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Chapter 1

From Cellulose Dissolution and Regeneration to Added Value Applications — Synergism Between Molecular Understanding and Material Development

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Additional information is available at the end of the chapter

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Abstract

Modern society is now demanding "greener" materials due to depleting fossil fuels and increasing environmental awareness. In the near future, industries will need to become more resource-conscious by making greater use of available renewable and sustainable raw materials. In this context, agro-forestry and related industries can indeed contribute to solve many resource challenges for society and suppliers in the near future. Thus, cellulose can be predicted to become an important resource for materials due to its abundance and versatility as a biopolymer. Cellulose is found in many different forms and applications. However, the dissolution and regeneration of cellulose are key (and challenging) aspects in many potential applications. This chapter is divided into two parts: (i) achievements in the field of dissolution and regeneration of cellulose including solvents and underlying mechanisms of dissolution; and (ii) state-of-the-art production of value-added materials and their applications including manmade textile fibers, hydrogels, aerogels, and all-cellulose composites, where the latter is given special attention.

Keywords: Cellulose, dissolution and regeneration, fiber, hydrogels, all-cellulose composites

1. Introduction

Cellulose was isolated for the first time by the French chemist Anselme Payen in 1838 [1], who extracted it from green plants and reported its elemental composition four years later [2]. Cellulose is the main component of the cell wall in higher plants, typically combined with

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lignin, hemicelluloses, pectins, proteins, and water. Apart from higher plants, cellulose can be synthesized by bacteria or be found in algae and tunicates. This readily available and renewable biopolymer is widely used in many applications such as paper, textiles, membranes, or packaging [3]. Cellulose is the most abundant and studied biorenewable material with an estimated annual production of 7.5 x 10^{10}t [4]. After more than 170 years of research into the "sugar of the plant cell wall", consumers, industries, and governments are increasingly demanding products from renewable and sustainable resources that are biodegradable, non-petroleum based, carbon neutral, and, at the same time, generating low environmental, animal/human health and safety risks [5].

Regarding its basic structure, cellulose is a linear syndiotactic homopolymer composed of D-anhydroglucopyranose units (AGU), that are connected by β(1–4)-glycosidic bonds (Figure 1) [5].

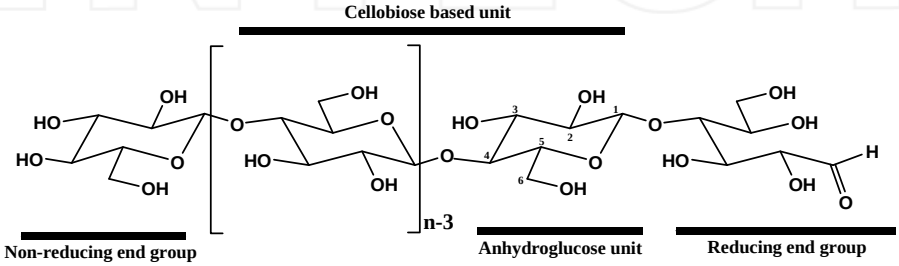


Figure 1. Molecular structure of cellulose (n = value of DP).

The size of the cellulose molecules can be defined by the average degree of polymerization (DP). The average molecular weight is estimated from the product of the DP and the molecular mass of a single AGU. Each AGU bears three hydroxyl groups (one primary and two secondary moieties that represent more than 30 % by weight), with the exception of the terminal ones. These structural features make cellulose surface chemistry quite intriguing and opens a broad spectrum of potential reactions, which typically occur in the primary and secondary hydroxyl groups [3].

From the single AGU up to the cellulose micro- and macrofibrils that constitute the cell walls, cellulose organizes in a rather dense and highly hierarchical fashion where an extended intra- and intermolecular network of hydrogen bonds is believed to constitute the basis of cohesion between cellulose molecules [6]. At the beginning of the biosynthesis, cells in higher plants are surrounded by a very thin outer wall, the primary (P) wall (0.1–0.5 μm thick), which envelops the cytoplasm. After completion of the elongation growth stage of the cells, the thickness of the cell wall increases significantly by the successive deposition of concentric inner layers, constituting the secondary (S1) and (S2) walls (0.1–0.3 μm and 1–10 μm thick, respectively). The last layer deposited, called the tertiary layer (T) in the case of wood fibers and (S3) layer in the case of cotton, is not always present and is very thin (< 100 nm). At the end of the biosynthesis, the cytoplasm dies, and the resulting central channel within the cells, so-called

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the lumen, is more or less narrow depending on the maturity of the fibers. In this layered structure, the different chemical components are distributed and organized, forming a complex and tri-dimensional composite microstructure [4, 6]. Cellulose microfibrils are reasonably oriented and hold together due to the cooperative function of the hemicelluloses, lignin, and pectins that act as matrix and adhesive components. The resulting fibrillar cells, also called elementary fibers, are usually gathered in fiber bundles as for wood or flax and hemp stems, or can be eventually found individualized in the elementary fibers as is in the case of cotton fibers.

A complementary perspective highlights the amphiphilic nature of cellulose [7–12]; the equatorial direction of a glucopyranose ring has a hydrophilic character because all three hydroxyl groups are located on the equatorial positions of the ring. On the other hand, the axial direction of the ring is hydrophobic since the hydrogen atoms of C–H bonds are located on the axial positions of the ring. Thus, cellulose molecules have an intrinsic structural anisotropy and due to intra- and intermolecular hydrogen bonding, there is a formation of rather flat ribbons, with sides that differ markedly in their polarity [10, 13, 14]; this is expected to considerably influence both the microscopic (e.g. interactions) and macroscopic (e.g. solubility) properties of cellulose.

As a semi-crystalline polymer, cellulose is able to adopt different forms in the cell wall of a plant such that amorphous regions (lower order) coexist with crystalline domains (higher order) [4]. The degree of crystallinity of cellulose, usually in the range of 40–60 %, depends on the origin and pre-treatment of the sample [6]. Interestingly, the parallel arrangement found in nature (so called cellulose I), is not the most stable structure for a cellulose crystal. Thus, when cellulose I is dissolved and recrystallized, cellulose chains may adopt an anti-parallel arrangement known as the cellulose II type crystal [15, 16]. This intriguing process is still not understood in detail. However, it has been postulated that the transition from cellulose I to cellulose II crystals does not require full chain swelling and coiling in solution; this transition could be reached by a simple translational movement of molecules, in particular during mercerization [4].

2. Cellulose dissolution

2.1. Solvents

The first attempts to dissolve cellulose or cellulose-containing materials were described about 150 years ago [3]. In many important cellulose applications, it is necessary to dissolve the biopolymer and normally this is a challenging step. Due to the complexity of such a biopolymeric network, the partial crystalline structure and the extended non-covalent interactions among molecules, chemical processing of cellulose is rather difficult. Cellulose is neither meltable nor soluble in water or a large range of organic compounds [17]. However, this biopolymer is soluble in more exotic media with no apparent common properties [18].

Cellulose solvents are usually divided in two main groups: non-derivatizing and derivatizing solvents [19]. Historically, derivatization came first. As the name suggests, the derivatizing

solvent group comprises all the systems where cellulose dissolution occurs via covalent modification giving an "unstable" ether, ester, or acetal intermediate, such as cellulose nitrate, cellulose xanthate or cellulose carbamate. The viscose process ($NaOH + CS_2$) is by far the most common derivatizing cellulose solvent system used [20].

The "non-derivatizing solvent" class, comprise systems capable of dissolving cellulose only via physical intermolecular interactions. This class of solvents is quite relevant for the organic chemistry of cellulose under homogeneous conditions. Historically significant, and of practical relevance for analytical purposes, is the system introduced by Schweizer in 1857 [21]. It was found that copper salts and concentrated ammonia effectively dissolve cotton. Among the most popular is cuprammonium hydroxide or simply "cuam". Fifty years later, ethylenediamine was found to be a good alternative to ammonia and also new complexing solvents were designed, such as the cadmium hydroxide in aqueous ethylenediamine, "cadoxen", or nickel oxide in the same aqueous ethylenediamine, "nioxen" [18, 22, 23]. Similar alternative systems have been reported using mainly other transition metals (such as palladium and zinc) and an amine or ammonium compound. However, none of these systems have been able to achieve full commercial success [18].

Since the work of Sobue et al., it is known that cellulose is soluble in aqueous NaOH below -5 °C within a specific concentration range of NaOH (7–10 %) [24, 25]. This system is potentially cheap, non-polluting, easy to handle and uses common chemicals. The aqueous alkali systems often, however, do not completely disrupt the semicrystalline regions of cellulose and the solubility is limited to cellulose of relatively low DP. The apparent solubility also depends on the degree of crystallinity and crystal type. Pre-treatments, such as steam explosion of the dissolving pulp, have been successfully used [26]. Other aqueous bases, such as LiOH [27], or quaternary ammonium hydroxides are also capable of dissolving cellulose [4, 18, 28]. More recently, the combination of aqueous NaOH solutions with other additives such as polyethylene glycol, PEG [29], urea [30], and thiourea [31] has been explored.

