed with water to remove (powder) MCC. The separated PET was hydrolyzed with water at 250 °C, and the terephthalic acid (TPA) purified.^[200]

PET was obtained with 96.2% recovery when polycotton was submitted to hydrothermal treatment with dilute HCl (1.5 wt%), at 150 °C, for 3 h. Increasing the temperature to

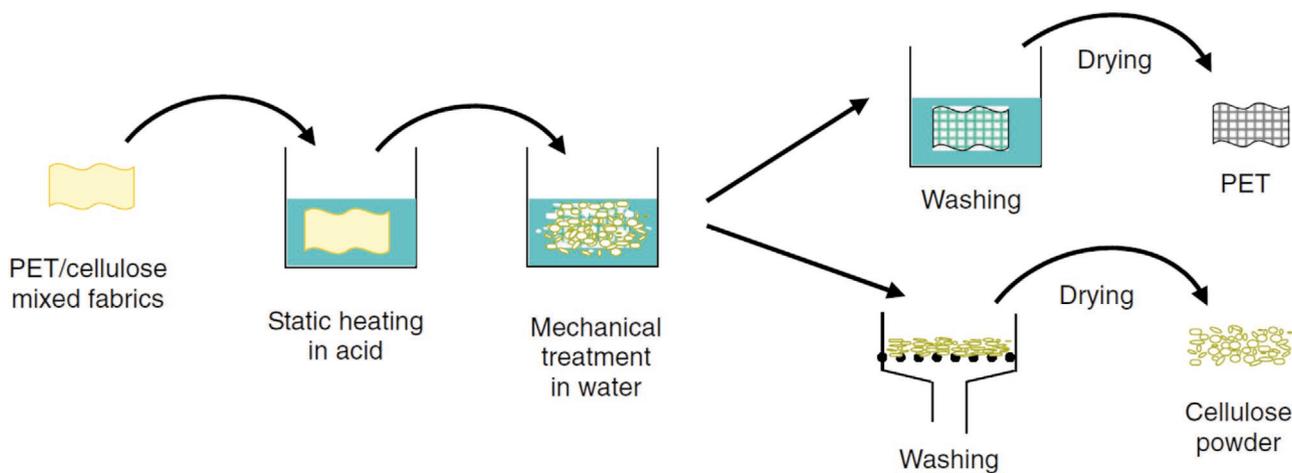


Figure 14. Schematic representation of the two-step separation of cellulose from PET. The steps are short-time acid hydrolysis, followed by beating in water at room temperature and separation of cellulose powder from PET. Reproduced with permission.^[197] Copyright 2010, Springer Nature.

170 °C decreased the cellulose powder yield, whereas increasing HCl concentration from 0.5 to 2.5 wt%, at a fixed temperature, produced the inverse effect. The PET was recovered with only slight decrease in its index of crystallinity and viscosity; MCC (48.2%) and glucose (15.6%) were obtained as cellulose hydrolysis products. The low acid concentration employed attenuates the equipment corrosion problem.^[201]

In order to address the process/environmental problems of using strong mineral acids, the cellulose component of polycotton was depolymerized in neutral (MgCl_2), or weakly acidic media, for example, $\text{MgCl}_2/\text{Al}_2(\text{SO}_4)_3$ and $\text{MgCl}_2/\text{citric acid}$. A two-step procedure was employed, namely pretreatment at 20–130 °C with aqueous solutions of the above compounds for 30 min, followed by heating at 150–180 °C. Cotton depolymerization efficiency followed the order: $\text{MgCl}_2/$

$\text{Al}_2(\text{SO}_4)_3 \geq \text{Al}_2(\text{SO}_4)_3 \gg \text{MgCl}_2$. Polycotton 50:50 blends pretreated at 20 °C with aqueous solution of MgCl_2 and $\text{Al}_2(\text{SO}_4)_3$ at composition of 1:5 (polycotton: solution), followed by heating at 180 °C gave the highest yield of cotton depolymerization, 95.5%. Pretreatment with $\text{MgCl}_2/\text{citric acid}$ at 130 °C followed by heating at 180 °C gave cotton depolymerization yield of 91.4%.^[202]

Rather than depolymerize the cellulose component in polycotton (35/65%, cotton/PET), the biopolymer was “extracted” from the blend via acetylation; leading to cellulose acetate (CA) and PET. Polycotton was cut into stripes, grinded into powder, acetylated with a mixture of acetic anhydride (anhydride/AGU molar ratio = 20/1) and *N*-methylimidazolium bisulfate catalyst, at 100 °C for 12 h, followed by product (CA plus PET) precipitation in ethanol. The produced CA was recovered by (Soxhlet)

