Green Modification of Surface Characteristics of Cellulosic Materials at the Molecular or Nano Scale: A Review

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Many current and potential uses of cellulosic materials depend critically on the character of their surfaces. This review of the scientific literature considers both well-established and emerging strategies to change the outermost surfaces of cellulosic fibers or films not only in terms of chemical composition, but also in terms of outcomes such as wettability, friction, and adhesion. A key goal of surface modification has been to improve the performance of cellulosic fibers in the manufacture of composites through chemistries such as esterification that are enabled by the high density of hydroxyl groups at typical cellulosic surfaces. A wide variety of grafting methods, some developed recently, can be used with plant-derived fibers. The costs and environmental consequences of such treatments must be carefully weighed against the potential to achieve similar performances by approaches that use more sustainable methods and materials and involve less energy and processing steps. There is potential to change the practical performances of many cellulosic materials by heating, by enzymatic treatments, by use of surface-active agents, or by adsorption of polyelectrolytes. The lignin, hemicelluloses, and extractives naturally present in plant-based materials also can be expected to play critical roles in emerging strategies to modify the surfaces characteristics of cellulosic fibers with a minimum of adverse environmental impacts.

Keywords: Surface modification; Cellulosic materials; Environmental impact; Reactions of wood; Adhesion; Life cycle analysis

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INTRODUCTION

Modification of cellulosic surfaces often can render the materials more suitable for subsequent processes that may involve wetting, coating, adhesion, or protection of the material. In an effort to be cost-effective and responsible, one attempts to meet the performance requirements of various applications at minimum cost and with minimum adverse impact on the environment. Such considerations suggest that emphasis ought to be placed on transformations that can be achieved with a sub- or mono-molecular layer of surface coverage. Also, given the great progress that has been achieved in nanotechnology in recent years, this review article includes approaches to surface modification that involve nano-scale layers of coverage on top of cellulose-based bulk materials.

Considering the environmental implications of manufacturing processes, scientists and engineers working with materials are facing a challenge. On the one hand they are motivated to employ cellulosic material as a key structural component in a wide range of current and future products in order to minimize adverse environmental impacts (Anastas and Warner 1998). Plants take up energy from the sun, along with the greenhouse gas CO_2, to manufacture cellulose fibrils, a material having relatively high values of elastic modulus and toughness. The choice of the cellulosic material affects property outcomes by way of the respective characteristic fiber dimensions, microfibril angles, and other physical and chemical aspects intrinsic to the fibers or wood. However, many of the potential uses for which materials scientists and engineers might wish to employ the cellulosic material – either as wood or as individual fibers – require that chemical reactions or adsorption have taken place at the surface. Each such reaction or interaction comes at an environmental price. A key part of that price involves how much energy is expended (Shah 2013). Ideally, one would want to be able to transform the surface of cellulosic materials to meet one's needs with a minimum input of energy, both in the reaction itself and also in the supply chain of procurement of the reagents to be used. A wide variety of different approaches could be used to modify cellulosic surfaces. So even though cellulosic materials themselves can be regarded generally as being ecologically-advantageous for manufacture, one runs the risk that such a description would no longer be justified from a green chemistry perspective after intensive alteration, especially if there were large inputs of energy, nonrecoverable solvents, or pollutants of various types.

To address this dilemma, the present review article adopts a strategy inspired by the presentation of consumer product performance data in a popular magazine and website (www.consumerreports.org). As in the cited example, the strategy is to consider each option in terms of a number of different aspects, each of which is rated on a scale of performance. Related multi-factor rating schemes have been employed when considering environmental impacts of various competing products and processes (Agostinho and Ortega 2013; Meyer and Priess 2014; Poveda and Lipsett 2014; Gibberd 2015). The goal in the present paper is to compare different possible interactions or reactions at the cellulosic surface. The different options will be rated in terms of various criteria contributing to their environmental desirability. Emphasis here will be placed on achieving a first beach-head with a suitable reagent that can have more than one functional group. If one side of an added chemical agent becomes associated with the cellulosic surface, by mechanisms to be discussed in this article, then there are essentially infinite possibilities for other functional groups within the same added molecules to enable further connections and structures that can be built outwards from the surface of the cellulosic material. To give one general example, if one forms an ester bond with –OH groups at a cellulosic surface, then the other end of the reagent chemical could have a wide range of different chemical nature, including hydrophobicity, acidity, basicity, or reactivity. It follows that, once one has achieved an initial connection (bonding or association) of something with the cellulosic surface, it is then possible to satisfy a wide range of goals in terms of wettability, adhesion, protection, or aesthetics, *etc.*

Why at the Molecular or Nano Scale?

Any modification of a cellulosic surface has to entail an initial molecular or nano-scale change at an interface, which is the focus of the present article. As will be discussed in the sections that follow, a variety of interactions, including covalent bonding, London dispersion forces, and ionic charge effects, *etc.*, may be involved. The manner and effectiveness of these primary interfacial interactions can be expected to affect a range of performance-related attributes of the cellulosic surfaces and the products that are made therefrom. As noted by Heinze and Liebert (2001), all large-scale industrial processes involving surface modification of cellulosic materials are essentially heterogeneous, depending on interactions between different phases. The cellulosic material is invariably present as a solid, and the reagents can be either in solution or in a gas phase. Due to the high specific surface areas of many cellulosic materials, especially in the case of nanocelluloses, the costs and other consequences of surface modification can be relatively large. To take an extreme example, based on its typical minimum dimensions of about 4 nm thickness (Habibi 2014), the specific surface area of a cellulosic nanocrystal (CNC) can be estimated to be of the order of magnitude of 1000 m^2/g. If one were to coat the surface of CNC with a dense layer of a fatty acid, which has a monolayer thickness of about 5.1 nm (Lee *et al.* 1992), one can estimate that the mass ratio might be about four parts of fatty acid to one part of cellulose. Thus it is very important to be able to achieve effects of modification with a minimum amount of added material.