In 1932, Letters et al. investigated the swelling and dissolution of cellulose in aqueous zinc chloride; dissolution was only observed at concentrations as high as 63 % (w/w) [32]. However, in later publications only three water/salt systems were described as effective cellulose solvents in more detail: $Ca(SCN)_2/H_2O$, $LiSCN/H_2O$, and $ZnCl_2/H_2O$. Among such classes of salts, $Ca(SCN)_2\,3H_2O$ showed a strong swelling and solvent action on cellulose [33]. Only the mixture of NaSCN/KSCN with $Ca(SCN)_2\,3H_2O$ or dimethyl sulfoxide (DMSO) was found to be able to dissolve cellulose. In addition, molten $LiSCN\,2H_2O$ is described as cellulose solvent [19]. Recently, Leipner et al. reported that $LiClO4\,3H_2O$ is a very effective solvent where transparent cellulose solutions can be obtained within a few minutes without pre-treatment or activation [34]. Moreover, mixtures of $LiClO_4\,3H_2O$ with $Mg(ClO_4)_2\,H_2O$ or $MgCl_2.6H_2O$ are also regarded as promising solvents.

Non-aqueous systems are also suitable to dissolve cellulose. Again, the solvent spectrum is broad and the number of possible combinations is high. From a historical point of view, combinations of some simple inorganic compounds, such as SO_2 and NH_3 with a suitable ammonium salt, can indeed be considered as the origin of two large groups of non-derivatizing non-aqueous solvent systems [35]. The first group worthy of mention generally comprises

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mixtures of a polar organic liquid, SO_2, and primary, secondary, or tertiary aliphatic or secondary alicyclic amines [36]. Alternatively, the sulfur component may be modified to $SOCl_2$. Suitable polar liquids employed are for instance N,N-dimethylformamide (DMF), DMSO, N,N-dimethylacetamide (DMAc) or formamide. From the wide variety of possible mixtures, DMSO/SO_2/diethylamine is one of the most versatile [35].

Relevant mixtures of two-component solvents containing DMSO [19] such as DMSO/methylamine, DMSO/KSCN, DMSO/$CaCl_2$, DMSO/formaldehyde, and DMSO/substituted ammonium fluorides, such as tetrabutylammonium fluoride, TBAF, a recently discovered powerful solvent capable of dissolving cellulose of reasonably high DP (650) within a few minutes without any pre-treatment at room temperature [37]. Non-aqueous solutions based on lithium salts are also very relevant for the analysis of cellulose and for the preparation of a wide variety of derivatives. In this regard, the DMAc/LiCl mixture, developed by McCormick in the late 1970s is noteworthy [38]. N-methylmorpholine-N-oxide (NMMO) emerged as the best of the amine-oxides in the late 1970's [3, 39]. Solutions up to 23 wt. % of cellulose were obtained by dissolving the polymer in NMMO/water mixtures, subsequently removing water under vacuum. This constitutes the basis of the Lyocell process whose commercial potential has been demonstrated and is now applied in large scale. Two main problems are still connected with the NMMO process; the instability of the solvent (demands costly investments for safety reasons) and the tendency of the regenerated fiber towards fibrillation [40].

Ionic liquids (ILs) are a very promising group of compounds in cellulose dissolution. These systems were first employed by Graenacher, in the form of N-alkylpyridinium salts, for the dissolution of cellulose and as media for homogeneous chemical reactions [41]. Almost seventy years passed before the work of Swatloski et al. where several low melting ionic liquids (below 100 °C) were reported as cellulose solvents [42]. This work triggered a new and exciting field in cellulose research and, since then, a huge variety of ILs has been developed. Note that the number of potential ion combinations available is estimated to provide around 10^{12} ILs [43]. Presently, the most efficient ILs for cellulose dissolution are mainly composed of a salt with halide [44], phosphonate [45], formate [46] or acetate [47] as anion, and imidazolium [48], pyridinium [6], choline [49], or phosphonium [50] as cation.

2.2. Swelling and dissolution mechanisms: From the cell wall structure down to the molecular level

2.2.1. Evidence of a heterogeneous swelling and role of the solvent quality

When placed in contact with a solvent, synthetic polymers dissolve in three main steps, *(i)* the solvent swells the solid phase that goes above its glass transition T_g, *(ii)* the swelling increases up to the disentanglement of the polymer chains, and finally *(iii)* the chains move out of the swollen phase to the solvent phase and the dissolution is completed [51, 52]. The dissolution occurs step by step from the outside to the inside of the bulk of the polymer, being the kinetics considerably different regarding the amorphous and crystalline zones.

Due to their complex hierarchical structures, cellulose fibers show a different picture characterized by a heterogeneous swelling and dissolution. The most peculiar effect of this hetero-

geneous swelling is the ballooning phenomenon, in which swelling occurs in specific zones along the fibers (Figure 2). The ballooning phenomenon has been observed and described long ago, first in 1864 by Nägeli [53], then by Pennetier [54], Flemming and Thaysen [55, 56], Rollins and Tripp [57, 58], Hock [59], Warwicker et al. [60]. According to these authors, this phenomenon is assumed to be caused by the swelling of the cellulose contained in the secondary wall of the fibers that leads to the bursting of the primary wall. As the cellulose swells, the primary wall rolls up in such a way as to form collars, rings, or spirals that restricts the uniform expansion of the fiber forming balloons.

Further studies of Chanzy et al. [61] and Cuissinat and Navard [62] showed that the swelling and dissolution mechanisms are strongly influenced by the solvent quality. Based on optical microscopy observations of the dissolution of wood and cotton fibers in a wide range of solvent qualities (i.e. in NMMO at 90 °C with increasing amount of water), the authors identified four main dissolution modes: *(i)* fast dissolution by fragmentation in good solvent (NMMO - < 17 % w/w water), *(ii)* swelling by ballooning and full dissolution in moderate solvent (NMMO - 19 to 24 % w/w water), *(iii)* swelling by ballooning and no complete dissolution in bad solvent (NMMO - 25 to 35 % w/w water), *(iiii)* low homogeneous swelling and no dissolution in non-solvent (NMMO - > 35 % w/w water).



Figure 2. Wood fiber swollen by "ballooning" in NMMO – 20 % w/w water at 90 °C (magnification of 200 times). (Pictures were taken by NLM at CEMEF - MINES ParisTech)

These mechanisms have also been observed in NaOH-water [63], ionic liquids [64], and for a wide range of other plant fibers [65] and some cellulose derivatives prepared by heterogeneous derivatization [66]. All these studies pointed out the leading roles of the solvent quality and the fiber microstructure on the dissolution mechanisms. As long as the native cell wall structure of cellulosic fibres is preserved, the swelling and dissolution mechanisms are found to be similar.

2.2.2. Gradient of dissolution within the cell wall structure and role of the chemical environment of cellulose chains

The role of the cell wall structure was investigated in detail by Le Moigne et al. [67, 68] by studying the dissolution mechanisms of cotton fibers extracted from cotton bolls at successive growth stages. When observing fiber dissolution in various solvent qualities, the authors

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showed that the primary P wall and the secondary S1 wall and S2 wall, which are successively deposited in concentric layers during biosynthesis, behave very differently upon dissolution. In good solvents (NMMO - 16 % w/w water), the whole fiber breaks into rod-like fragments and dissolves fast. In contrast, cellulose fibres in moderate solvent (NMMO – 20 % w/w water) dissolve by ballooning following the steps (1, 2, and 3) illustrated in Figure 3. Three main areas are implied in the ballooning phenomenon: *(i)* the fragments that are made of the secondary S2 wall and dissolve easily and quickly within the balloons, *(ii)* the membrane of the balloons that is made of the swollen secondary S1 wall and dissolves slowly, and *(iii)* the helices and collars surrounding the balloons that are made of the primary P wall do not dissolve easily and break under the expansion of the secondary wall. These observations revealed a centripetal radial gradient of the dissolution capacity from the inside to the outside of the fiber, being the inside layers from the secondary S2 wall easier to dissolve.

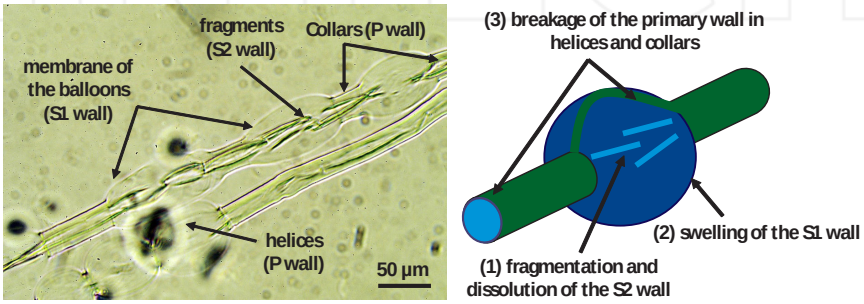


Figure 3. Optical microscopy observation of a cotton fiber in NMMO – 20 % w/w water at 90 °C: (left) description of the zones implied in the ballooning phenomenon; (right) successive dissolution steps (1, 2, and 3). (Pictures were taken by NLM at CEMEF - MINES ParisTech)

Considering that the degree of polymerization and the crystallinity of cellulose increase during the biosynthesis of the secondary S2 wall [69, 70], the dissolution capacity of cellulose fibers does not depend, in a first instance, on thermodynamics (molar mass), or kinetic (crystalline or amorphous) parameters. The gradient in dissolution capacity of the successively deposited cell wall layers has to be related with the specific hierarchical and multi-component structure of cellulose fibres. The primary wall is indeed composed of cellulose and hemicellulose as well as pectins and proteins, while the secondary S2 wall contains almost only cellulose and hemicelluloses [71]. Dynamic FTIR spectroscopy experiments showed that all these components are strongly linked together [72]. As described by Klemm et al. [4], the cellulose microfibrils are also differently arranged and packed within the cell wall structure. The dissolution capacity of cellulose fibers must thus be considered at two structural levels, *(i)* the cell wall structure that needs to be dismantled for improving dissolution, and *(ii)* the chemical environment of cellulose chains. In this sense, it has been shown that the dismantlement of the cell wall layers induced by steam explosion, acidic hydrolysis, or a simple shearing of the solution eases the dissolution of wood pulps in bad quality solvents such as NaOH-water mixtures [73–76]. Based on a selective separation by centrifugation of insoluble and soluble cellulose

fractions in cellulose-NaOH-water mixtures and further analyses by size exclusion chromatography, Le Moigne et al. [76] also showed that cellulose chains of similar molar masses can be either dissolved or remain as insoluble fractions. Some of the cellulose chains are thus less accessible than others and embedded in structural regions difficult to dissolve. The carbohydrate composition analysis of the various insoluble fractions revealed that it may contain higher amount of non-cellulosic components than the soluble ones [76, 77]. Beyond thermodynamic considerations, the dissolution capacity of cellulose chains is thus highly influenced by their localization in the cell wall structure. Additionally, their chemical environment has to be regarded as an important parameter in the dissolution efficiency.

