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The Surface and In-Depth Modification of Cellulose Fibers

Alessandro Gandini and Mohamed Naceur Belgacem

Abstract This review updates the most relevant advances achieved in the field of surface and in-depth modification of cellulose fibers during the last 5 years. It reports work dealing with cellulose substrates on the nano- to micrometer scale, namely cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs), microfibrillated cellulose (MFC), and bacterial cellulose (BC), as well as conventional lignocellulosic fibers. Several approaches have been applied for surface modification of these substrates, namely hydrophobization and oleophobization, physicochemical adsorption, oxidation, cationization, esterification, urethane and siloxane formation, and grafting-from and grafting-onto macromolecular sequences. In-depth modification can be achieved by both partial esterification and partial oxypropylation.

Keywords Bacterial cellulose · Cellulose nanocrystals (CNCs) · Cellulose nanofibrils (CNFs) · In-depth modification of cellulose · Lignocellulosic fibers · Nano- and microfibrillated cellulose · Surface modification of cellulose

Contents

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1 Introduction

This review provides an updated description of the state of the art in research dealing with different approaches related to the modification of cellulose fibers using both physical and chemical processes. It covers both classical lignocellulosic fibers from wood and annual plants and the different nanocellulose counterparts that have gained such a prominent status in recent years. Two strategies are covered here, namely alterations limited to the macromolecules present on the surface of the fibers and those involving deeper modifications leading to the formation of a sleeve of modified material, but without transforming the entire thickness of the fiber, which would otherwise generate a bulk cellulose derivative. In other words, the purpose of the latter approach is to induce an in-depth modification, while preserving the pristine morphology of the unmodified inner regions of the fibers and, hence, their original mechanical properties.

The purposes of these investigations are related to a number of alternative outcomes and, hence, to various properties and applications, including hydrophobization; lipophobization; super-absorbency; interfacial compatibilization with other macromolecular materials (mostly for the elaboration of high-performance composites); the selective sequestration of industrial effluents or marine pollutants; hybrid, magnetic, conductive, and other "intelligent" materials; and the possibility of generating single-component composites based exclusively on cellulose. Other types of surface modifications, such as dyeing or the manufacture of chromatography substrates, fall outside the scope of this review.

The literature on cellulose fiber surface modification is very rich and several reviews cover the field up to 2010 [1–5], with particular emphasis on the elaboration of composite materials, although the latest contribution covers a wider scope [5]. Given this quantity of information, only a brief summary is given here on the developments achieved up to about 5 years ago and the review concentrates on the important advances reported since 2010. Although this seems a relatively short period of time, the quantity of original contributions, attesting to the importance of the topic, justifies the need for a detailed and critical update.

The interest in altering the surface of cellulose fibers began in the middle of the last century with studies of graft polymerizations in aqueous media, in which surface-generated free radicals initiated the polymerization of various monomers. Hebeish and Guthrie [6] thoroughly reviewed this field up to 1980. Subsequent work, including excursions into anionic and cationic grafting, was described by Belgacem and Gandini in 2005 [3]. Despite significant efforts, these processes did not materialize into viable applications. The advent of controlled radicals has reopened this dormant topic with new perspectives, as discussed below.

Revival of the field took place after a lull of a few decades, with a sudden crop of studies at the beginning of the 1990s and the trend has not stopped, nor slackened, since then, enriched moreover by investigations related to the blooming of interest in nanocelluloses [7–11]. In the context of conventional chemical modifications, the obvious reactive moieties are, of course, almost exclusively the hydroxyl functions, usually comprising both the primary and the secondary species. Small molecules, oligomers, and polymers have been appended to the outer layer(s) of the fibers by a variety of mechanisms [5], and the ensuing materials often characterized in a rigorous fashion using a battery of complementary techniques. Physical treatments using a variety of energy sources are covered in a more modest number of studies and, inevitably, also produced structural modifications, albeit in a less predictable and precise fashion [5]. Some reports also described approaches that did not involve any attack on the fiber surface, focusing instead on the building of a polymer cover around it to mask its specific structural features (i.e., the OH groups), which were replaced by those of the coating. Recent progress associated with all these strategies is discussed and subdivided on the basis of the primary aim of each of strategy.

2 Surface Modification

Surface modification dominates the field covered by this review. This section is concerned with investigations in which the depth of the modification is ideally limited to the outer macromolecular layer of the fiber surface. Strictly speaking, it is more realistic to view these treatments as affecting what one could call its "outer skin" (i.e., the most superficial cellulose molecules). Even when the main purpose of the study clearly addresses a specific application, the nature of the modification sometimes generates properties that are also exploitable for other uses, as in the case of certain types of hydrophobization, which create conditions also appropriate for surface compatibilization with a nonpolar polymer matrix in the construction of a composite material. The following subdivision is therefore not entirely univocal, but is nevertheless deemed sufficiently rational to justify its use, with the proviso that broader situations, as defined above, are clearly identified and discussed.

2.1 Hydrophobization and Oleophobization

Making the surface of cellulose fibers hydrophobic can be an end in itself, as in the case of the treatment of paper, or it can combine two aims, such as the decrease in affinity for moisture and the transformation of a polar surface into a nonpolar counterpart in order to improve its compatibility with a similarly nonpolar polymer. An example is the elaboration of a composite material in which the reinforcing fibers must display a strong interfacial adhesion to the macromolecular matrix by minimizing their interface energy. The publications surveyed in this section often relate to the latter situation.

It is generally acknowledged that in order to generate a highly hydrophobic (or superhydrophobic) surface, two complementary features must be imparted to it, namely a chemical contribution arising from the presence of nonpolar moieties and a morphological complement consisting of the development of micro- or nano-asperities that inhibit wetting of the corresponding valleys and, hence, the spreading of water. The hydrophobic character of a surface can be assessed by measurement of the contact angle formed by a droplet of water deposited on it, although other criteria are also employed. Values higher than 90° conventionally define a surface as hydrophobic. When a contact angle of 150° is reached, the surface is said to be superhydrophobic.

Much research has been devoted to the hydrophobization of cellulose [12, 13] because of its intrinsic affinity to water and, hence, its classical moisture uptake or wicking, which dramatically affects the mechanical properties of the fibers. This is a problem also encountered with starch-based materials and other polysaccharides [14].

The necessity to confer hydrophobic characteristics to fibers or fibrils that assemble into a hydrophilic biopolymer such as cellulose has always been part of the development of papermaking, particularly with respect to the sizing operation. Sizing is generally conducted at the wet-end part of the process in order to reduce the tendency of paper to absorb liquids (e.g., to ensure the drying of an ink without smudging or excessive in-depth penetration, or to retain the mechanical strength of cardboard in a damp atmosphere, as with egg containers). The most common sizing agents used in papermaking are alkenyl succinic acid anhydride (ASA), alkyl ketene dimer (AKD), and rosin, which are added to the fiber suspension in the form of emulsions [15, 16] or delivered from the vapor phase [17].

AKD has also been employed to prepare superhydrophobic papers using three alternative introduction techniques: (1) air-blasting with cryoground microparticles, (2) crystallizing from organic solvents, and (3) spraying with rapid expansion of supercritical solutions (RESS) [18]. The green character and simplicity of the cryogrinding–airblasting method is favored over the use of an organic solvent, but the RESS technique produces a higher hydrophobicity; moreover, this approach provides the additional advantage of a continuous application (i.e., has potential industrial implementation).

Whether AKD actually reacts with the surface OH groups of the paper cellulose fibers or is simply adsorbed on them through polar interactions is still a source of debate among specialists [15, 16]. However, a recent alternative to conventional sizing [19] involves an entirely physical process consisting of sizing and coating paper with poly(3-hydroxybutyrate), a readily biodegradable material, using a heat press. The high price of this polymer, however, constitutes a serious drawback to possible applications, particularly in the realm of papermaking where cost-effectiveness is paramount.

The interest in making cellulose fibers hydrophobic in a more general context began some 40 years ago with numerous studies on surface esterification using aliphatic and aromatic carboxylic reagents, mostly in organic media, although recent reports also deal with gas–solid reactions using carboxylic anhydrides [12, 13]. Depending on the degree of substitution (DS) and the specific moiety appended, contact angles increased to different levels, reaching values above 90° in the best situations [12, 13]. A particularly detailed study dealing with the use of aliphatic fatty acid chlorides of different chain lengths [20–24] showed that the combined use of two renewable resources as both the fiber substrate and the reagent can open the way to fully green systems with properties that go beyond mere hydrophobization, which is nevertheless attained at good levels. The modified fibers displayed excellent compatibility with polyolefins in the construction of composite materials, given the structural affinity between the grafted aliphatic "hairs" and the matrix macromolecules. Furthermore, these hairs were sufficiently long (C12–C22) to generate physical entanglements with the polymer surrounding them, thus enhancing the strength of the fiber–matrix interface. A later study applied the same approach to cellulose nanocrystals or whiskers instead of conventional fibers [25]. Results showed that long appended aliphatic chains actually crystallized at the surface of the modified cellulose nanocrystals and that their incorporation into poly(ethylene) improved the mechanical properties of the matrix.

Esterification with the perfluorocarbonyl compounds shown in Fig. 1 leads to cellulose surfaces with enhanced hydrophobicity compared with those discussed above, as expected, because of the low surface energy associated with the presence of fluorinated moieties. Indeed, the polar component of the surface energy (γ_s^p) fell to practically zero and the dispersive contribution (γ_{ds}) to values as low as 8 mJ/m^2. This explains the fact that these treatments also generate a strong lipophilicity and thus the fiber surface becomes "omniphobic," with high contact angles for polar and nonpolar liquids. Trifluoroacetylation is readily reversed by hydrolysis following prolonged contact with water, a feature that favors recycling of the original fibers after their life cycle (e.g., in packaging resist to both moisture and grease). Pentafluorobenzoylation, on the other hand, gives surfaces that are much more stable toward hydrolysis [12, 13].