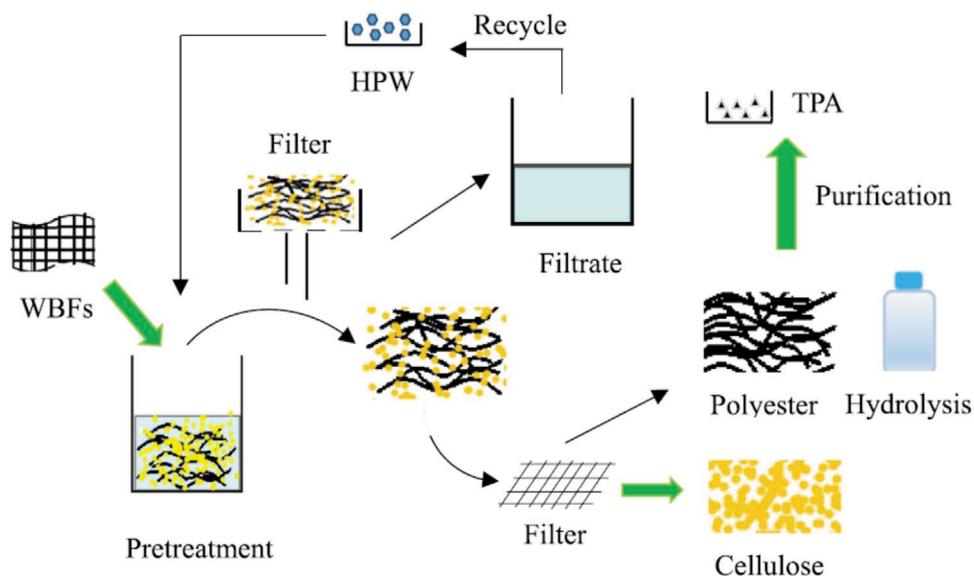


Figure 15. Schematic representation of separation of polycotton components by $\text{H}_3\text{PW}_{12}\text{O}_{40}$ -mediated hydrolysis of cellulose. WBF, HPW, and TPA refer to the polycotton fabric, phosphotungstic acid, and terephthalic acid, respectively. The pretreatment step is the acid hydrolysis of cotton. Reproduced with permission.^[200] Copyright 2019, Elsevier.

extraction with acetone. PET recovery was 96.2%, while cellulose conversion into CA was 84.5%. The DS of the produced CA was as high as 2.62 when the molar ratio catalyst/AGU was 0.4. Extraction of the solid mixture with acetone plus DMF (instead of acetone) gave similar CA recovery results (84.5% and 87.40%, respectively), showing that the major fraction of the produced CA had DS between 2.0 and 2.7, that is, acetone soluble.^[203]

Hydrolysis of the cellulosic part of polycotton was carried out enzymatically. The high crystallinity of cotton, however, hindered the enzymatic hydrolysis. This problem was attenuated by a pretreatment with alkali or alkali plus additive before the enzymatic hydrolysis step. This pretreatment is akin to mercerization that is frequently employed to activate cotton toward derivatization.^[5] Examples of the alkalis employed were aqueous LiOH and NaOH, alone or in the presence of urea and thiourea.^[204–206] Thus, alkali pretreatment of polycotton was performed using NaOH (12 wt%), NaOH/urea (7/12 wt%), NaOH/thiourea (9.5/4.5 wt%), and NaOH/urea/thiourea (8/8/6.4 wt%) at –20, 0, 23, and 100 °C for 1 h. The alkali was removed by filtration, the solid product washed with water, air dried, and then treated with a buffered solution of cellulase (pH = 4.8) at 45 °C for 72 h; PET was separated by sieving. To demonstrate the advantage of fabric pretreatment, simultaneous saccharification and fermentation were carried out on polycotton without and with pretreatment with NaOH, NaOH/urea, and NaOH/thiourea at –20 °C, as well as NaOH/urea/thiourea at 0 °C. The results showed much higher PET recovery and ethanol production when polycotton pretreatment was used (PET = 96.4 ± 1.4%; ethanol 68 ± 2%; 72 h incubation time) than without (PET = 54.5%; ethanol = 30–38%, 72 h incubation time). Thus, this (consecutive) treatment produces PET, glucose and ethanol (**Figure 16**), in all cases lower pretreatment temperature and presence of urea enhanced the yields.^[207]