2.2.3. Molecular mobility and cellulose/solvent interactions

The dissolution of cellulose substrates implies that the solvating molecules have sufficient accessibility within the fiber structure to approach cellulose chains, and that the latter are able to gain conformational entropy to be further dissolved. However, the spinning process used for regenerated cellulose fibers as well as the naturally occurring bio-deposition mechanism in native cellulose fibers imply that cellulose chains are well aligned and strongly oriented in an extended conformational state, out of equilibrium. Considering the large number of hydroxyl groups available per AGU, this results in a strong intra- and intermolecular hydrogen bond network [7] that links all the cellulose chains together achieving a long range order. As postulated by O'Sullivan [1], even the chains in non-crystalline regions most likely still possess a certain degree of order. All these features strongly restrict the molecular mobility of cellulose chains.

Evidence of this long range order is the large contraction usually observed during swelling and dissolution of cellulose fibres in moderate quality solvent [68], which can be interpreted as the release of the stresses stored within the fiber structure during fiber processing or biosynthesis, and the return to the equilibrium conformational of individual chains that force the whole fiber structure to contract. If this contraction mechanism is restricted by holding the fiber under tension [78], it has been shown that full dissolution can be prevented and a large decrease of the chemical derivatization efficiency was also observed. The acetylation of Lyocell fibers without tension indeed led to degree of substitution (DS) values up to 1.3, while under tension, lower DS values of ca. 0.2–0.5 were estimated. Thus, the local molecular motions needed for the solvatation and the chemical reactions of cellulose chains were inhibited under tension. These observations highlight the key role of the molecular mobility and the need to find efficient ways to break the abovementioned intra- and intermolecular hydrogen bond network and prevent its reformation [79, 78] for improving cellulose dissolution and reactivity.

Apart from the hydrogen bonding role, there are also several indications regarding cellulose amphiphilicity, and thus a careful examination of the interactions involved suggests that hydrophobic interactions may also play a significant role in governing cellulose solubility. In fact, hydrophobic interactions have been shown to markedly contribute to the crystal-like structure of cellulose and its stability over a hypothetical solution state; from free energy simulations in oligomers it has been estimated that there is a 2.0 kcal/mol/residue contribution for hydrophobic stacking, while the estimated hydrogen bonding contribution is about eight times less [7].

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From a thermodynamic point of view, the dissolution of a polymer, such as cellulose, in a solvent is, of course, governed by the free energy of mixing [18]. A negative value of the free energy change on mixing means that the mixing process will occur spontaneously. Charging up a polymer is always expected to help solubility in many solvents; thus dissociated counterions contribute strongly to the translational entropy of mixing. This seems to be the main reason why cellulose tends to be more soluble or be more penetrated by water at either high or low pH. However, the pK values are such that rather extreme conditions are needed for either deprotonation or protonation of the hydroxyls; a pKa of ca. 13.3 has been found assuming that only one hydroxyl group per AGU dissociates [80].

A reasonable solvent for cellulose dissolution must be able to overcome the low entropy gain by favorable solvent/polymer interactions, and better dissolution results are obtained using amphiphilic solvents that are not only able to eliminate hydrogen bonding but also eliminate hydrophobic interactions. Both the amorphous and the crystalline regions can be affected by the solvent. However, the amorphous domains, due to a higher free energy, are preferentially and more easily accessed [8]. Therefore, it is not surprising that quite often, prior to dissolution, different activation processes are applied to mainly transform the more ordered and less accessible (crystalline) domains of cellulose into disordered and more accessible regions. It is argued that these alterations of the cellulose structure facilitate the solvent molecules to get access to the cellulose chains [81]. The crystallinity effect in dissolution is still controversial despite some supportive evidences of its effect. For instance, it is argued that sisal pulp (e.g. fibers extracted from the leaves of the *Agave sisalana* plant) dissolves more readily than cotton linters in a particular solvent as its crystallinity index and crystallite size are smaller than that of the latter. After pre-treatment of cotton linter (e.g. mercerization), dissolution was considerably improved and this observation was related to the decrease in both the crystallinity index and average crystal size [82].

In the majority of the cases, cellulose is not dissolved down to a molecular level but rather forms stable colloidal dispersions where ordered cellulose aggregates of, at least, several hundred chains, are present. The structure in solution has been proposed to consist of aggregates of "fringed micelle" type characterized by a highly ordered cylindrical core of aligned chains, which is insoluble in the solvent, and two spherical coronas surrounding the core ends [83]. Reaching molecularly dispersed systems has been challenging for nearly all known solvent systems. Recently, Cohen et al. showed that ionic liquids are able to dissolve cellulose down to a molecular level [84]. Typically, the cations of IL are bulky species with amphiphilic properties. Proof of this is that most literature agrees on the formation of aggregates or micelles of ionic liquids in water, similar to a surfactant behavior [85]. Such amphiphilicity is normally not considered when discussing the mechanism of dissolution of cellulose. This is particularly relevant since crystalline cellulose has an amphipathic-like structure; hydrophobic surfaces consisting of pyranose ring hydrogens and hydrophilic regions arising from the hydroxyl groups directed towards the sides of the ring. In fact, this also follows the earlier discussion on the effect of additives such as PEG, urea, and thiourea on NaOH solutions. Recent molecular dynamics simulation reveals that urea is preferentially adsorbed on the hydrophobic faces of the anhydroglucose rings but has the same affinity as water to the

hydroxyl groups. Thus, the simulations suggest that urea acts primarily by mitigating the effect of the hydrophobic portions of the cellulose molecule [86, 87]. In the same direction, a recent molecular dynamics simulations study carried out on cellulose oligomers and 1-ethyl-3-methylimidazolium acetate (C2mimOAc) indeed suggest that the cations are in close contact with the cellulose through hydrophobic interactions [88].

2.2.4. Improving cellulose dissolution: Towards targeted activation treatments

The challenge faced by generations of scientists and numerous companies is to find a simple, cheap, and non-polluting cellulose dissolution process. As pointed out in the previous sections, one of the crucial aspects in cellulose dissolution is the capacity of the fibers to be accessible for reagents in order to perform the subsequent transformation stages. Consequently, several chemical and physical methods, so-called ''activation", have been developed to ease cellulose dissolution, e.g. acid hydrolysis [24, 89], ball or vibration milling [4, 90], steam explosion [73–75], and electron beam irradiation [91–93]. The main goal is to disrupt the cell wall structure and the hydrogen bond network in order to increase the accessibility of the solvent within the fiber structure, while preserving the original macromolecular structure of cellulose chains. Although such methods improve cellulose dissolution, typically these activation treatments are accompanied by a strong degradation of the cellulose chains leading to low DPs, ca. 600–1200 for dissolving wood pulps and ca. 100–200 for cellulose powders. Such reduction in molecular weight may adversely compromise the properties of the final cellulose-based products [4]. This is mainly due to the lack of selectivity of the activation treatments that strongly affect the integrity of cellulose substrates at the different scales of their structure depending on the procedure employed. Thus, there is a need for more targeted activation methods.

In this respect, the recent advances in biotechnology with the use of enzymes are expected to bring new insights for the development of targeted activation treatments. As it was previously discussed, the chemical environment of the cellulose chains, as well as their localization within the cell wall structure, plays a key role in their dissolution capacity. Due to their specificity, enzymes should thus be an alternative strategy to improve the selectivity of activation treatments towards "non-dissolving" areas within the fiber structure. Several studies have showed that enzymatic treatments can increase cellulose solubility basically due to changes in DP and hydrogen bond density [94, 95]. However, in these studies, the potential specific action of enzymes within the fiber structure for the improvement of their dissolution capacity was not exploited.