Another coupling reaction involves isocyanates. The most thorough investigation on the preparation of omniphobic cellulose surfaces using this coupling deals with the reaction of (3-isocyanatopropyl)triethoxysilane with cellulose fibers [26], followed by sol–gel treatments with different reagents to generate the most appropriate conditions for superhydrophobicity and superoleophobicity, particularly

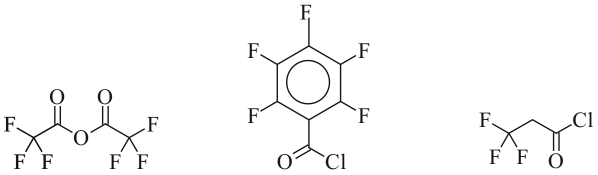


Fig. 1 Three perfluorocarboxyl reagents used for the hydrophobization and lipophobization of cellulose fibers [12, 13]

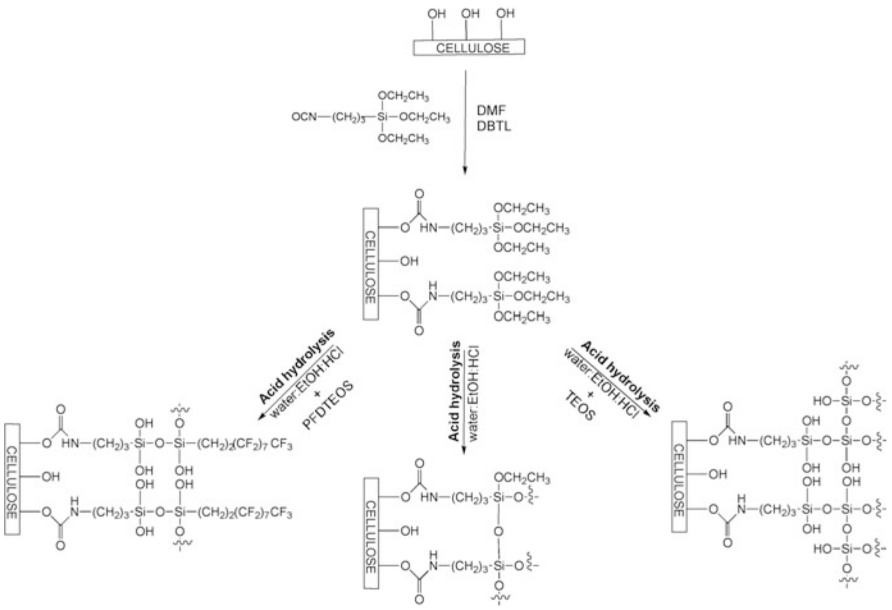
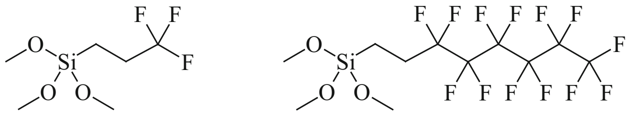


Fig. 2 Pathways implemented to prepare differently modified cellulose fibers, following the initial coupling with (3-isocyanatopropyl)triethoxysilane (reproduced by permission of Elsevier. Copyright 2010. Reprinted from Cunha et al. [26])



TFPS PFOS

Fig. 3 Chemical structures of 3,3,3-trifluoropropyl trimethoxysilane (*TFPS*) and *1H*,*1H*,*2H*,*2H*-perfluorooctyl trimethosysilane (*PFOS*)

when using perfluorosiloxanes for the final step (see Fig. 2). This process ultimately generates micro- or nanosurface asperities on the fibers, which, when complemented by incorporation of perfluoro moieties, results in strongly biphobic surfaces with contact angles as high as 140° for water and 134° for the nonpolar diiodomethane.

A different treatment involving the siloxane reaction with the cellulose OH groups, aimed at producing a highly hydrophobic surface [27], enabled grafting of the surface of two models for cellulose fibers (Avicell and Whatman paper) with two fluorine-bearing alkoxysilanes, 3,3,3-trifluoropropyl trimethoxysilane (TFPS) and *1H*,*1H*,*2H*,*2H*-perfluorooctyl trimethosysilane (PFOS) (Fig. 3).

These fluorinated moieties append onto the surface of the cellulose macromolecules and produce a strong hydrophobic effect, as revealed by the increase in water contact angles on both model substrates. Contact angles changed from about 50° before modification to 115° and 125° for TFPS- and PFOS-modified samples, respectively. Moreover, determination of the polar contribution to the surface energy (γ_s^p) using the Owens–Wendt approach showed a dramatic decrease from about 20 mJ/m^2 for the pristine celluloses to practically zero after modification. A similar approach was implemented with the aim of preparing a superhydrophobic and self-cleaning cotton fabric [28] using treatment with *1H,1H,2H,2H*-perfluorooctyl triethoxysilane (FOS). Water contact angle measurements revealed the formation of a highly hydrophobic surface after modification with different concentrations of FOS. A superhydrophobic character was only attained when the FOS concentration was 20% with respect to the cotton weight. The self-cleaning ability of the FOS-modified cotton fabric was also investigated, with encouraging results.

Two original alternative strategies for generating a pronounced hydrophobic character on the surface of cellulose fibers combine the introduction of nonpolar moieties and the formation of micro- to nanoscale topographies. One strategy involved physical adsorption of silica nanobeads onto the fibers (nanoroughness), followed by the reaction of TFPS or FOS with the silica surface (low surface energy structures) [29], as illustrated in Fig. 4. Each modification step was followed by SEM and AFM imaging. Water contact angles close to 150° were attained, confirming the effectiveness of combining the two approaches.

The second strategy has the advantage of a remarkable ease of implementation and green connotations [30]. The cellulose surface was subjected to short contact

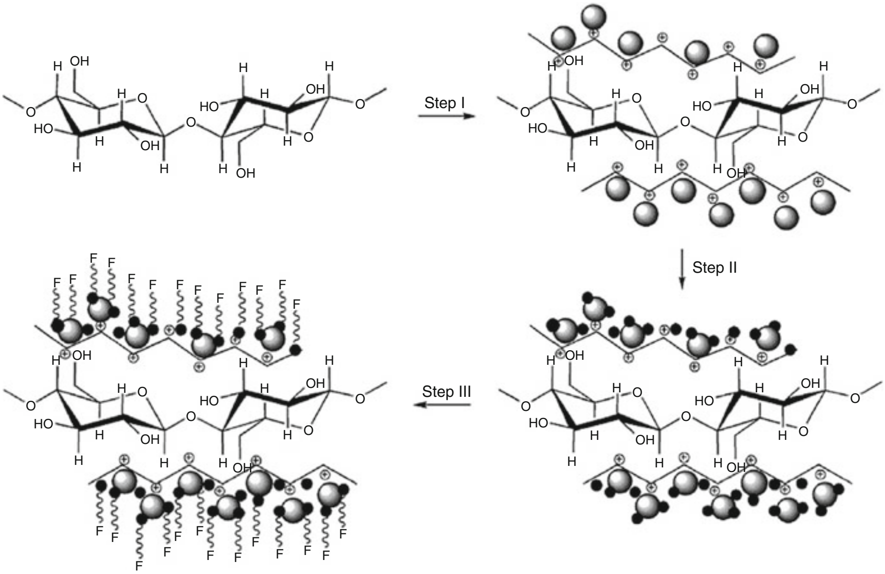


Fig. 4 Sequence of steps applied for preparation of highly hydrophobic rough cellulose surfaces (reproduced by permission of Elsevier. Copyright 2008. Reprinted from Gonçalves et al. [29])

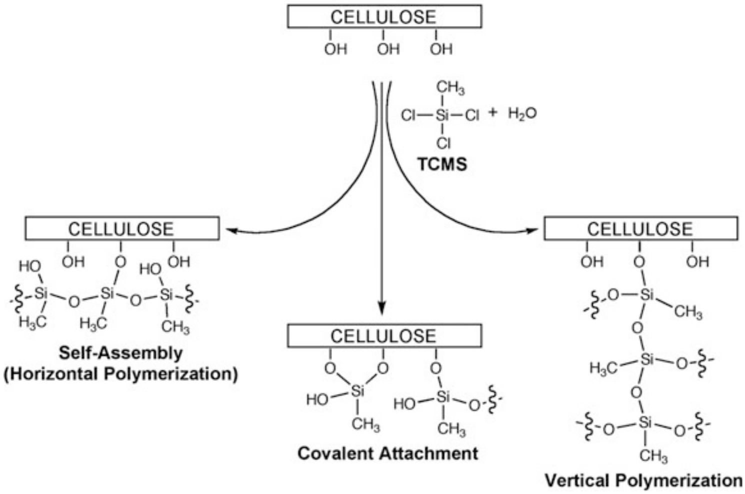


Fig. 5 Alternative structures generated by the reaction of hydrolysed trichloromethylsilane (*TCMS*) with the surface of cellulose fibers (reproduced by permission of Elsevier. Copyright 2010. Reprinted from Reference [30])

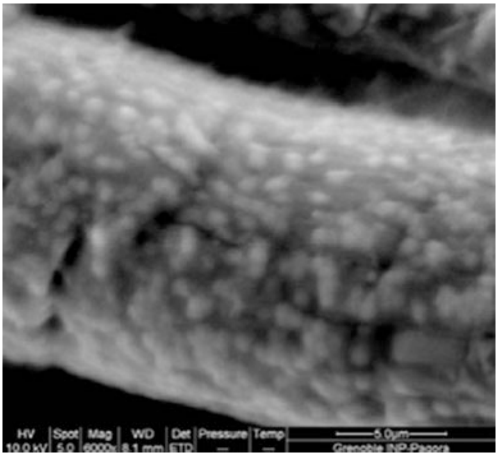


Fig. 6 A cellulose fiber covered by nano-asperities associated with the structures shown in Fig. 5 (reproduced by permission of Elsevier. Copyright 2010. Reprinted from Cunha et al. [30])

with trichloromethylsilane (TCMS) vapor in the presence of moisture at room temperature, and the hydrolyzed silane rapidly reacted with the surface OH of the fibers. The set of structures arising from this process, as shown in Fig. 5, contribute to the generation of nano-asperities on the cellulose fibers (Fig. 6).

In the process of switching to nanocelluloses, the use of aliphatic isocyanates has been reported for appending relatively long methylene sequences onto their surfaces [31, 32]. The reaction of *n*-octadecylisocyanate was conducted in toluene on both cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) and, despite a fairly low DS as a result of steric hindrance of the appended long aliphatic chains, the water contact angles were raised to values as high as 100°. This study also included incorporation of the modified fibers into a poly(caprolactone) (PCL) matrix and characterization of the ensuing composites. The results clearly showed the benefits of modification in terms of a superior gain in mechanical properties compared with the two untreated nanocelluloses.