The enzyme-catalyzed hydrolysis scheme was extended to blends of cotton (50–90%)/PET (5–40%)/wool (5–10%). The samples were grinded, suspended in boiling water for 30 min, filtered, and dried. First, the wool component was hydrolyzed by agitating the powder with protease at 50 °C for 2 days. The resulting solid was filtered, washed, dried, and then agitated

with a cocktail of cellulases at 50 °C for 5 days. This consecutive enzymatic treatment led to depolymerization of ≈90% of the wool component, 60–89% of the cellulose present in the blends. Further enzymatic hydrolysis of the products was carried out to produce bioethanol (*Saccharomyces cerevisiae*) and partially hydrolyze the produced PET (*Humicola insolens*).^[208]

As shown above, acid-catalyzed hydrolysis of the cellulosic component of polycotton produces oligomer and glucose that cannot be re-polymerized chemically. As shown by the last examples, however, these degradation products can be further fermented to biofuels (bioethanol and biogas),^[209] or as a feedstock for the production of bacterial cellulose.^[210,211] Consequently, if the aim of the recycling is to produce material with high molar mass, oligomer and monomer chemical re-polymerization is needed; this is feasible for depolymerization of the PET component,^[212] as shown in the following section.

3.3. Chemical Recycling through PET Depolymerization and Recovery of Cellulose

The third approach to recycle polycotton chemically is base-catalyzed hydrolysis of the PET component to recover cellulose. This recycling approach is advantageous because many polycotton articles, in particular hospital towels, pillow cases, and bed sheets were already subjected to a very large number of washings under relatively harsh conditions (high alkalinity and temperature), leading to partial degradation of the PET component of polycotton.^[39] That is, PET of low quality (low DP and index of crystallinity) would have been obtained if the cellulose-acid-catalyzed hydrolysis strategy was employed.

In their work on polycotton recycling, Palme et al. used the alkaline hydrolysis approach with and without the PTC benzyltri(*n*-butyl)ammonium chloride.^[188] Thus, 5–15 wt% aqueous NaOH was used for the hydrolysis of the blend at 70–90 °C, producing sodium terephthalate (TPA-Na) and ethylene glycol (EG). The alkaline hydrolysis of PET was completed in 40 min when performed in the presence of the PTC. PET hydrolysis products are soluble in water and remained in the aqueous phase, while cellulose was separated by filtration. This

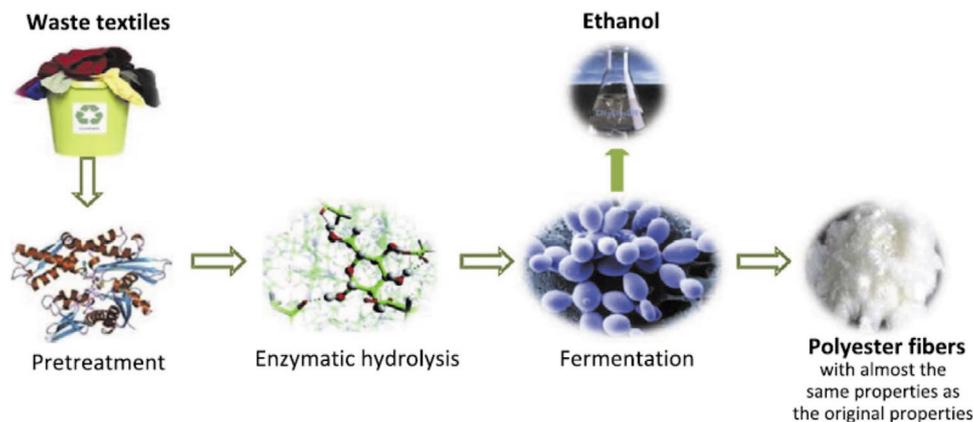


Figure 16. Polycotton treatment to produce PET and ethanol as end products. Alkali pretreatment activated the cotton component toward enzymatic hydrolysis to sugars that were fermented to ethanol. Reproduced with permission.^[207] Copyright 2014, Elsevier.