Based on the observations that the external cell wall layers, i.e. the primary and S1 walls, prevent the efficient dissolution of cellulose fibers [67], Le Moigne et al. have recently investigated the possibility to perform a targeted enzymatic peeling treatment in order to remove the external walls and to improve the dissolution capacity of cellulose fibers without degrading their whole structure [96]. The alkaline solubility of the different enzymatically treated samples was investigated in NaOH–water solution. The results showed that the enzymatic peeling has two effects at short treatment times, *(i)* a digestion of the primary wall that was assessed by the near absence of ballooning and *(ii)* a degradation of the fiber structure that was supported

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by the decrease in the DP. At longer treatment times, the external walls were totally digested and the fiber structure totally dismantled. As expected, a direct correlation was found between the cellulose solubility and its DP and degree of crystallinity. Nevertheless, the removal of the external walls and the macrostructural disruption of the fibers must be regarded as important factors for the improvement of cellulose dissolution. The alkaline solubility of wood pulps having similar intrinsic viscosity values was indeed two times higher when the external walls were removed by the enzymatic peeling.

Interesting results were also obtained by the use of endopectinase and endoglucanase mixtures to improve dissolution of wood pulps in NaOH-water solution [97]. Although the mechanisms are not fully elucidated, it was suggested that endopectinases have a targeted hydrolyzing action on the pectic network present in the primary and S1 walls. This resulted in an enhanced accessibility and diffusion of the solvent through the external walls of the fibers and a significant increase in their swelling and dissolution capacity, while having a limited effect on the cellulose DP.

The use of enzymes for the improvement of cellulose dissolution is thus of great interest due to their high specificity and potential targeted action on the fiber structure that should allow to preserve the solid state of cellulose while improving its processing and the properties of final cellulose based products. As underlined by Koivula et al. [98], the future role of enzymes in lignocellulosic polysaccharide processing will depend on their added value and economical feasibility, as well as the wide industrial acceptance of biotechnologies.

3. Understanding the cellulose regeneration process

Typically, the regeneration of cellulose occurs when contacting the cellulose solution with a coagulation medium. The polymer profile at the point of precipitation exhibits a very high interfacial concentration, thus favoring the formation of a dense polymer "skin". The bulk of the sample is at near the initial concentration and is in a fluid state. Thus, a rapid inflow of the coagulant can take place through the weak points at the skin interface. Rapid growth of finger-like voids in the fluid region is expected to occur due to the moving interface created by the coagulant (less viscous) and solution (more viscous). The kinetics of regeneration is mainly controlled by the relative velocities of the counter-diffusion process; diffusion of the solvent from the solution into the coagulation bath and the coagulant from the bath into the solution [99].

The exchange of solvent with non-solvent leads to a desolvation of the cellulose molecules and supposed reformation of the intra- and intermolecular hydrogen bonds [100]. The regenerated mechanical and surface chemical properties are known to depend strongly on the type of cellulose solvent and coagulant. The reader is directed to the work of Isobe et al. and references therein [101].

Regenerated cellulose is highly wettable and has been identified as one of the most hydrophilic polymers. The contact angles of water droplets on regenerated cellulose such as cellophane and cuprophane are 11.6° and 12.2°, respectively. In contrast, the wetting angle of commodity polymers such as poly(styrene) are 83 and 108.5°, respectively. The high hydrophilicity of

cellulose is due to 3 hydroxyls per glucose unit, although this alone is not sufficient to explain the high wettability. A further reason for high hydrophilicity could be due to the uniplanar orientation of the (1 $\bar{1}$ 0) crystal plane when parallel to the material surface as many hydroxyl groups are on this plane [102]. Despite its hydrophobic nature, the structural anisotropy of cellulose may provide regenerated cellulose with hydrophilic properties [10]. As described by Yamane et al. [103] through wide angle X-ray diffraction (WAXD) analysis, glucopyranoses in the (1 $\bar{1}$ 0) crystal plane are stacked together by hydrophilic interactions and van der Waals forces. As a result, the density of hydroxyls on this plane surface is very high, resulting in the highest surface energy of crystal planes among cellulose I and cellulose II polymorphs. Molecular dynamics (MD) simulations are often used to elucidate on the mechanistic aspects of cellulose regeneration. Cousins and Brown have [104] suggested that a molecular sheet is the starting structure for the formation of native cellulose. Additionally, it is stated that the potential energy of the molecular sheets formed by hydrophobic interaction is far lower than that of hydrogen-bonded molecular sheets in water and therefore the former case was suggested to constitute the initial structure of crystallization.

Cellulose chains exist in a folded form and once chains are packed into particles their length can be more than ten-fold larger than their diameter [105]. Therefore, it is possible that the regenerated cellulose chains are also folded and, in the case of the cellulose II polymorph, chains align in an anti-parallel fashion. Studying the cellulose chain folded structure and ring conformers through MD, Yamane et al, proposed a mechanism for the structural formation of regenerated cellulose from a polar solution based on three stages, as schematically illustrated in Figure 4 [106].

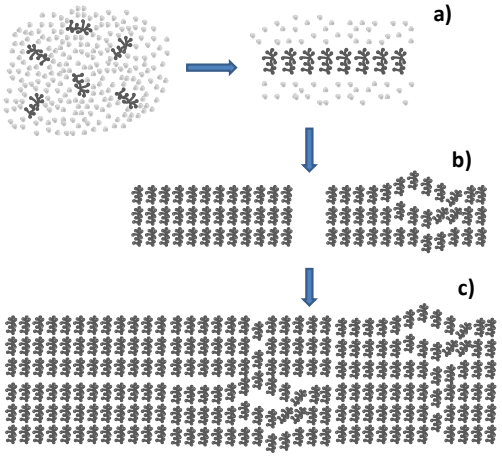


Figure 4. Schematic model of the structural formation of regenerated cellulose in an aqueous environment. The dark grey symbols schematically represent cellulose molecules, while the light grey represent water molecules. a) Glucopyranose rings stacking by hydrophobic interactions, forming a sheet-like structure; b) ordered and less ordered domains; c) regenerated material with a mixture of crystalline and amorphous regions (adapted from reference [106]).

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Firstly, when the aqueous cellulose solution is set under unstable conditions (i.e. addition of a coagulant or via marked changes in temperature), cellulose molecules appear to aggregate side by side, with glucopyranose rings stacking by hydrophobic interactions, forming a sheet-like structure (Figure 4.a). Secondly, as the coagulation process proceeds, many sheet-like structures are progressively stacked by hydrogen bonds to form thin planar crystals incorporating amorphous regions. These structural domains are simultaneously laid down parallel to the surface of the shrinking cellulose gel due to their sheet-like shapes. Some aggregates that are tightly stacked with each other and free of defects transform into the crystalline regions (Figure 4.b on the left), while those that incorporate defects in their structure become less ordered domains or amorphous regions (Figure 4.b on the right). This mechanism suggests that the amorphous regions in regenerated cellulose could be defined as being composed of molecular sheets with distances that have substantial distributions, as originally described by Hermans in the late 1940s [107]. In the final stage, these randomly dispersed structural units make contact with other units and, by a diffusion cluster-cluster aggregation mechanism, form a regenerated material with a mixture of crystalline and amorphous regions (Figure 4.c) [108, 109].

As previously mentioned, in the course of coagulation the solvent is squeezed out from the precipitating cellulose gel, resulting in shrinkage, which causes the uniplanar orientation of the $(1\bar{1}0)$ crystal plane. There is also recent experimental evidence for the molecular sheet formation process in cellulose regeneration [101]. The regeneration of cellulose triggered either by a coagulant or upon heating was followed in an aqueous alkali-urea solvent and monitored by time-resolved synchrotron X-ray scattering. It is suggested that when the medium surrounding the cellulose molecules becomes energetically unfavorable for molecular dispersion, the regeneration starts, and the initial process would consist of stacking the hydrophobic glucopyranoside rings (driven by hydrophobic interactions) to form monomolecular sheets, which then would line up by hydrogen bonding to form Na-cellulose type IV crystallites, a hydrate form of cellulose II (Figure 4) [110]. This may constitute one of the first experimental findings that is evidence of the development of hydrophobically stacked monomolecular sheets as hypothesized first by Hermans [107], later by Hayashi [111], and also discussed by Yamane et al. The work of Isobe et al. not only elucidates the regeneration mechanism of cellulose but also provides an alternative vision to the typical regeneration mechanism found in literature that essentially focuses on the reformation of the broken inter- and intramolecular hydrogen bonds among cellulose molecules [101]. Independently of the solvent system used, different studies concluded that both the coagulation medium and the post-treatment influence the regenerated cellulose films regarding the pore size distribution and crystallinity [112, 14, 113, 114]. Furthermore, the crystallinity, porosity and density of regenerated cellulose depend on the temperature and solvent concentration of the coagulation bath, which affect the diffusion rate and slower regeneration leads to higher crystallinity and density [115, 116]. The precipitation method affects cellulose formation as well, with remarkable differences between immersion and vapor precipitation. Song et al. show that crystalline cellulose spherulites can grow from concentrated cellulose solution in IL by very slow precipitation in vapor [117].

Typically, water is the most suitable coagulation agent but often the presence of certain additives (such as salts and amphiphiles) is required in order to tune the mechanical and morphological properties of the regenerated material.