An investigation aimed at the synthesis of so-called continuous fiber-reinforced composites led to the elaboration of new cellulose-based hydrophobic materials. The approach involved attaching a polymeric matrix to the surface of cellulose fibers via chemical coupling, in such a way that the long chains appended to the fiber surface formed macromolecular entanglements with those of the polymer matrix. In particular, the grafting of cellulose fibers by PCL followed a reaction pathway in which phenyl isocyanate was used as an OH-blocking agent, and 2,4-toluene diisocyanate (TDI) as the PCL–cellulose coupling mediator (Fig. 7) [33]. After modification, the water contact angle was higher than 90° and was found to be quite stable with time. This material was biodegradable, albeit with slower kinetics than those of the pristine fibers.

The use of high-energy physical sources, such as cold plasma, lasers, and UV light, in the presence of a specifically selected compound in the gas phase has been exploited to increase the hydrophobicity of cellulose surfaces [12, 13]. In all these processes, the mechanisms leading to chemical modification of the fiber surface are ill defined and certainly not confined to a single process [12, 13]. Plasmas involving styrene and a number of its homologs [34] have been tested successfully as sources of hydrophobization. A systematic study using this approach showed that the water contact angle increased up to 100°. There was clear evidence of surface modification, as shown by X-ray photoelectron microscopy (XPS) and elemental analysis. In the case of cold plasmas involving fluorinated reagents, the presence of grafted fluorine moieties or individual atoms were unambiguously detected and considered to be the main cause of the observed increase in hydrophobicity. However, these techniques, with rare exceptions [34], are difficult to control for good reproducibility, although this might not be a major drawback for certain applications where a positive qualitative outcome is considered adequate.

The purely physical deposit of a hydrophobic material onto cellulose fibers is the last type of treatment discussed in this section. The noncovalent attachment of different polymers or nanosized particles has been carried out using several techniques, such as Pickering emulsions, layer-by-layer or multilayer deposition, dip-coating or immersion in the polymer solution, impregnation, physical deposition, or simply heating [12, 13]. The advantages of these techniques stem from their relative simplicity and the possibility of using aqueous media. However, the mechanical stability of these thin coatings following prolonged utilization under mechanical stress raises concerns, which to the best of our knowledge have never been thoroughly addressed.

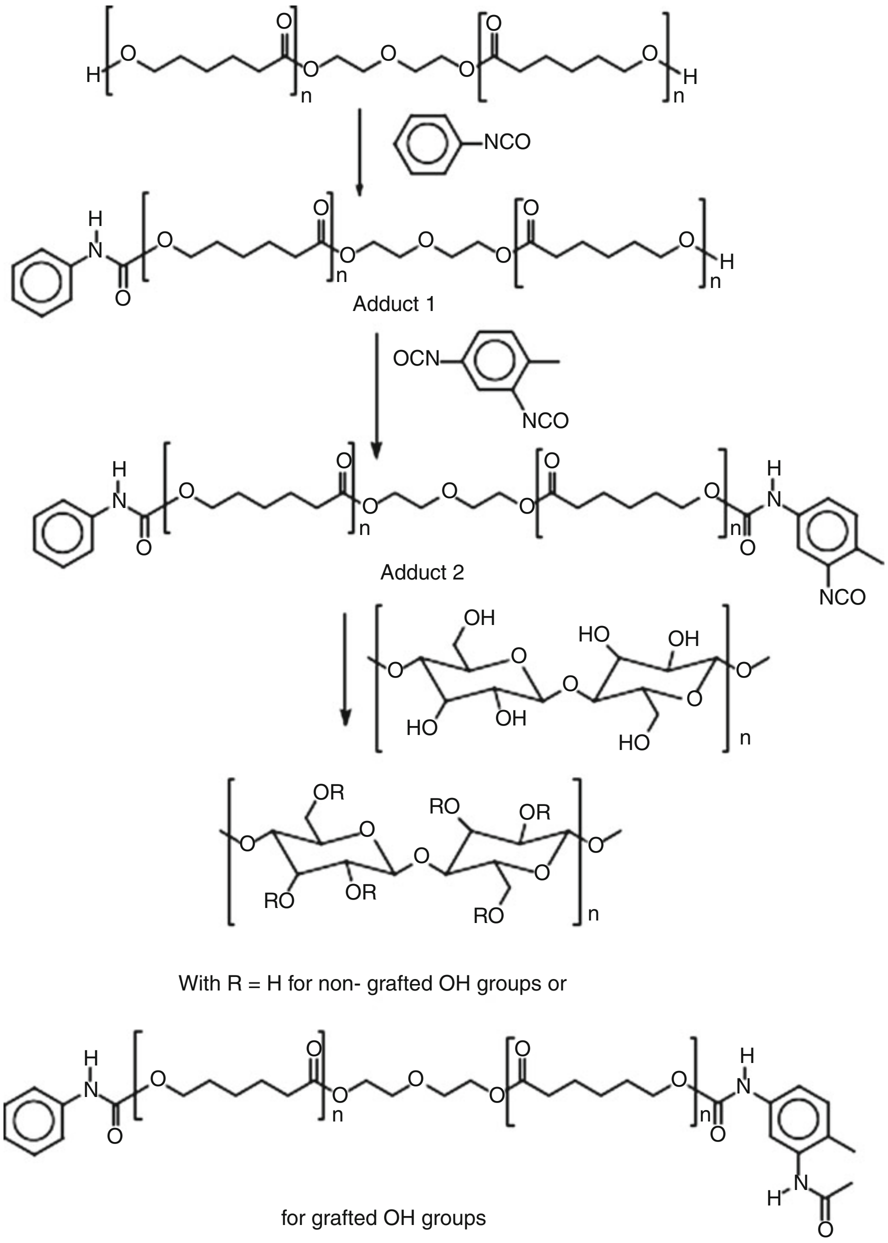


Fig. 7 Process leading to the grafting of poly (caprolactone) onto cellulose fibers (reproduced by permission of Elsevier. Copyright 2010. Reprinted from Paquet et al. [33])

The application of admicellar polymerization to cellulose fibers was first reported more than 10 years ago [35]. The process, formerly used to coat inorganic substrates such as oxides, involves generating an admicellar double layer of surfactant onto the solid surface to be modified and then filling it with a nonpolar monomer from its water suspension. The subsequent free radical polymerization generates a thin sleeve of the corresponding polymer around the substrate. Poly (styrene) and poly(acrylate)s were thus efficiently wrapped around conventional cellulose fibers, with a considerable gain in hydrophobicity after washing and drying the material [35]. Polymers with a low glass transition temperature are obviously preferred in this context in order to ensure flexibility of the sleeved fibers. The purpose of this study was to associate two possible applications, namely the increase in hydrophobicity for packaging papers and the incorporation of the treated fibers into a macromolecular matrix to form a composite material with good interfacial properties. This investigation was not pursued any further until 2013, when the same process was applied successfully to the three types of nanocellulose (CNCs, CNFs, and bacterial cellulose (BC) filaments [36, 37]). This is an original, simple, and green method for enveloping fibers with different polymers of low polarity without recurring to cumbersome techniques involving the transfer of nanofibers from their natural aqueous habitat to an organic medium. Figure 8 shows unpublished SEM images of BC fibers before and after undergoing the admicellar polymerization of styrene, and highlights the formation of a sleeve of poly(styrene) around the fibers.

The rewarding repercussions of this strategy are clearly illustrated by a subsequent study in which poly(styrene)-coated BC nanofibers were incorporated into natural rubber in order to enhance its mechanical properties [36, 37]. The presence of the polymer sleeve around BC improved the quality of its interface with the nonpolar natural matrix and provided a notable improvement in the mechanical properties of the ensuing composites in terms of Young’s modulus and tensile strength, even with modest nanofiber loadings. This investigation resulted in the preparation of materials going progressively from typical elastomers to stiff thermoplastics, as a function of the extent of incorporation of modified BC.

2.2 Modification by Physical-Chemical Adsorption

Noncovalent interactions have received much attention in the context of nanocellulose surface modification [7–11], on the one hand to facilitate dispersion in nonpolar media and, on the other hand, to develop viable bioengineering interactions. The former strategy was introduced in 2000 [38] by using surfactants consisting of the mono- and di-esters of phosphoric acid, with alkyl phenols tails to adsorb onto CNCs, with excellent results in terms of ease of dispersion in organic solvents. The incorporation of these surfactant-coated CNCs into either atactic or isotactic polypropylene produced very good compatibilization [39, 40], with specific interactions between charge and matrix in the latter type of composite. The use

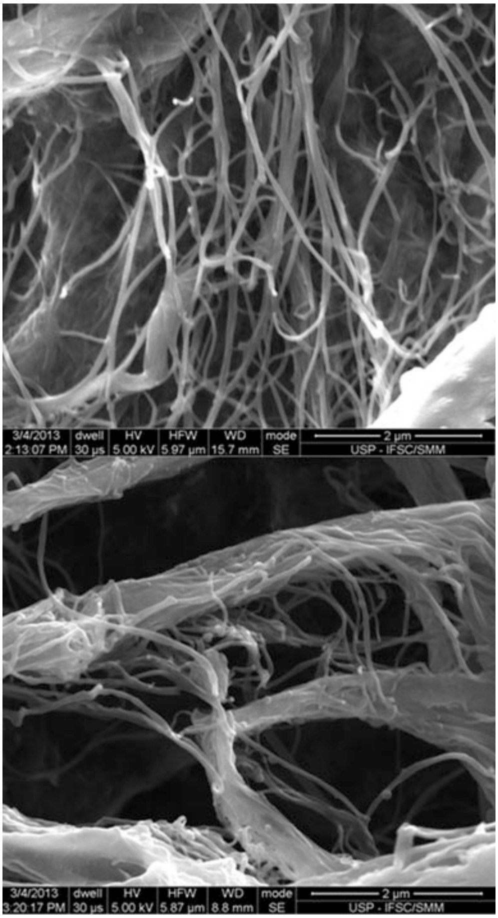


Fig. 8 SEM images of bacterial cellulose fibers before (*above*) and after (*below*) being subjected to the admicellar polymerization of styrene

of anionic surfactants was found to improve the dispersion of the modified CNCs in poly(lactic acid) [41], and nonionic counterparts provided the same beneficial effect when the matrix was poly(styrene) [42, 43]. Macromolecular amphiphilic block copolymers were also tested in this context and found to be an efficient aid for the dispersion of modified CNCs in nonpolar solvents [44]. The deposition of a cationic surfactant, cetyltrimethylammonium bromide, onto oxidized BC enhanced the strength of the interfacial interaction (thanks to the anionic–cationic electrostatic coupling) to such a degree that the surfactant was not removed by repeated aqueous washings [45, 46]. A similar study [47] described the interaction of oxidized CNCs with various cationic surfactants in an aqueous medium, simulating the process of organic modification of layered silicates.