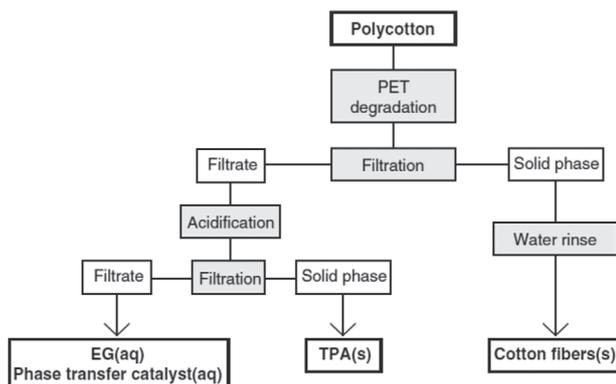


Figure 17. Chemical recycling of polycotton via PET alkaline hydrolysis in the presence of a PTC. The process leads to separation of cotton and recuperation of PET monomers, namely EG and TPA. Reproduced with permission.^[15] Copyright 2017, Springer Nature.

aqueous phase is then acidified (pH = 2.5–3.0) to precipitate TPA, see **Figure 17**. The results obtained showed that: i) PET can be completely hydrolyzed within 40 min in 10% NaOH at 90 °C with the addition of 52 mmol PTC per kg hydrolysis solution; it can be recovered as pure TPA; ii) increasing the temperature, NaOH concentration, and the PTC concentration increased the reaction rate; iii) hydrolysis without the PTC also yielded pure streams, albeit at a slower rate; iv) The isolation of pure cotton and TPA implies that PET production can be accomplished through re-polymerization of the TPA with EG.^[188]

A recycling process for (50/50) cotton/PET blend through alkaline hydrolysis of PET and separation of the cotton component from EG and TPA-Na by filtration was proposed. The experimental hydrolysis conditions were 3 M NaOH, 95–108 °C, 200–1600 min. TPA was recovered from the aqueous phase by filtration after solution acidification, whereas the filtrate was concentrated to an aqueous solution

of EG. The cellulose separated was dissolved in NMMO and spun to produce fibers.^[213]

3.4. Chemical Recycling of Polycotton without Degradation of the Components

As indicated above, preferential dissolution of PET requires solvents that are either corrosive or inconvenient environmentally. Recently, the alternative approach of preferentially dissolving the cellulose component physically with an environmentally acceptable solvent was introduced. After dissolution, PET is separated, and the dissolved cellulose is regenerated. This strategy is superior to the above-mentioned ones because both polymers are recovered, albeit with lower DP than the starting polymers. Its industrial application requires cost reduction of the solvents employed, optimization of the process conditions to decrease polymer degradation during preferential dissolution of cellulose, and development of efficient, low energy solvent recycling methods. The scheme below (**Figure 18**) is typical for simultaneous recovery of cellulose and PET from polycotton using the IL 1-allyl-3-methylimidazolium chloride (AlMeImCl).^[187]

Several reports are available in the literature that use ILs to separate the PET from the textile waste through preferential dissolution of cellulose. For example, there is a report on separating PET from polycotton by dissolving the cellulose component using NMMO. The biopolymer solution is then separated by filtration and used for spinning of high-quality regenerated cellulose fibers.^[211] AlMeImCl and 1-allyl-3-methylimidazolium acetate were used for selectively dissolving the cellulosic component of the blend, PET was separated by filtration of the mixture while cellulose was recovered through coagulating in water or alcohol. Dissolution of cellulose required 6 h, at 120 °C.^[187] Enzymatic degradation of cellulose produces 94% of glucose when the blends were pretreated with AlMeImCl at 110 °C for 90 min.^[214]

Recently, the cellulose component of polycotton was dissolved in DBNAClO, containing excess acetic acid to suppress the