4. Brief overview of some cellulose applications

4.1. Fibers for textile and non-woven applications

The forest industry is facing a paradigm shift, where fast growing short fibers from the southern hemisphere are claiming more room in a matured paper pulp market. Margins are under pressure and profitability will inevitably decrease. Simultaneously, paper consumption is ever decreasing. For the world leaders within the area of forestry and refining of forest raw materials, identifying new products and processes has become paramount. One very interesting alternative is the use of cellulose for the production of man-made fibers. Even though regenerated cellulose fiber has confirmed its position as one of the most dynamic segments of the century, achieving an average annual growth rate of 5.4 % since the year 2000, the demand for cellulose fibers is predicted to exceed the available supply by 3.3 million tons in the year 2020! This is due to population growth and increased prosperity megatrends, along with stagnating cotton production. Currently the global fiber consumption within the textile industry is about 80 million tons where only 5 % of the fibers are originated from dissolving pulp. Since petrochemically-derived fibrs are not sustainable in the long run and the cotton production is being increasingly questioned, sourcing sustainable raw materials has become increasingly difficult for global players in the textile market. In this respect, regenerated cellulose is regarded to potentially play a leading role as a replacement for cotton and synthetic fibres for textile and non-woven applications. Cellulose fibres are known to have good strength properties and a relatively high stiffness, while being only of moderate density, due to the hollow nature of the fiber composition. While the properties of natural fibers have an inherent variability in properties due to differences in species, as well as growing and harvesting conditions, the properties of regenerated cellulose fibers are homogeneous and can be adjusted by processing parameters. However, the successful use of this rapidly renewable, abundant, and biodegradable material will depend on the development of economically and environmentally advantageous processing technologies. Historically, one of the first solvent systems developed for cellulose was based on aqueous complexing agents (such as cupper salts in concentrated ammonia solutions, also referred to as cuprammonium solution). This discovery by Schweizer essentially triggered the cellulose fiber industry [21]. Three years later, H. Despassie developed another process to produce fibers from the same solvent system (aqueous cuprammonium solution-Cupro). A few years later, with the "stretch-spinning process" invention by Thiele, the process became commercialized. A competitor to this process, was the viscose route developed by Cross, Bevan, and Beadke in 1891 that is based on a reaction between cellulose and carbon disulfide (CS_2) in alkali media. A labile and soluble intermediate in aqueous sodium hydroxide solution is formed (e.g. cellulose xanthogenate) and during precipitation of the shaped product, the substituent is cleaved off, and high purity non-modified cellulose is regenerated [102, 118]. The viscose method is still the most important procedure for cellulose shaping and dominates the supply of regenerated cellulose fiber accounting for more than 90 % of the annual production volume.

This route is technologically complex, requiring reasonably high-quality dissolving pulp and leading to problematic environmental loads from the use of CS_2, heavy metal compounds in

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the precipitation process, and resultant by-products [119]. Due to the emergence of the synthetic fiber industry in the 1940s and to the environmental pollution during the production of regenerated cellulose fibers, caused by the generation of harmful gases, the production of fibers based on Viscose and Cupro processes decreased in the 1960s. In order to overcome these disadvantages, many new solvents have been discovered and studied [120, 121]. A reasonably successful example in the commercial scale production is the Lyocel, a type of rayon fiber [39,122]. The underlying process has been in industrial use for several years, but the production is relatively small. One of the reasons is the thermal instability of the solvent (N-methylmorpholine-N-oxide), which demands major investments in safety technology [40]. A very interesting alternative based on the viscose spinning technology is the CarbaCell process, which does not require the use of sulfur-containing compounds and has been developed to commercial maturity [119]. In this process, a new reaction variant employs the urea to convert cellulose into cellulose carbamate, which can be subsequently processed on existing viscose spinning systems.

As discussed before, the use of ionic liquids to dissolve and produce cellulose based fibers seems very attractive. An example of a recently synthesized ionic liquid with great potential for fiber spinning is the 1,5-diaza-bicyclo[4.3.0]non-5-enium acetate ([DBNH][OAc]), which is described as a powerful direct cellulose solvent [123]. The development of a process designated as Ioncell-F produces regenerated cellulose fiber with properties comparable (or even superior) to Lyocell [124].

4.2. Bioethanol

Cellulose dissolution is typically required for one of the following reasons: analytical characterization of cellulose; shaping in a different format (such as fibers); homogenous chemical modification or degradation to obtain the elementary sugars. In the latter case, it is therefore possible to obtain ethanol from cellulose. In theory, this can be simply achieved by hydrolysis of cellulose-based materials using, for instance, enzymes to break cellulose into simple sugars, followed by fermentation and distillation. In reality, the process is not that straightforward. A pretreatment is typically necessary as cellulose usability is limited due to its structural rigidity, partial crystallinity, and complex network of interactions. This pretreatment also liberates cellulose from the lignin so it becomes more accessible for hydrolysis [125]. During enzymatic hydrolysis, the cellulose chains are broken into small oligomers or even into the elementary sugar units through cellulase enzymes in a similar process as occurring in the stomach of some ruminants. Some species of bacteria, such as *Clostridium thermocellum*, can promote an immediate conversion of cellulose into ethanol. These species break down cellulose and synthesize ethanol. Research in this area has also focused on genetically engineering bacteria that are capable of optimizing ethanol production and inhibit the formation of side products [126]. The environmental benefits of cellulosic ethanol are considerable as it can reduce carbon dioxide emissions to nearly zero and it can impressively reduce green house gas emissions compared with fossil fuels [127]. For instance, corn ethanol reduces green house gas emissions by 13 %, while this value exceeds 85 % if ethanol is of cellulosic origin [128]. The long-predicted arrival of cellulose-based fuels might be very close as several companies are initializing the production of ethanol from biomass while others are producing efficient enzymes.

4.3. Aerogels

Aerogels are low-density solids (0.004–0.15 g/cm3) with high porosity (90–99.8 % air) and a large internal surface area [129–131]. Being one of the most attractive materials, aerogels are also referred to as frozen smoke, solid smoke, or solid air. Some of the most interesting applications include NASA missions, where silica aerogels are used to collect comet particles, insulators in semi-transparent roofs, thickening agents in paints and cosmetics, thermal protections for clothes and materials, drug delivery systems and water purification systems. The low density and high porosity (air takes up the majority of the space in an aerogel) permit the aerogel to be almost weightless. Most aerogels exhibit a slight color due to Rayleigh scattering and they can show a thermal conductivity smaller than the gas they contain, due to the Knudsen effect [132]. Aerogel shows superior insulation and can be used as alternative to the current home insulation. One windowpane (2.5 cm thick) composed of silica aerogel is equivalent to the insulation provided by 20 windowpanes of glass [133]. This will have a strong impact on energy saving to keep houses warm. Additionally, it has obvious impact in the worldwide production of carbon dioxide and other greenhouse gases. Aerogels can be extremely tough, able to hold up to 4,000 times their weight. These systems are typically prepared by a sol-gel process, involving crosslink formation between the components. Firstly, a colloidal suspension or solution of particles with diameter in the range of 1–1,000 nm are subjected to polymerization reactions and/or crosslinking that leads to the formation of a gel with a three dimensional network. The pores of the network contain the solvent of the suspension, usually water. The solvent in the gel can then be removed by exchanging with a CO_2 miscible liquid such as ethanol, followed by liquid CO_2 and then tuning CO_2 above its critical point. An alternative method is to direct inject the supercritical CO_2 into the gel. The pore solvent is replaced with air without altering the gel network structure or the volume of the gel. An alternative way to remove the solvent from the pores is by freeze drying the suspension. Such materials are typically called “cryogels” [134]. Normal evaporation of the pore solvent is inadequate to obtain common aerogels with high porosity: such methods result in xerogels that exhibit large amounts of shrinkage after drying, since the magnitude of the surface tensions of the liquid-solid interfaces can destroy the network.

Aerocellulose is a biodegradable aerogel composed of cellulose. The first aerocellulose known was prepared in 1971 from cellulose pulp [135]. The water from the wet cellulose pulp was exchanged with ethanol and then with CO_2, which was removed by critical point drying, as described above. A cellulose aerogel with a specific surface area of 206 m^2/g was obtained. Since then many aerocellulose derivatives were reported. Tan et al. have developed cellulose acetate aerogels [136]. Jin et al. have developed highly porous cellulose aerogels consisting of cellulose nanofibrils with an approximate pore size of 500 nm [132]. Transparent aerocellulose that combine mechanical toughness and good heat insulation was reported by Kobayashi et al. [137]. Novel aerogels (or aerocellulose) based on all-cellulose composites were prepared by partially dissolving microcrystalline cellulose (MCC) in LiCl/DMAc solution [138]. The inclusion of nanocellulose as a building block for aerogels has also motivated several studies in particular because nanocellulose is able to provide mechanical reinforcement to the material among other advantages [139–145]. Also aerogels of regenerated cellulose prepared through molecular dissolution processes have attracted attention [146, 147]. It is clear that the interest in these materials is considerable and this is probably motivated from the vast range applica-

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tions and unique features of aerogels. Thus, it is not surprising that these materials have already started being produced on an industrial scale.

4.4. Hydrogels

Renewable raw materials have immense potential for the development and research of new products. Development of new techniques together with the knowledge of traditional methods can facilitate the production of, for example, super-sorbent gels or hydrogels [148]. Cellulose-based hydrogels are biocompatible and biodegradable materials which are promising for a large number of industrial uses, in particular the cases where environmental issues are concerned, as well as in biomedical applications. Several water-soluble cellulose derivatives can be used, alone or combined, to form robust hydrogel networks possessing highly specific properties in terms of swelling capability and sensitivity to external stimuli. The current trend in the design of cellulose hydrogels mostly related to the use of non-toxic crosslinking chemicals or treatments, to further improve the safeness of both the end product and the productions processes. Structurally, due to the extended crosslinked network of polymers (intimately related to previously discussed aerogels), hydrogels are similar to the extracellular matrix of the human body [149]. These structures may be modified or designed in accordance to the external physical and chemical factors that may influence their activity during a certain application. Hydrogels are generally categorized into functional and synthetic on the basis of their formation [150]. Self-assembled natural polymers are termed as functional hydrogels whereas synthetic hydrogels are programmed to have desired functionality with multiple interactions.