Studies related to biologically inspired composites using nanocelluloses include the interaction of BC with poly(ethylene oxide) (PEO) [48] and hydroxyethylcellulose [49], the association of CNCs with PEO [50], and the adsorption of carboxymethylcellulose or chitosan on cellulose film surfaces [51]. The treatment of CNCs with a quaternized thermoresponsive acrylic copolymer [52] imparted this important property to the coated nanocrystals.

The by-now classical strategy of assembling monomolecular strata via layer-by-layer (LbL) deposition, based on electrostatic interaction between oppositely charged molecules or polyelectrolytes, has also been applied to both CNCs and microfibrillar cellulose (MFC) [53–59], as well as to carboxymethylated MFC, a highly negatively charged surface [60]. A variety of cationic polyelectrolytes, and even cationized MFC, were used, and the ensuing assemblies characterized in terms of specific structures and properties and, hence, possible applications.

The attachment of inorganic nanoparticles, including metals and oxides, onto the surface of cellulose fibers is another topic of growing interest. The first thorough study described the deposition of Ag, Au, Pt, and Pd particles with a narrow size distribution below 10 nm and the characterization of these novel hybrid materials [61]. Further work on this topic developed progressively [5] and the most notable advances reported the electrostatic deposition of Au nanoparticles on wood pulp and BC [62], the preparation of cellulose/SiO_2 nanocomposites by the LbL process [63], and the surface modification of cellulose fibers with TiO_2 [64] to give solar light photostable nanocomposites. Another promising application involves the antibacterial activity of cellulose/Ag nanocomposites. Ag concentrations as low as 5×10^{-4} wt% provided effective antibacterial action [65]. Further investigations have focused on increasing the fiber surface coverage [66] and exploring alternative deposition processes [67]. The most recent original contributions in this area deal with the use of LbL to first attach various polyelectrolytes to CNFs, in order to use them as attachment sites for the deposition of Ag and ZnO nanoparticles capable of providing antimicrobial properties to the ensuing assemblies [68, 69].

2.3 Chemical Modification of the Surface Chemical Moieties

2.3.1 Oxidation

The most relevant aspect of controlled modification of the chemical structure of cellulose fibers is the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-catalyzed oxidation of cellulose to generate carboxylic groups, particularly in view of its usefulness in handling nanocellulose suspensions and their reactivity. The reaction is known to exclusively affect the primary OH groups and is ecologically advantageous because it is carried out in water and in the presence of NaBr and NaOCl and calls upon the strategic role of the stable nitroxyl radical TEMPO to mediate the oxidation. Figure 9 illustrates the mechanism as applied to cellulose.

Isogai's group has been at the forefront of this research area [70] and developed an optimized technique to treat wood and other lignocellulosic fibers under mild basic conditions in order to facilitate their progressive unraveling as a consequence of the electrostatic repulsion generated by the formation of carboxylic groups.

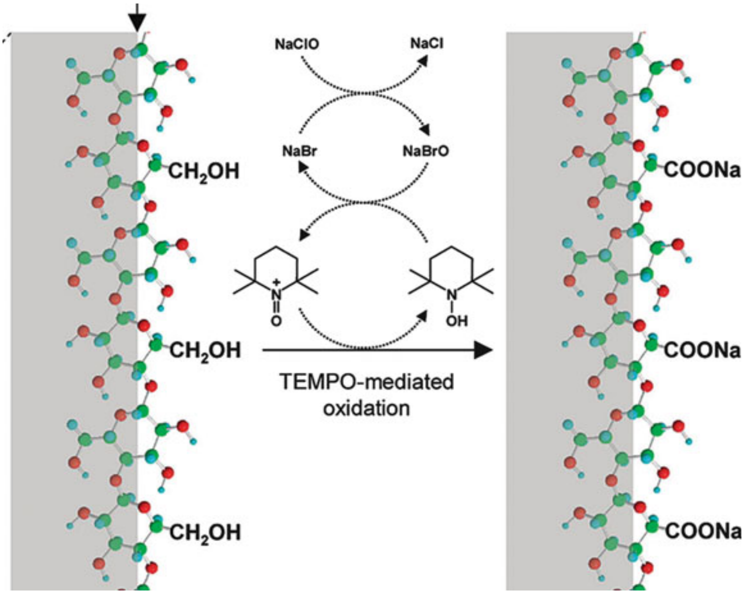


Fig. 9 Mechanism of the TEMPO-catalyzed oxidation of the primary hydroxyl groups of cellulose

Coupled with mechanical shearing, as in the preparation of CNFs, this green process gives rise to individual microfibers in a couple of hours at room temperature. The fibers are typically several nanometers wide, several micrometers long, and have a crystallinity of 70–90%. Numerous applications have been found for this relatively cheap nanocellulose, including nanoelectronics, healthcare, cosmetics and, not least, their incorporation into polymer matrices as reinforcement, to impart gas-barrier properties, and to improve thermal stability [70]. This process has also been applied to CNCs [71] and CNFs [72] with the purpose of facilitating their dispersion in both aqueous and organic media, and also to generate surface COOH groups in order to graft different moieties onto them.

2.3.2 Cationization

The introduction of positive charges on cellulose macromolecules [73, 74] is more cumbersome than similar cationizations of other polysaccharides such as starch and chitosan, because of solubility problems, as highlighted in a recent review [75]. However, this problem is largely alleviated if only the surface of the fibers is involved. The typical reagents used for this purpose are epichlorohydrin in conjunction with tertiary amines (as shown in Fig. 10), or an ammonium oxirane such as epoxypropyltrimethylammonium chloride, via nucleophilic addition of the alkali-activated cellulose hydroxyl groups to the epoxy moiety. As in the case of the

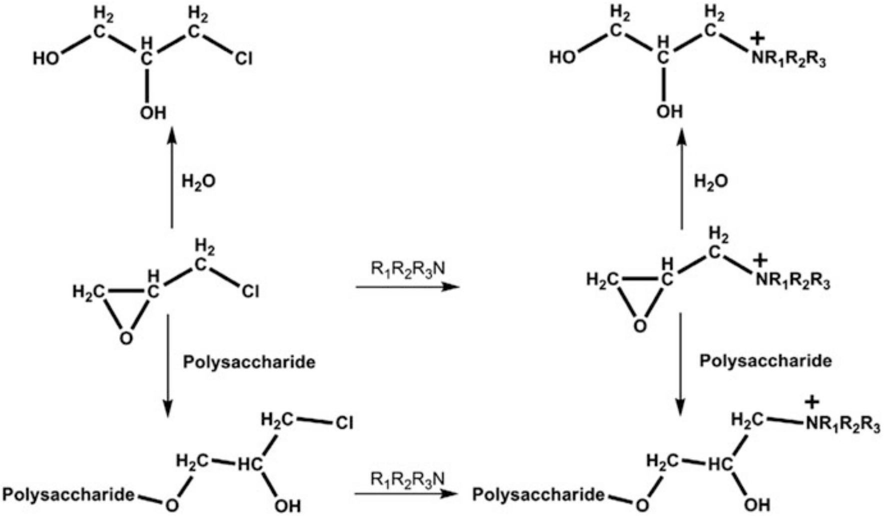


Fig. 10 Synthesis of cationized polysaccharides with epichlorohydrin and tertiary amines

cationization of CNCs [76], the surface grafting of chitin nanocrystals by appended cationic moieties leads to stable aqueous suspensions of these particles with original thixotropic properties. Given the fact that in this process the original anionic sites on the cellulose molecules are preserved, the ensuing fibers can be considered as amphoteric, but, of course, with a predominant cationic character. A similar process was applied to cellulose fibers before their mechanical shearing in order to reduce energy consumption in the preparation of CNFs [77, 78].

2.4 Grafting with Molecular Moieties

The numerous studies dealing with the chemical condensation of nonpolymeric molecular structures at the surface of cellulose fibers have been reviewed on several occasions [1–5], apart from the specific investigations discussed in the section on hydrophobization (Sect. 2.1). Only the advances reported in the last 5 years, which are predominantly related to the use of nanocelluloses as substrates [7–11], are therefore reviewed here. Many of these contributions are concerned with improvements in the compatibilization of the nanocellulose used as a reinforcing element in composites based on polymer matrices, but other strategies have been put forward with a variety of other purposes in mind.

2.4.1 Esterification

This chemical transformation has been discussed in the section on hydrophobization (Sect. 2.1). Work on the acetylation of different CNFs, typically involving acetic anhydride in the presence of strong acids as catalysts, has shown that the morphology of the substrates is not substantially altered, even under rather severe conditions. In general, the purpose of these esterification processes is primarily to improve compatibilization of the ensuing nanofibers with different macromolecular matrices in the construction of nanocomposite materials. The most original idea in this context stems from a pioneering investigation [79, 80] in which the authors coupled the acetylation reaction with the splicing and size reduction of lignocellulosic fibers in order to prepare esterified nanocellulose in a single step, as sketched in Fig. 11.

This approach inspired a recent study in which esterified CNFs were prepared by the application of both the fiber ball milling and chemical processes [81]. The use of different organic media, reagents, and other experimental conditions enabled modified CNFs with various features and properties to be attained.