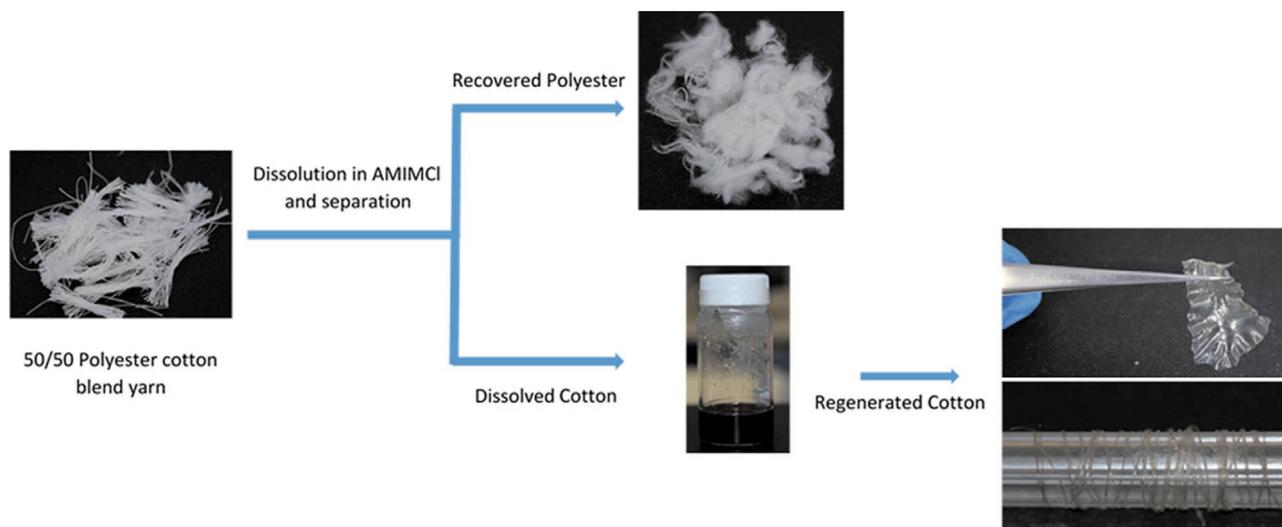


Figure 18. Separation and utilization of polyester/cotton blends using AlMeImCl. Reproduced with permission.^[187] Copyright 2014, The Royal Society of Chemistry.

degradation of PET. The cotton/PET blend was mixed with the IL at 80 °C for 1 h in a vertical kneader system; PET was separated using hydraulic pressure filtration, yielding 6.5 wt% cellulose solution. The latter was employed for dry-jet wet spin textile grade cellulose fibers down to the microfiber range (0.75–2.95 dtex) with breaking tenacities (27–48 cN per tex) and elongations (7–9%) comparable to commercial Lyocell fibers made from high-purity dissolving pulp. Under these experimental conditions the recovered PET had low cellulose content (1.7–2.5 wt%). Its molar mass, tensile strength, and tenacity decreased to <51%, <52%, and 47%, respectively of their original values. The degradation of PET can be reduced through optimizing the process conditions.^[215]

4. Conclusions and Perspectives

There are exciting recent developments in the fields of regeneration of cellulose, production of its fibers, and chemical recycling of cotton and polycotton. Use of various sub-classes of ILs and their mixtures with MSs is an important development because the resulting (low viscosity) biopolymer solutions can be processed into different (physical) shapes, including nanospheres, films, nonwovens (mats), and fibers with high tenacities. Aqueous alkali solutions, especially in the presence of urea and thiourea show potential use as cellulose solvents; this constitute a promising alternative to the traditional viscose process. Chemical recycling of polycotton reached the pilot scale, and initial commercialization.^[216,217] Additionally, there are commercial schemes for recycling cellulose, for example, from used clothes.^[216,218] Undoubtedly, ILs have considerable potential for ecofriendly recycling of textile wastes and, particularly, post-use items (garments, service clothing, items used hospital, e.g., clothing, towels, pillowcases, bed sheets, and coats). Judicious selection of the constituting ions of the ILs will minimize the cost and increase the dissolution efficiency of cellulose. These novel cleaner textile-recycling processes will lead to strengthening both sustainability and innovation in the textile industry. Efficient recovery and recycling of the solvents employed still need further development to improve process economy, in addition to a thorough assessment of their environmental impact.^[155,219] We hope that this account provides useful data and information for researchers and industrialists working to develop novel cleaner regeneration/recycling processes for cellulose-based materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

O.A.E.S. and M.K. thank FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) for financial support, grant numbers 2014/22136-4, 2016/22869-7, and 2017/06394-1. O.A.E.S. thanks CNPq for research productivity fellowship (grant number 307022/2014-5). K.J. thanks the Swedish Research Council Formas, grant number 942-2015-388. N.I.M. thanks the Consortium for Scientific Research, University Grants Commission (UGC-DAE) Collaborative Research Scheme, grant number UDCSR/MUM/AO/CRS-M-276/2017.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

cellulose blends, cellulose fibers, cellulose nanoparticles, cellulose regeneration, chemical recycling, films, nonwovens

Received: December 8, 2019

Revised: January 24, 2020

Published online:

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