The acrylamide-based hydrogels are currently all over the market but such systems raise serious environmental and societal concerns [148]. As stated above, cellulose is naturally available and abundant resource in nature. Even though cellulose is a biocompatible, biodegradable, and sustainable polymer, cellulose itself cannot be reabsorbed by human cells due to the lack of cellulases.

The stability of hydrogels is altered by changing the type of cross-linker (in the case of chemical hydrogels) and number of cross-linking sites per unit volume. The free hydroxyl groups present on the cellulose backbone enable a rich surface chemistry and cellulose derivatives that are typically water-soluble [151]. Common examples are carboxymethyl cellulose (CMC), hydroxypropyl methylcellulose (HPMC), and hydroxyethyl cellulose (HEC) and these systems have the capacity to produce ultra fine gel networks, particularly when mixed with other polymers, resulting in high water retaining capacities and remarkable mechanical properties [152]. The water holding capacity is determined by the chemical composition and the manufacturing procedures of the starting material. The "smart" behavior of some cellulose-based systems regarding response to physiologically relevant variables (e.g. pH, ionic strength, temperature) makes the resulting hydrogels particularly appealing for in vivo applications.

4.4.1. Hydrogels in agriculture

A common concern nowadays in agriculture is related to the adequate supply and use of pesticides, herbicides, and fungicides, and the use of non-effective agrochemical products since

these are devastating the agricultural economy. Additionally, the crop uptake of micronutrient should be balanced. Encapsulation in agriculture is a delivering method that seems to hold a promising targeted approach. This will enable, for instance, the decrease of losses of agrochemicals by erosion, being advantageous from an economic and sustainability point of view. Hydrogels can be specifically synthesized to give a sustainable delivery of water, nutrients, or agrochemicals in adequate amounts in an undisturbed fashion [153]. In this respect, cellulose-based systems (e.g. CMC- and HEC-based hydrogels) can be, for example, effective water reservoirs in agriculture. For instance, tomatoes have been successfully cultivated using these hydrogels in soil without any other water supply. The water absorption and conserving capacity seems to be enhanced. The development of super absorbent polymer (SAP) gels aim at reducing the release of water from the network. It has been reported that CMC and starch, when cross-linked with aluminium sulphate octadecahydrate, produce super absorbent gels [154] that can even be used in extreme drought conditions [155]. Other successful applications in agriculture include the so-called root-targeted delivery vehicle systems. These systems can be formed by dissolving CMC, iron, and calcium salts and are used, for instance, to grow wheat in nutrient depleted soil media. Additionally, when mixed with fertilizers, an efficient and increased growth rate is often observed. Another promising cellulose-based hydrogel is composed of methyl cellulose, polyacrylamide, and calcium montmorillonite that has been shown to be an efficient nutrient carrier. The addition of urea can make the hydrogel more porous, thus enhancing its capability for absorption [156].

4.4.2. Hydrogels in biomedicine

Biomedical, healthcare, and pharmaceutical industries extensively use cellulose derivatives as release matrices, tablets, granules, delivery systems, stabilizers, semi solid gelling agents, artificial wound dressing, for cell encapsulation, and in many other applications [148]. A cellulose hybrid hydrogel having doped phosphor (PP) and epichlorohydrin as a cross-linker was reinforced in a lightly alkaline solution. This PP-based cellulose hydrogel was found to have great potential for bioimaging applications [157]. This system is particularly promising due to its high intensity in green florescence and extended glowing periods. This is relevant because it not only avoids the use of harmful radiation but can also be detected under the skin and/or in the stomach. A hydrophobic hydrogel network formed by cellulose nanowhiskers (extracted crystalline fractions of cellulose), acrylamide, and stearyl methacrylate possess unique properties of self-healing and remolding. This system has a wide extensibility and good mechanical strength making it highly suitable for different applications within the biomedical field [158]. Zhou et al. found that cellulose extracted from bamboo (*Phyllostachys heterocycla)* shows high swelling rates at human body temperature and intestinal pH. Thus, hydrogels based on this cellulose exhibit an immense potential as an oral drug model [159]. According to Sannino et al., edema problems can also be treated using cellulose-based hydrogels as these systems have improved water absorbing and holding capacity [160]. In several examples, no arachidonic acid release is identified confirming that inflammation does not occur and the cellulose-based hydrogel is biocompatible. Different studies have also given the prospect of using cellulose-based hydrogels as encapsulating agents for probacteria and its sustainable delivery after incorporation in different food matrix systems [161–163].

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4.5. Cellulose-based composite materials

Composite materials have gained tremendous interest over the last decades and are found in numerous lightweight, structural applications ranging from aerospace to automotive and sports equipment. A large body of research has focused on replacing the traditional reinforcement of composites, such as glass fibers, with lignocellulosic fibers [164–167]. The most commonly used natural fibers are flax, hemp, sisal, jute, and wood [168, 167]. The high specific strength and stiffness of bast fibers, such as hemp, flax, and ramie, give natural fiber reinforced composite properties that compare favorably with glass fiber reinforced composites [169]. The advantages of natural fibers over synthetic fibers, include lower energy usage during production, reduced hazards during handling, less abrasion on machinery, lower density, and a neutral CO_2-balance [169, 164]. However, a drawback of natural fiber is the large inherent scatter in properties due to differences in growing and harvesting conditions, necessitating rigorous quality management to ensure consistent composite properties [167].

In addition to bio-based reinforcements, there has been much effort on the development of naturally derived biopolymers as matrix systems [166, 170] in order to achieve a completely bio-based, biodegradable, and CO_2-neutral material. Composites that are a mix of bio-based and synthetic materials are referred to as *biocomposites* or *eco-composites*, while those completely composed of bio-based materials are elevated to *green composites*.

4.5.1. All-cellulose composite materials

The replacement of synthetic fiber by natural fiber is a promising advancement. However, chemical incompatibility may exist between a hydrophilic fiber reinforcement and hydrophobic polymer matrix that leads to weak fiber-matrix bonding. Poor fiber-matrix bonding leads to inefficient load transfer between the two phases such that the high mechanical properties of natural fibers are not fully exploited [168]. The relatively poor mechanical performance of biocomposites is significantly improved by chemically treating the fiber and/or matrix. Common procedures include chemical grafting, corona discharge and silane or alkaline treatments. However, such procedures add process complexity and costs [171–173].

Single polymer composites (SPCs) overcome the issue of chemical incompatibility by using the same polymer for both fiber and matrix. The main advantage of using the same polymer for both phases is the high level of bonding, resulting in high interfacial strength and efficient load transfer. A further advantage of SPCs is the ease of recycling as the fiber and matrix components do not require extraction and separation. An overview of the field of SPCs is presented in several reviews [174–176].

All cellulose composites (ACCs) are green composites that have been developed using the SPC concept. In ACCs, both the reinforcing and matrix phases are based on cellulose, leading to high chemical compatibility at the fiber-matrix interface. Although high performance ACCs have recently appeared in the literature [177–179], there are historically a number of materials that could be categorized as ACCs. For example, currently used materials such as vulcanized fiber and paper were patented in 1859 [180], cellophane was patented in 1918 [181], and the processing of vegetable parchment is a technology dating back to the 19th century [182].

4.5.2. Processing of all-cellulose composites

Generally, ACCs are processed *via* one of two different pathways, as illustrated in Figure 5. The first pathway involves two distinct processing steps in which (i) cellulose is first dissolved in a solvent and then (ii) regenerated in the presence of an undissolved cellulose reinforcement. The first example of this two-step method was reported by Nishino et al. [177], in which unidirectional ramie fiber was combined with fully dissolved wood pulp. The regeneration of the wood pulp created a matrix phase that provided adhesion between the undissolved ramie fibers. The second pathway is essentially a single processing step that involves wetting a cellulose reinforcement with a solvent and partially dissolving the cellulose. Regeneration of the dissolved portion of cellulose leads to the *in situ* formation of a matrix phase that binds together the undissolved fraction of cellulose. Gindl and Keckes [183] were the first to report the use of the one-step method for creating an ACC, and it has been variously referred to as partial dissolution [184], surface-selective dissolution [185] and natural fiber welding [186]. The one-step method results in ACCs with a relatively high volume fraction of fibers (e.g. ≤ 88 vol. %) [179]. Thus, the volume fraction of fibers in an ACC approaches the theoretical maximum of 90.7 % that exists for a hexagonal packing arrangement [187].