An alternative way to avoid the laborious aqueous–organic medium change before the chemical transformation, a procedure that typically requires such steps as water–acetone–toluene exchange, has been put forward, namely a gas–solid reaction. CNCs and CNFs were exposed to the in vacuo attack of palmitoyl chloride at 160–190°C [82, 83] and the extent of esterification assessed by SEM and X-ray characterization. By altering the reaction conditions, the authors were able to ensure near-complete surface condensation without affecting the inner layers of the

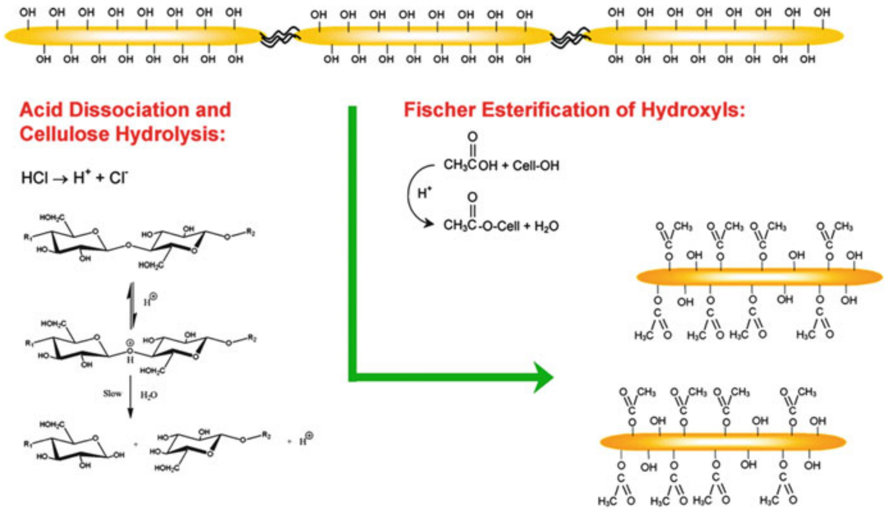


Fig. 11 Concomitant hydrolysis of amorphous regions and acetylation in a single-step process, leading to esterified cellulose nanocrystals (reproduced by permission of the American Chemical Society. Copyright 2010. Reprinted from Braun and Dorgan [79] and Sobkowicz et al. [80])

nanocellulose substrates. Further work by the same group used nanocrystal aerogels as starting cellulose material to provide a convenient way of dispersing the ensuing esterified product in nonpolar media [82, 83].

Exploitation of the classical transacetylation reaction using vinyl acetate was extended to CNCs in a study conducted in DMF suspension with potassium carbonate as catalyst [84]. This simple procedure provided a means to control the extent of esterification, as well as the severity of the attack.

Another interesting strategy with ecological advantages uses an ionic liquid ([bmim][PF6]) as the reaction medium for the surface esterification of CNFs by different aliphatic carboxylic anhydrides [85]. After optimization, surface DS values of around unity were attained, as assessed by XPS. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used as a novel complementary tool for the characterization of esterified nanofibers, and the authors also showed that the solvent could be adequately recycled.

2.4.2 Reactions with Isocyanates

The same group that carried out the reactions mentioned above in the context of hydrophobization [31, 32], also pursued reactions with isocyanates on both CNCs and CNFs in bulk at around 100°C [86–88] in order to find the optimal grafting conditions for compatibilization of the modified nanocelluloses with nonpolar matrices.

A more detailed and thorough investigation by another group from the same laboratory [89] was carried out in which a toluene suspension of CNFs was reacted with *n*-octadecyl-isocyanate (with the aid of the classical dibutyltindilaurate catalyst) in order to enhance the degree of surface grafting. One of the interesting outcomes of this study was that the morphology of the nanofiber assemblies was a function of the DS of the long aliphatic chains on their surface, as shown in Fig. 12. At high DS, steric crowding favored their organization to form crystalline domains based on dispersive interactions. This conclusion was reached from X-ray evidence and further corroborated by contact angle and thermogravimetric measurements [89].

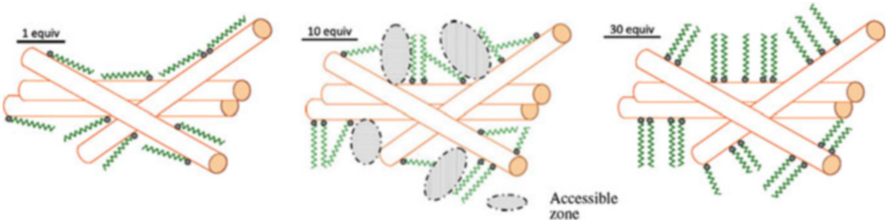


Fig. 12 Morphology of modified cellulose nanofibers as a function of the extent of grafting of octadecyl chains (reproduced by permission of Springer. Copyright 2012. Reprinted from Missoum et al. [89])

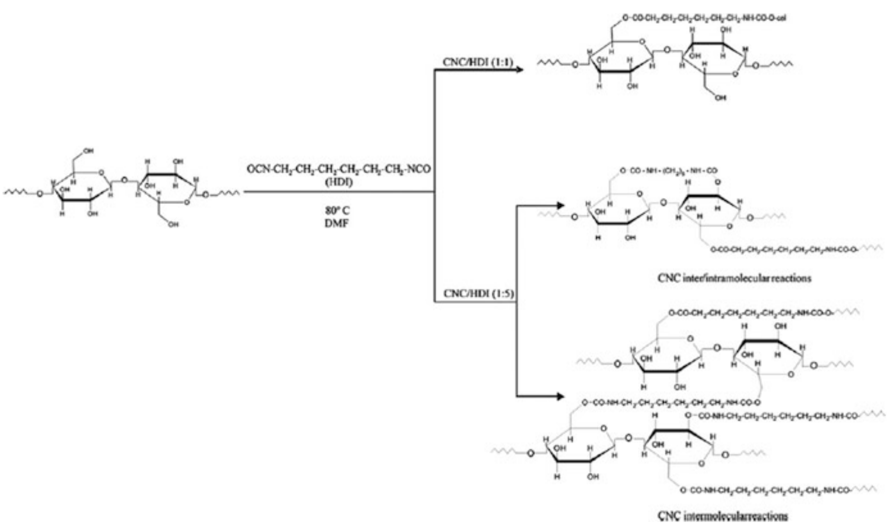


Fig. 13 Reaction between the surface OH groups of cellulose nanocrystals (*CNC*) and hexamethylenediisocyanate (*HDI*) in different molar ratios (reproduced by permission of Elsevier. Copyright 2011. Reprinted from Rueda et al. [92])

An extension of this work used the same aliphatic isocyanate to treat conventional lignocellulosic fibers used for the reinforcement of cement-based composites for roofing and cladding panels. The treated fibers created a protective shield against water swelling and the strongly basic medium of the matrix, which promotes degradation of cellulose [90, 91]. This strategy gave satisfactory results in terms of high chemical and physical stability of the fibers and enhanced mechanical properties.

The use of an aliphatic diisocyanate as the surface-coupling agent for CNCs [92] showed that, as the amount of 1,6-hexamethylene diisocyanate was increased with respect to the available surface OH groups, intra- and inter-CNC condensations took place (see Fig. 13). The incorporation of untreated CNCs into a polyurethane matrix resulted in an even dispersion, yielding a tough material without loss of ductility. Counterparts modified with an excess of diisocyanate appeared to migrate preferentially toward the matrix hard segments, increasing their crystallinity and enhancing the stiffness and thermal stability of the composite.

Another double reagent (3-isocyanatepropyltriethoxysilane), but this time made up of different moieties, was grafted onto CNCs through its more OH-reactive NCO side, thus leaving the siloxane end dangling and awaiting further modification [93]. This occurred as a sol–gel hydrolytic coupling and generated a silica-type coating on the nanocrystals, as shown in Fig. 14.

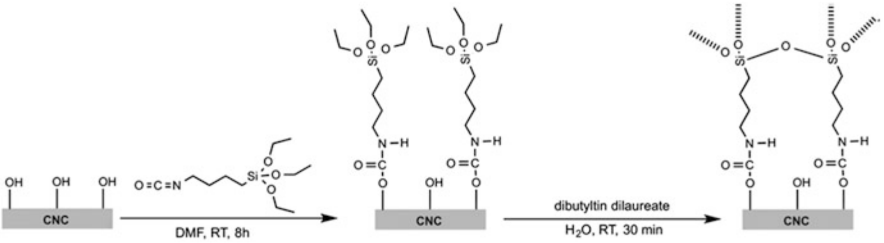


Fig. 14 Double reaction leading to silica-coated cellulose nanocrystals (*CNC*)

2.4.3 Reactions with Silanes and Siloxanes

Pioneering work of Chanzy's group dealt with the treatment of CNCs with a series of alkyldimethylchlorosilanes that resulted in stable suspensions with birefringent behavior. The same modification was applied to CNFs and provided nanocelluloses with a flexibility akin to that of conventional polymers [94, 95]. Research in Stenius' laboratory pursued this topic with the aim of giving the silylated CNFs the capacity of stabilizing water-in-oil emulsions [96, 97].

CNCs functionalized by coupling with *n*-dodecyldimethylchlorosilane gave a good dispersion in poly(L-lactide) and accelerated its crystallization rate [98]. Chemical vapor deposition of perfluorodecyltrichlorosilane or octyltrichlorosilane onto CNF aerogels provided a means to reduce considerably their wetting by nonpolar liquids [99, 100].

Regrettably, there is often some confusion in the literature regarding both the terminology and the reactivity of silicon-based reagents for cellulose. In order to clarify the following observations, it is therefore important to distinguish between *silanes*, where the silicon atom is bound to carbon and halogen atoms, and *siloxanes*, where Si–O bonds are also present. This is not trivial, because the generic use of the term silane for both types of compounds can lead to the wrong assumption of a similar reactivity toward the cellulose hydroxyl groups.

All the systems discussed above are based on the very efficient silylation reaction:

$$\equiv\mathrm{Si}-\mathrm{Cl} + \text{Cell-OH} \rightarrow \equiv\mathrm{Si}-\text{O-Cell} + \mathrm{HCl}.$$

This is, however, not the case when the reaction involves an alkoxysilane, despite numerous unverified claims to the contrary:

$$\equiv\mathrm{Si}-\mathrm{OR} + \text{Cell-OH}$$

The latter is an exceedingly sluggish interaction (if it does take place at all), as clearly shown in a thorough study on the issue [101]. However, if the siloxane has been partly hydrolyzed, the condensation reaction does occur, albeit at a lower rate than that involving the Si–Cl link [101]:

$$\equiv Si - OH + Cell\text{-}OH \rightarrow Si - O\text{-}Cell + H_2O$$

It follows that the studies quoted below bear an uncertainty related to whether the used siloxane had undergone some degree of hydrolysis, because otherwise its coupling with the cellulose OH remains doubtful.