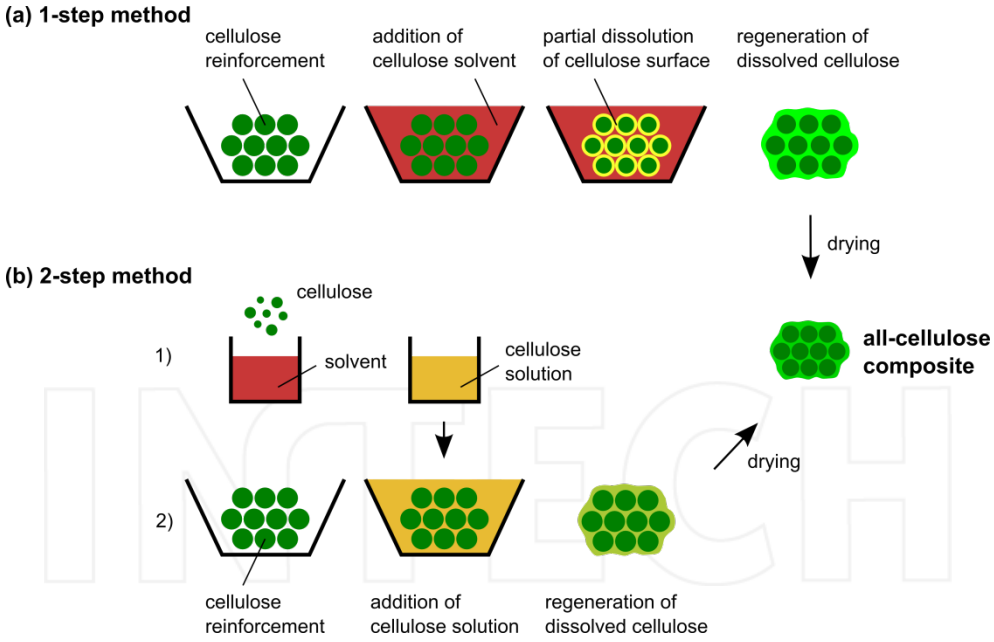


Figure 5. Schematic of processing pathways of ACCs: (a) One-step method and (b) Two-step method. Adapted from Nishino et al. [177].

A number of different cellulose solvents and cellulose types have been used for processing ACCs. The most commonly used solvents are NMMO, LiCl/DMAc, IL, and NaOH aqueous

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solution [188], of which NMMO, IL, and NaOH based solvents are advantageous because they do not require an activation step before dissolution.

The choice of cellulose source mainly determines the type of composite that will be obtained. Isotropic ACCs have been created from micro- or nanofibrillated cellulose [183, 189–192], wood pulp [193], bacterial cellulose [194, 195] and filter paper [189]. Uni- or multidirectional ACCs have been prepared from natural fibre including ramie [177, 178, 185] and flax [196], and regenerated cellulose fibers including Lyocell [196], Cordenka [184, 197], and Bocell [179].

The use of man-made regenerated fiber in ACCs is beneficial for several reasons: man-made regenerated cellulose fiber can be synthesised to be highly consistent in terms of purity, microstructure, morphology, and mechanical properties [198, 199]. Moreover, the homogeneous microstructure of man-made regenerated cellulose fiber results in a uniform dissolution from the skin to the core [200]. In contrast, the dissolution of natural fiber can be inhomogeneous, with ballooning, contraction, and rotation of cotton and wood fibers as an example [63, 68]. Furthermore, the structural integrity of the cell wall components of natural fiber is severely affected by partial dissolution, which is detrimental to the mechanical properties of flax fiber-based ACCs [196]. ACCs based on regenerated fibers (Lyocell) have a higher mechanical performance, and their mechanical properties compare favorably with epoxy-based composites [196].

The structural form (or polymorph) of the precursor cellulose may undergo a phase transformation during the processing of ACCs. An obvious example is the transformation of cellulose I to cellulose II following dissolution and regeneration. Thus, it is possible for a mixture of different polymorphs to be present in the final ACC. However, the transformation of cellulose I following dissolution and regeneration may follow different pathways depending on the starting materials and processing conditions. For example, Duchemin et al. reported that the partial dissolution and regeneration of MCC leads to the formation of a paracrystalline matrix phase, rather than the expected cellulose II [201].

The nature of the interface between different polymorphs within an ACC has not been studied in detail. Interestingly, Qin et al. observed improved mechanical properties of ramie fiber-based ACCs after a mercerisation treatment of the composites [178]. During mercerisation, cellulose I is transformed to cellulose II, which is concomitant with a decrease in the mechanical properties of cellulose [202]. Therefore, it is supposed that the resulting increase in mechanical properties is due to improved chemical compatibility between the cellulose II in the fiber and that of the matrix formed after partial dissolution. However, several other factors may play a role including the removal of hemicellulose, fiber strengthening, or elimination of defects [178].

Pullawan et al. investigated the micromechanics of the fiber-matrix interface of all-cellulose nanocomposites [203, 204]. Interestingly, the overall crystallinity of the cellulose increased from 26 % in the pure matrix film to 48 % in the ACC with the addition of 1 vol. % of highly crystalline cellulose nanowhiskers. However, a simple calculation based on the rule of mixtures shows that the upper limit of crystallinity of the nanocomposite is 27 %. Thus, the presence of nanowhiskers appears to assist in the nucleation of crystallites during the regen-

eration of the dissolved cellulose [203]. Chemical compatibility between cellulose I and II is also suggested by the successful stress transfer from fibre to matrix [203, 204].

4.5.3. Developing industrial scale manufacturing pathways for all-cellulose composites

The majority of literature studies of ACCs have produced and characterized films of ACCs with thicknesses that are ca. 0.5 mm. However, the expansion of ACCs into different applications will likely require greater thicknesses of material. The manufacture of ACCs relies on wet processing and necessitates a washing and drying step. The removal of solvent and subsequent drying result in a volumetric shrinkage approximately equal to the ratio of cellulose to solvent. ACC films are typically cast from 5 to 25 vol. % cellulose and hence a shrinkage of > 80 % is to be expected, that is significantly higher than the shrinkage of 1 to 3 % observed during injection moulding of thermoplastics [205]. Furthermore, the removal of solvent from the dissolved portion of cellulose also results in *differential* shrinkage due to large differences in the shrinkage of the reinforcing and regenerated matrix phases. Differential shrinkage is problematic for two reasons: (i) internal residual stresses are generated that compromise the mechanical performance of the composite; and (ii) dimensional stability of the material is decreased following the final drying step (i.e. warpage occurs). Hence, it is clear that extensive experimental studies and development of predictive models of shrinkage in ACCs are still required in order to meet the requirements of the composite industry. Finally, the disposal and/or recycling of the solvent and identification of cost-effective sources of cellulose are important aspects in the context of industrial manufacturing that require further research and development.

Processes based on the one-step method seem more promising for larger scale manufacture of ACCs, due to the higher cellulose/solvent ratio and minimal transformation of cellulose precursor to matrix, which limits the overall and differential shrinkage. Industrial-scale composite manufacturing techniques (e.g., compression moulding, resin infusion) have been explored and adapted for larger scale one-step manufacturing of ACCs, although the technology is still in its infancy. A common characteristic of these processing routes is the application of pressure to consolidate the material during all stages of processing so as to manage the shrinkage and ensure dimensional stability. Conventional compression moulding of composites involves the use of a rigid double-sided mould through which pressure and heat are applied to consolidate the reinforcement and matrix materials [206]. Compression moulding of ACC laminates was carried out by Huber et al. [197]. Initially, several layers of a woven regenerated cellulose fiber textile were impregnated with an ionic liquid as the solvent, followed by stacking and compression of the layers. The application of heat and pressure (110 °C, < 2.5 MPa, 80 min) leads to the partial dissolution of the fibers within the textile layers, resulting in the in situ formation of the matrix phase. The compression-moulded ACC laminates were formed into dimensionally-stable, flat sheets with a final thickness of 2 to 8 mm, tensile strength of 70 MPa, and Young's modulus of 2.5 GPa.

Vacuum-assisted resin transfer moulding (VARTM) is a liquid moulding process that is used to fabricate complex-shaped, high quality composite laminate parts [207, 208]. Typically, a woven textile preform is placed on a one-sided rigid mould that is then covered with a vacuum

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bag. A low pressure vacuum forces resin to flow through the textile preform, while also acting to remove voids and compact the laminate stack. As an adaptation of the VARTM process, a method called solvent infusion processing (SIP) was developed for the fabrication of dimensionally-stable ACC laminates. During SIP, a cellulosic textile is homogeneously wetted by a solvent (rather than resin). Further compaction and partial dissolution of the cellulose reinforcement are then achieved using external pressure and heat. SIP results in ACC laminates with a high fiber volume fraction (70 to 90 vol. %) with minimal void content [184]. The thickness of the ACC laminates is easily adjusted by varying the number of textile layers. The mechanical properties of the final laminate can be tailored through the choice of precursor (i.e. fiber preform). ACCs based on rayon fiber processed *via* SIP have been shown to exhibit high tensile and flexural strength of 95 MPa and 135 MPa, respectively, and outstanding impact resistance with a puncture impact strength of 2 kN mm^{-2} and an unnotched Charpy impact strength of 42 kJ m^{-2} [184, 209].

4.5.4. Mechanical properties of all-cellulose composites

The mechanical properties of ACCs strongly depend on the type of reinforcement and processing conditions. One of the main factors is the dissolution time and its effect is best explained with the example of a unidirectional ACC. With increasing dissolution times, a higher fraction of the fibers is transformed into the matrix, which decreases the longitudinal tensile strength due to the reduction of the fiber cross-sectional area, and simultaneously leads to an increase in transverse strength, due to a higher matrix-volume fraction and better interfacial adhesion [177, 185]. The dissolution time has a pronounced effect on the microstructure and crystallinity of ACCs, as well as the DP of the processed cellulose [185, 190]. A similarly important parameter is the regeneration rate, with ACCs formed by slow precipitation displaying higher crystallinity, Young's modulus, and tensile strength [190].