The use of the fluoroalkoxysilane TFPS and PFOS (see above) as grafting agents on model cellulose fibers or filter paper was investigated and the coupling clearly shown to occur, because the two reagents had indeed partly hydrolyzed [27]. The reaction of 3-aminopropyltriethoxysilane with both CNCs and CNFs [102] was studied in order to enhance their compatibility with poly(lactic acid), but the proof that it actually took place was not provided convincingly. In contrast, the coupling of CNC with a variety of siloxanes for the same purpose, carried out in an aqueous medium, was shown to occur [103].

An interesting route for the preparation of fluorescent nanocellulose is the reaction of aminosiloxanes with CNCs, followed by grafting of the fluorescent moiety onto the appended amino groups [104]. Additionally, the use of siloxanes bearing SH groups has been described in two studies with the aim of appending thiol functionalities to CNC [105, 106]. In both instances, the first modification was carried out with the purpose of applying the thiol-ene click reaction to the ensuing SH-decorated CNCs, as discussed further in the next section.

2.4.4 Other Molecular Graftings

Two independent approaches have been proposed for attaching pH-sensitive structures onto nanocellulose. The first method used succinimidyl ester dyes introduced onto the surface of CNCs through a thiol-ene reaction [107], whereas the other exploited the azide-alkyne 1,3-dipolar cycloaddition to graft 1,2,3-triazole-4-methanamine to CNFs [108]. The latter click mechanism was also adopted to incorporate cationic porphyrin [109] and an imidazolium salt [110] onto the surface of CNCs for antimicrobial purposes and ion-exchange applications, respectively.

A recent addition to the numerous ways of appending reactive moieties to nanocellulose surfaces is the reaction of TEMPO-oxidized CNFs, embedded in an electrospun poly(acrylonitrile) nanofibrous scaffold, with cysteine [111], as shown in Fig. 15. The aim of this study was to use the material as an efficient scavenger of chromium (VI) and lead (II) pollutants in water.

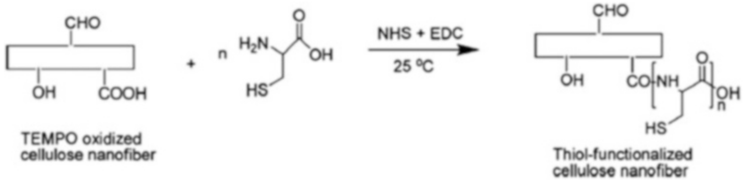


Fig. 15 Reaction of oxidized cellulose nanofibers with cysteine (reproduced by permission of Elsevier. Copyright 2014. Reprinted from Young et al. [111])

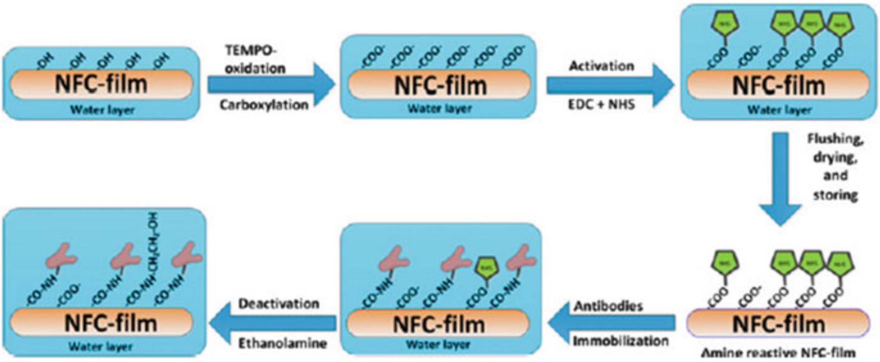


Fig. 16 Sequence of steps for the immobilization of antibodies on the surface of a nanofibrillar-cellulose film (*NFC-film*) (reproduced by permission of AIP Publishing LLC. Copyright 2012. Reprinted from Orelma et al. [113])

The possibility of exploiting nanocelluloses as bioactive surfaces has been carefully reviewed by the group of Rojas [112]. An original example of this strategy [113] deals with the reaction of TEMPO-oxidized CNF thin films with *N*-hydroxysuccinimide (NHS), in the presence of 1-ethyl-3-[3-dimethylamino-propyl]carbodiimide hydrochloride (EDC) to catalyze the condensation reaction. The amino groups thus appended were used to anchor antibodies, as sketched in Fig. 16. The same type of surface modification with NHS and EDC was applied to oxidized CNFs [114], but the purpose of this investigation was to apply the amidation reaction to amino-functionalized carbon dots, which were thus chemically incorporated at the nanofibril surface. The result of this study was the preparation of transparent and fluorescent nanopaper with tunable luminescence.

Another contribution from this USA–Finland research collaboration proposed a general method for attaching a chemical graft onto nanocellulose [115, 116] in an aqueous medium. Carboxymethyl cellulose was functionalized with either azido or propargyl moieties and then adsorbed onto CNFs or ultrathin cellulose films before proceeding to click the grafted moieties with a variety of complementary molecules using the Cu(I)-catalyzed 1,3-dipolar azido-alkyne cycloaddition.

Yet another stimulating piece of research from the same group looked into a strategy for building CNCs bearing a thiol group at one end of their rodlike morphology [117]. The process required the transformation of surface OH groups into sulfate anions, leaving the reducing aldehyde end ready for transformation into an aliphatic thiol tail that could be placed in contact with a gold surface. Under appropriate medium conditions, these end-SH functionalized nanorods could be aligned perpendicularly to a gold surface (as shown in Fig. 17), but other orientations were also available given the flexibility of the SH–gold junction.

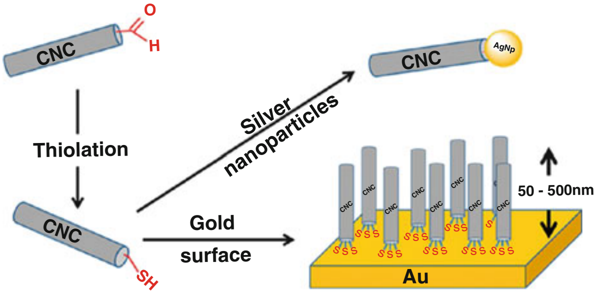


Fig. 17 The principles associated with building cellulose nanopillars on a gold surface (reproduced by permission of the American Chemical Society. Copyright 2013. Reprinted from Lokanathan et al. [117])

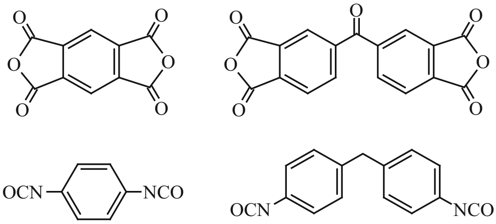


Fig. 18 Stiff bifunctional molecules suitable for reacting with only one of their moieties in heterogeneous contact with cellulose fibers

2.4.5 The Use of Stiff Bifunctional Reagents

Bifunctional reagents have been reviewed before [3–5], but the interest in them and their applications justify a reminder here. The strategy is based on the use of bifunctional molecules with a rigid core, which hinder any flexibility with respect to the availability of both reactive groups [118]. When such reagents are placed in contact with a solid substrate bearing complementary functions in a heterogeneous medium, only one of the active moieties can statistically graft itself onto the solid surface, thus leaving the other available for further exploitation.

In the specific case of a cellulose surface, the obvious reactive moieties are carboxylic anhydrides and isocyanates, as in the structures given in Fig. 18. One of the most obvious applications of this principle is the preparation of composite materials in which the surface of the modified cellulose fibers is covalently linked to the macromolecular matrix, demonstrating the best means of ensuring an optimized interface.

Apart from the examples of applications given in the original study [118], some recent exploitations of this idea include a study in which each of the four molecules shown in Fig. 18 was appended onto the surface of cellulose fibers before incorporating them into a cellulose aceto-butyrate matrix [119].

2.5 Grafting with Oligomers and Polymers

The chemical attachment of macromolecular strands to the surface of cellulose fibers has witnessed an important revival. This is because of the opportunities arising from the recent advances in controlled radical and ring-opening polymerization techniques and, also, because of the stimulating perspectives associated with grafting nanocelluloses. Again, given the availability of previous overviews [3–5, 120, 121], the present treatment of this topic concentrates on notable progress in the last few years. The grafting strategies have either exploited the reactivity of the cellulose superficial hydroxyl groups directly, or their preliminary transformation into other functional moieties, following the concepts discussed in the previous section. In both instances, the classical approaches of grafting-from and grafting-onto have been applied. The grafting-through counterpart is not possible in these heterogeneous systems because the cellulose macromolecules are immobilized on the fiber surface and can therefore only provide access to the growth of the appended polymer in the outward direction.

2.5.1 Grafting From

The surface activation of cellulose fibers to generate initiating species for free radical and ionic polymerization of different monomers [3, 6] had lost impetus because of rather unsatisfactory results in terms of the possible applications of the ensuing materials. However, the development of novel quasi-living mechanisms and the current relevance of nanocelluloses have spurred a flurry of fresh research initiatives.

Chain polymerization reactions bearing a free radical nature have been studied using traditional techniques based on the OH-oxidative power of Ce(IV) salts or the persulfate–sulfite couple, applied to different nanocelluloses and acrylic monomers [122–126], but gave rather poor yields because of the important interference of homopolymerization reactions. By contrast, controlled approaches such as atom-transfer radical polymerization (ATRP) and single-electron living radical polymerization (SE-LRP), have provided interesting results. Thus, poly(styrene) [127] and acrylic polymers [128, 129] were efficiently grafted onto nanocellulose surfaces using these procedures, namely, poly(butylacrylate) was attached to MFC [130, 131] and both poly(butylacrylate) and poly(methylmethacrylate) were linked to BC [132]. A variety of specific mechanisms and conditions were selected for these processes and the ensuing degree of branching, as well as the properties of the grafted nanocelluloses, varied accordingly. An interesting example among these studies [129] is that of a two-step procedure to attach isobutyl bromide moieties at the CNC surface, which resulted in optimization of the extent of grafting and relative uniformity in the chain length of poly(*tert*-butylacrylate) chains.

The ring-opening polymerizations (ROP) of ε-caprolactone and L-lactide are other relevant contributions to recent grafting-from investigations, as recently

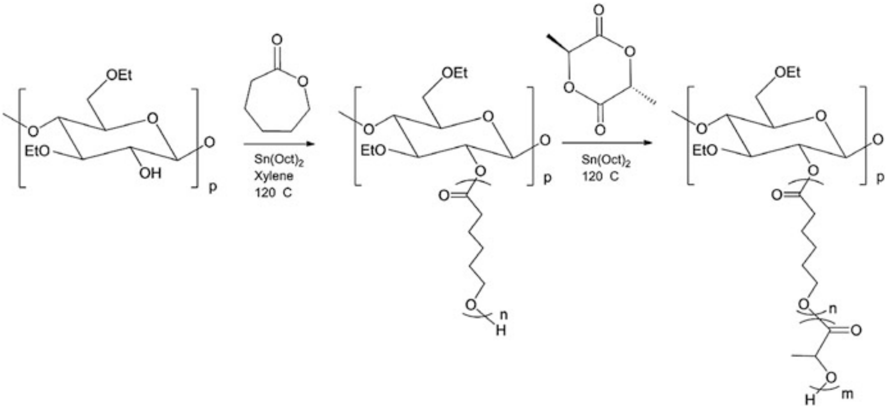


Fig. 19 Example of sequential ring-opening polymerization grafting of a cellulose surface to append block copolymer chains (reproduced by permission of the American Chemical Society. Copyright 2007. Reprinted from Yuan et al. [133] and Goffin et al. [134])

reviewed [120]. The principle of these processes, applicable equally well to conventional lignocellulosic fibers and nanocelluloses, consists of activating the surface OH groups in order to promote the ROP of these cyclic esters. Tin (II) 2-ethylhexanoate, Sn(Oct)$_2$, is by far the preferred catalyst and operates through a coordination–insertion polymerization mechanism, but carboxylic acids have also been utilized. These ROPs do not display any termination reaction and the hydroxyl-bearing end group of each chain can therefore be exploited to initiate the polymerization of a second monomer. This expedient has been applied to cellulose surface grafting (both common fibers and CNCs) by using ε-caprolactone and L-lactide in succession to generate block copolymers [133, 134], as shown in Fig. 19.

The most important aim behind these studies is, of course, optimization of the interface quality arising from the incorporation of the modified fibers or nanofibers into polyester-type matrices, including the attainment of continuous covalent bonding [120, 135].

2.5.2 Grafting Onto

Interestingly, the grafting of PCL chains at the surface of conventional cellulose fibers was also carried out by coupling the polymer bearing isocyanate end-functions with the outer OH groups of the fibers. This is a grafting-onto strategy, which is an alternative to the grafting-from counterpart discussed above [33] and shown in Fig. 7 (a three-step procedure using a PCL macrodiol prepared from diethylene glycol).

The grafting of oligo- or poly-ether chains onto (nano)cellulose fibers is arguably the most investigated item within the present subject. In the first report on this

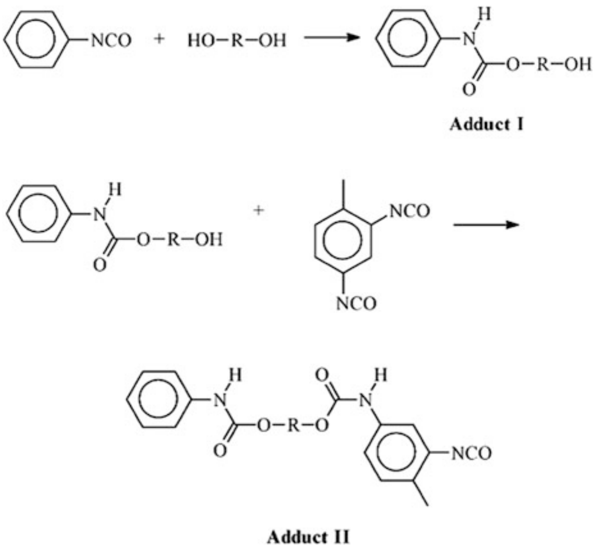


Fig. 20 Synthesis of polyethers bearing an isocyanate end group to be reacted with the superficial cellulose hydroxyl functions (reproduced by permission of Elsevier. Copyright 2010. Reprinted from Ly et al. [136])

topic [136], the surfaces of lignocellulosic fibers were decorated with PEO, poly (propylene oxide), and poly(tetrahydrofuran) (PTHF) with molecular weights of 2,000–4,000, employing the same principle used for grafting PCL chains [33]. More specifically, toluene diisocyanate played the role of coupling agent between the polyether and the OH groups on the fiber surface, as sketched in Fig. 20, where HO-R-OH is the polyether diol. Adduct II was then grafted to the fiber surface.

CNCs were grafted with PEO chains by the condensation reaction of PEO-NH_2 ($M_w = 5{,}000$) with the TEMPO-oxidized surface of nanocrystals bearing COOH groups [137], in order to improve their dispersability in melt-extruded poly(styrene). The same strategy was adopted to append PEO chains (M ~1,000 and ~2,000) to ultrafine CNFs [138], which were then used to prepare poly(L-lactide) composites displaying enhanced mechanical properties.

The direct elaboration of nanocomposites of CNFs chemically linked to a thermoplastic polyurethane (PU) matrix, based on a grafting-onto process, was recently described [139]. A PTHF macrodiol ($M_w = 1{,}000$) was reacted with an excess of an aromatic diisocyanate and the ensuing PU with NCO end groups was mixed in situ with the CNFs, whose surface OH moieties condensed with some of the NCO functions. Chain extension of all the PU chains was then induced by adding 1,4-butanediol to the medium, before casting and solvent evaporation. The procedure is illustrated in Fig. 21. The composites displayed a considerable increase in strength, even with incorporation of only 1% nanocrystal, without loss of extensibility and transparency.

In a similar vein, biomimetic capsules designed to hold liquids were prepared by reacting CNFs directly with an aliphatic diisocyanate using an original one-pot two-phase process, as sketched in Fig. 22 [140].

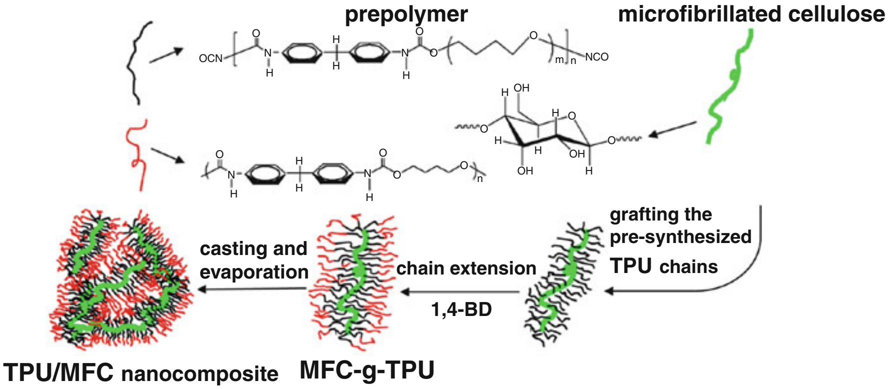


Fig. 21 In situ preparation of a polyurethane/cellulose nanofiber composite (reproduced by permission of the American Chemical Society. Copyright 2014. Reprinted from Yao et al. [139])

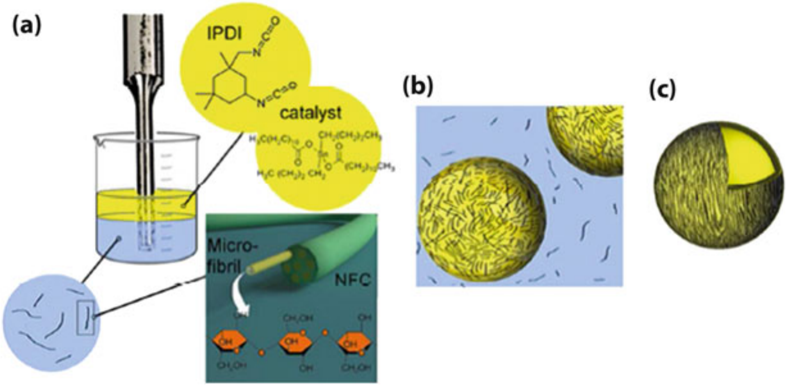


Fig. 22 Preparation of liquid-holding capsules based on cellulose nanofibers (reproduced by permission of the American Chemical Society. Copyright 2014. Reprinted from Svagan et al. [140])

In a different vein, β-cyclodextrin moieties were attached to the surface of various conventional types of celluloses, including paper and cotton bandage. This was accomplished through the catalytic action of citric acid, which played the role of polycondensation agent thanks to its three COOH groups. The growth of cyclodextrin chains was promoted while, at the same time, joining them covalently to the substrate fibers [141]. The cup-like shape of cyclodextrin (see Fig. 23) bearing hydroxyl functions was exploited to insert chlorhexidinedigluconate, a widely used antiseptic molecule whose shape fits appropriately into the cavities. Release of the bioactive agent was studied by immersing the modified cellulose in water and measuring its escape kinetics. This simple procedure, based on a surface grafting-onto mechanism, enabled the performance of bactericidal aids to be

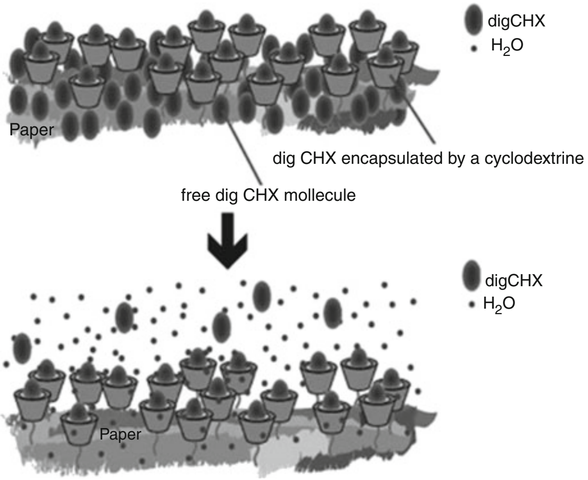


Fig. 23 Massive release of chlorhexidine digluconate (*digCHX*) from cyclodextrin grafted on cellulose (reproduced by permission of Wiley Periodicals, Inc. Copyright 2012. Reprinted from Cusola et al. [141])