The mechanical properties of ACCs can also be influenced by wet drawing. Stretching a regenerated, but still wet ACC leads to a preferred orientation of the cellulose crystallites in the direction of stretching [210, 192]. The crystalline orientation is maintained after drying and a linearly increasing relationship of tensile strength and Young's modulus with the applied draw ratio was found. Applying a draw ratio of 1.5 leads to an increase in tensile strength from 202 to 428 MPa and Young's modulus from 9.9 to 33.5 MPa [210]. Similarly, the orientation of nanowhiskers within an ACC can be influenced by a magnetic field to achieve an increase in mechanical properties in a preferred direction [211, 212].

The comparison of mechanical properties of ACCs in the literature is problematic due to variations in cellulose type and processing parameters. A broad overview of the mechanical properties of ACCs was presented by Huber et al. [188]. A comparison of ACCs with other biocomposites shows that ACCs are highly competitive in terms of their properties (Figure 6a). The Young's modulus of isotropic ACCs is relatively high when compared to conventional biocomposites; this can be attributed to the high properties of the regenerated cellulose matrix [188]. The situation is different for unidirectional composites, where the Young's modulus of ACCs falls in the same range as that of biocomposites (Figure 6b). This may be due to either a decrease in the fiber modulus caused by solvent interaction in the processing of ACCs or the

modulus of biocomposites is mainly determined by the fiber modulus and the interfacial strength is of little influence [188]. When it comes to ultimate tensile strength, ACCs perform significantly better than isotropic and unidirectional biocomposites.

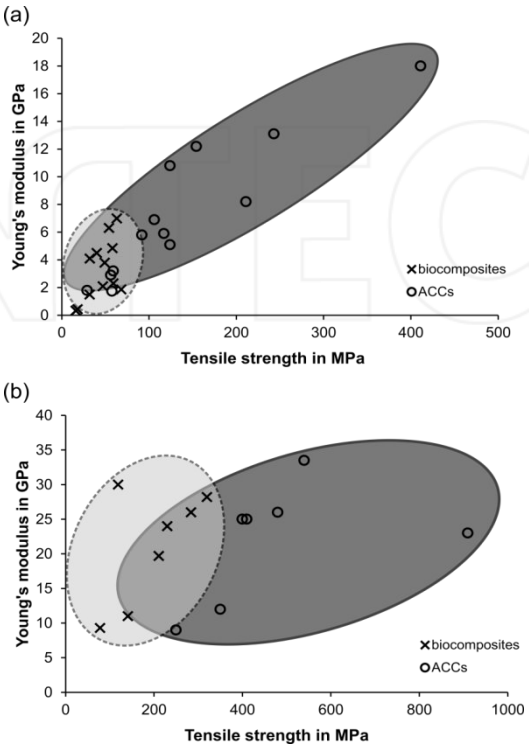


Figure 6. Comparison of mechanical properties of (a) isotropic and (b) unidirectional biocomposites and ACCs. Underlying data is presented in the review by Huber et al. [188].

In terms of viscoelastic behavior, ACCs exhibit a storage modulus that decreases with increasing temperatures. Nevertheless, the storage modulus remains considerably high, up to a temperature of around 250 °C (Figure 7), indicating that ACCs may have relatively high thermal performance as polymer-based composites [190, 213]. The thermal stability strongly depends on the cellulose source. For example, ramie-based ACCs have a higher thermal resistance [177] than flax and Lyocell-based ACCs [196]. Dynamic mechanical analysis of cellulose reveals three separate glass transitions, labeled as α_1, α_2, and α_3 (Figure 7). The α_3 transition occurs at ca. 30 °C and has been assigned to cooperative motions of cellulose chains and water molecules in the non-crystalline regions. The transitions α_2 and α_1 are observed around 140 °C and 300 °C, respectively, and have been assigned to micro-Brownian motions of polymer segments in non-crystalline regions [214]. Duchemin et al. observed that the α_1 transition is composed of two contributions, $\alpha_{1,1}$, and $\alpha_{1,2}$ [213]. Interestingly, the amplitude of

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the $\alpha_{1,2}$ viscoelastic relaxation at 303 ± 2 °C decreases with increasing crystallinity in ACCs made by partial dissolution of MCC. This relaxation was assigned to the molecular motion of non-crystalline domains during thermal decomposition. Composites with a higher crystallinity thus showed a better retention of the dynamic storage modulus when tested at 300 °C, which translates to a better thermo-mechanical stability in this temperature range.

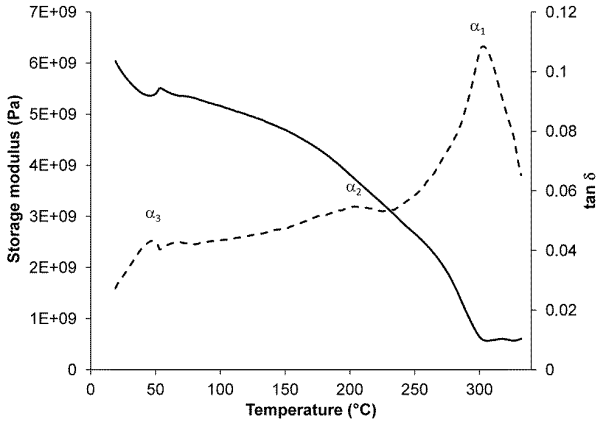


Figure 7. Storage modulus (solid line) and damping (dashed line) of dry all-cellulose composites prepared by partial dissolution of 15 wt. % MCC in DMAc/LiCl for 8 h and followed by precipitation in water. Adapted from Duchemin et al. [213].

4.5.5. Biodegradability

A key advantage of green composites that are based on biopolymers is their inherent biodegradability. However, many synthetic biopolymers (e.g. polylactides, PLA) require energy-intensive composting temperatures (ca. 60 °C) for biodegradation to occur rapidly [215, 216]. In contrast, native cellulose and regenerated cellulose can degrade rapidly at ambient temperatures (i.e. 20–30 °C) due to the hydrophilicity of cellulose [217, 218].

Kalka et al. were the first to demonstrate the rapid biodegradation of ACCs using soil burial trials. Initially, the ACC laminates increased in mass due to moisture uptake, although this was followed by significant mass loss as the material degraded. The percentage mass loss of the ACCs following 70 days of soil burial varied between 39 and 73 % at temperatures of 20.8 and 33.5 °C, respectively. Comparatively, the mass loss of a PLA-matrix composite using the same rayon fiber as reinforcement was minimal (< 2.4 %) under the same conditions [219].

Kalka et al. observed delamination and discoloration of the surface of the ACCs as evidence of microbial activity during the soil burial trials. Furthermore, the surface of ACCs was found to be colonized by filamentous bodies of cellulose decaying fungi and spherical fruit bodies. Microscopic analysis also revealed that clusters of fibers had separated from the composite. The mechanism of fiber-matrix debonding may be the preferential degradation of a more

disordered matrix phase that permits greater accessibility to microorganisms compared with that of the original rayon fiber [219].

The rapid biodegradation of ACCs is a distinct advantage over other bio-based composites. However, the high potential for degradation also limits the use of ACCs in some applications. The development of bulk modifications or surface treatments are likely to be required to protect the high mechanical properties of ACCs from the influence of water. For example, Yousefi et al. found that immersion treatment of ACCs with a silane coupling agent (3 wt. % dodecyltriethoxysilane solution) leads to an increase in water contact angle from 59 to 93° and reduces the percentage water uptake from > 4 % to < 1 %. These results demonstrate the efficacy of a silane treatment for the protection of ACCs from moisture ingress, while additionally resulting in higher mechanical properties due to a lower equilibrium moisture content of treated samples and the closure of voids by the silane [220].

5. Conclusions

The dependence of mankind on depleting fossil resources is a problematic issue, and based upon its criticism, a high demand for more sustainable engineering materials has arisen. Cellulose is a decidedly interesting alternative raw material to petrochemical-derived materials due to its high strength and stiffness, wide availability, and biodegradability. Due to the complexity of the biopolymeric network, as well as the partially crystalline structure and extended noncovalent interactions among molecules, chemical processing of cellulose is rather difficult. A wide variety of suitable solvents for cellulose is already available. Nevertheless, most solvent systems have important limitations and there is an intense activity in both industrial and academic research aiming to optimize existing solvents and develop new ones. The problem of obtaining a picture of molecular processes is not trivial since cellulose solvents are of remarkably different nature and thus the understanding of the subtle balance between the different interactions involved becomes non-trivial. The dissolution and regenerative precipitation of cellulose appear to both depend upon a subtle interplay of forces, among which hydrogen bonds are only one of the important factors, and do not seem to be the most significant driving force. Key factors instead include hydrophobic interactions, due to the amphiphilic character of cellulose, as well as the entropy of the counterions for the case that cellulose molecules have a net charge; this net charge can arise from protonation or deprotonation as well as association with charged species. Cellulose can find applications in many and different areas as the ones briefly discussed in this treatise. However, it becomes clear that the understanding of the interplay between all the interactions is very important not only from a fundamental point but particularly for the creation and development of enhanced materials.

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