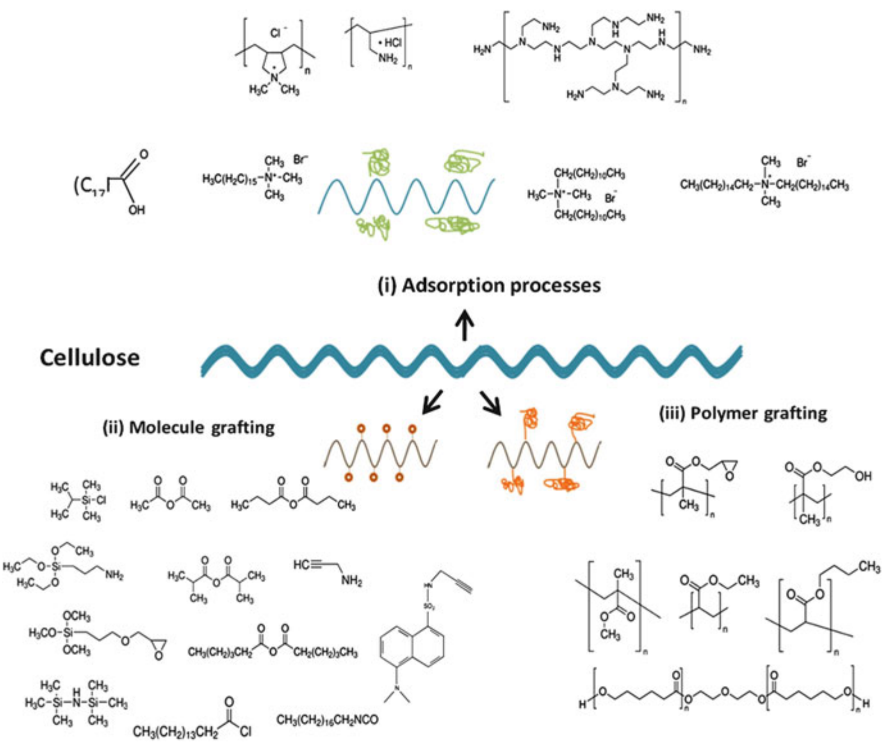


Fig. 24 Strategies for cellulose surface modification: (*i*) adsorption processes, (*ii*) molecule grafting, and (*iii*) polymer grafting (adapted from Missoum et al. [142])

optimized without affecting the mechanical properties of their inner cellulose structure and morphology.

Before introducing in-depth modification of cellulose, we finalize this section by presenting a summary of the different approaches and main moieties that can be used for cellulose surface modification. Figure 24 displays graphically the various approaches discussed in Sect. 2, including physical adsorption as well as molecular and polymer grafting.

3 In-Depth Modification

In contrast to the working hypothesis discussed in Sect. 2, which is based on limiting any cellulose modification to the surface, or to a few outer molecular layers, the strategy discussed here consists in carrying out modification reactions that proceed through part of the fiber thickness, in a controlled fashion. Although these ideas have generated relatively few concrete results up to now, further implementation seems likely given the potential development of interesting novel materials, hence our decision to incorporate this topic in the review.

3.1 Physical Modification

The idea of elaborating a composite material in which both the matrix and the reinforcing elements are from the same polymer was originally proposed by Ward and Hine [143,144], who applied it to poly(ethylene). Reports about the application of this concept to cellulose [145–148] describe the impregnation of uniaxially aligned cellulose fibers with a cellulose solution, selectively dissolving the surface of cellulose fibers and then compressing and drying the system. This gives rise to an all-cellulose composite in which the crystalline inner core of undissolved fibers is surrounded by an amorphous sleeve. Similar approaches have been implemented, all based on embedding highly crystalline fibers into a matrix of regenerated cellulose, albeit using different solvents and fibers [149–152]. The modulus of elasticity and the strength of these original materials in some instances reached values well above those of the best cellulose-reinforced thermoplastics, namely more than 10 GPa and about 100–500 MPa, respectively.

An extension of these concepts to the preparation of cellulose aerogels involves the partial and controlled dissolution of microcrystalline cellulose in a LiCl/ *N*,*N*-dimethylacetamide (DMAc) solvent system, followed by precipitation of the ensuing gels and freeze-drying to preserve their open morphology [153]. These highly porous materials had densities of 100–350 kg m^{-3}, flexural strengths as high as 8 MPa, and a maximum stiffness of 280 MPa.

3.2 Chemical Modification

To the best of our knowledge, two different methods for in-depth chemical modification of cellulose fibers have been tackled successfully. The first is an extension of the study on surface esterification with fatty acid chlorides discussed above [20–24], in which the reaction medium was changed from toluene (which does not swell cellulose) to the cellulose-swelling *N*,*N*-dimethylformamide. Under these conditions, the esterification reaction could proceed beyond the surface of the fibers and thus produce a thermoplastic sleeve around them. The crucial aspect of this process is careful control of the extent of penetration, to avoid the total transformation of cellulose into its corresponding esters. Optimization of the system gave a morphology consisting of an inner core of untouched residual fibrous cellulose, which therefore preserved its pristine mechanical properties, and an outer shell of thermoplastic material. Hot pressing this two-layer product generated a novel composite arising entirely from the starting cellulose fibers in a one-pot operation. Figure 25 illustrates this sequential transformation.

The second approach is a variation on the theme of oxypropylation. This process has received considerable attention as a very useful way of valorizing biomass rejects by turning them into useful polyols for rigid polyurethane foams [155]. Any OH-bearing solid substrate can be readily converted into a viscous polyol by the straightforward grafting-from of propylene oxide (PO) through its anionic oligomerization. Figure 26 shows the principle of this reaction, which is always accompanied by some PO homopolymerization. The green aspects of the process are coupled with the interest in using a straightforward method of exploiting a large number of industrial side products associated with vegetable resources such as sugarbeet pulp, lignin, cork rejects, olive stones, low-quality chitin, and chitosan.

In these applications, the substrate is treated in order to be converted entirely into the corresponding oxypropylated polyol, whereas the partial reaction provides an original means of turning cellulose fibers into a source of one-component composite. The system was thoroughly studied [156–158] and yielded interesting fiber morphologies, characterized by a sleeve of thermoplastic poly(PO) surrounding the inner unreacted core (as shown in Fig. 27), which could be hot-pressed into a composite. The same treatment was also applied to starch granules, with similar results [157].

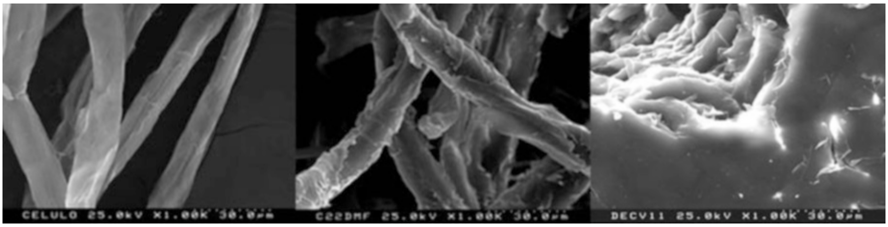


Fig. 25 In-depth esterification of cellulose fibers and formation of a composite. Pristine fibers (*left*), esterified fibers before (*center*) and after (*right*) hot pressing (reproduced by permission of Elsevier. Copyright 2005. Reprinted from Gandini et al. [154])

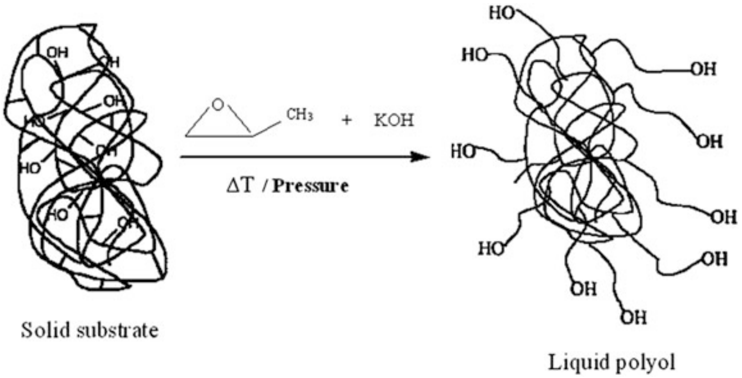


Fig. 26 Oxypropylation of an OH-bearing solid substrate by gaseous propylene oxide

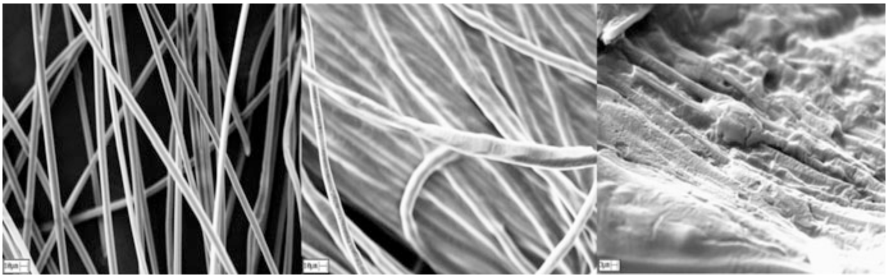


Fig. 27 From *left* to *right*: regenerated cellulose fibers before and after partial oxypropylation, and after hot pressing (reproduced by permission of Elsevier. Copyright 2005. Reprinted from Belgacem and Gandini [155])

4 Conclusions

This review shows clearly that modification of cellulose substrates, either limited to their surface or involving a sleeve of numerous macromolecular layers, is a steadily growing area of research and development that is applicable to conventional fibers and, more importantly, to their nanocellulose counterparts. This trend is driven by the benefits associated with the large specific surface area offered by the latter, which results in enhanced mechanical performance and other properties of macromolecular matrices when nanofibers are incorporated. The various strategies for surface modification discussed here can bring about an improvement in properties and widen the domains of application of the ensuing materials in such fields as packaging, composites, selective adsorption, optoelectronics, biomedicine, and catalysis.

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