Surface Characteristics of Cellulosic Materials

Key aspects of the surfaces of cellulosic materials have been considered previously (Krässig 1993; Hubbe and Rojas 2008; Shen 2009; Gamelas 2013). Surface-sensitive analytical methods have revealed much about the chemical composition of such surfaces both before and after chemical modification (Ostenson *et al.* 2006; Gamelas 2013). Several review articles have discussed chemical strategies for surface modification of these biomaterials (Mohanty *et al.* 2001; Freire and Gandini 2006; Renneckar *et al.* 2006; Nishio 2006; Tizzotti *et al.* 2010; Kalia *et al.* 2009, 2011, 2014; Cheng *et al.* 2012; Gandini and Pasquini 2012; Lam *et al.* 2012; Renneckar 2013; Shah 2013; Eyley and Thielemans 2014; Hu *et al.* 2014). George *et al.* (2001) reviewed work showing that physical modification methods, in addition to chemical modifications, must not be neglected when seeking ways to change the performance of cellulosic surfaces in various applications. Several review articles have emphasized chemical approaches to imparting or increasing a hydrophobic character to cellulosic surfaces (Cunha and Gandini 2010; Wang and Piao 2011). Other review articles have focused on types of surface modifications to facilitate the preparation of cellulose-reinforced composites or nanocomposites (Lu *et al.* 2000; Xie *et al.* 2010b; Dufresne 2010, 2011; Kabir *et al.* 2012). Cellulosic materials also can be surface-modified at the nano scale by means of adsorption of polyelectrolytes or colloidal particles; such approaches have been reviewed (Cunha and Gandini 2010; Lam *et al.* 2012; Hubbe 2014).

Factors Affecting Environmental Impact

As has been noted by Anastas and Warner (1998), among others, some chemical processes can be regarded as being more “green” than others due to their minimization of adverse environmental impacts. Connel (2005) provides good background about how different chemical processes and the resulting pollutants can affect the environment. Many such green manufacturing strategies can initially appear to be more expensive than so-called conventional technologies. However, part of this apparent higher cost may be because the full costs related to environmental damage have not been fully borne at the point of manufacture. Systems of life-cycle assessment (LCA) have been developed in an attempt to quantify and fairly compare different process options relative to environmental friendliness (Ciambrone 1997; Bauman and Tillman 2004; Horne *et al.* 2009).

Though the present review considers environmental impacts, this is not intended to be a life cycle analysis. A full LCA generally would include a careful evaluation of the environmental costs associated with each component in an integrated process, *i.e.* not just the procedures associated with the “methods” section of a scientific article, but also the underlying procedures, transportation, and other environmental aspects associated with the selection of materials and the often overlooked disposal aspects of the process as well (Bauman and Tillman 2004). Factors to be emphasized in sections that follow will include: whether the treatment agent comes from a photosynthetically renewable source, whether harmful solvents are used (Andrade and Alves 2005), whether toxic materials are used, whether the modification requires extensive use of energy, whether the modified cellulosic material still is biodegradable, whether it is still suitable for recycling, as in the manufacture of paper, whether materials are wasted during the modification process, whether non-renewable substances (petrochemicals) are used in the course of modification, whether the treatment damages the cellulose at a molecular level, and whether the modification is suitable for scale-up to industrial scale. Some factors that might be considered in a full LCA, but which will not be considered here, include odor, noise, radiation, water consumption, land use, occupational safety and health, ozone depletion, acidification, eutrophication, habitat alterations, and biodiversity.

Table A, which is placed in the Appendix of this review article, provides a listing of treatments from a large number of scientific articles describing different technologies for modification of cellulose-based materials. In each case the first column indicates what cellulose-based material was being modified in a given study. The second column indicates the manner of modification. The final column provides a citation in author-year format. The corresponding references can be found in References Cited. In addition, the table also provides qualitative ratings for 11 categories related to environmental sustainability. In each category the cited systems were assigned a score of -, 0, +, or ++, depending on the authors’ overall judgment, as shown below in Table 1.

Table 1. System for Rating of Modification Methods

Rating Code	Meaning
++	Highly favorable to minimize environmental impacts
+	Favorable relative to environmental impacts
0	Neutral or mixed effects on the environment
-	Unfavorable relative to environmental impacts

Subsections that follow describe the general process by which the authors assigned the ratings. However, as a disclaimer, it needs to be emphasized that one needs to read the cited articles in order to obtain a comprehensive understanding. Since the studies cited in this work differed greatly with respect to both goals and methods, many aspects defy easy categorization or comparisons. Rather, the ratings in Table A can be regarded as signposts that may draw one's attention to treatment systems that merit further study.

Green origin of the treatment agent

The first-listed category in the rating grid of Table A is "Green origin of treatment". Here the attention is placed on the nature of the substance or condition used as the agent of modification. A positive indication (+) is assigned, for the most part, when a treatment employs a photosynthetically renewable material. For example, a fatty acid treatment would generally receive a rating of "+" on account of its likely sourcing from a living plant. By contrast, a rating of "-" usually would be assigned if an acrylamide or silane product was employed, since such chemicals are not ordinarily obtained from plant sources. A neutral score (0) might be assigned, for instance, if the treatment just involves heating or the addition of clay, with no clear involvement of an organic chemical additive. Also, a neutral score sometimes is assigned if the treatment involves two agents, one plant-based and the other one petroleum-based but not present in major amount.

Some selected examples will be mentioned, showing how the rating scale was applied, for purposes of illustration. Dancovich and Hsieh (2007) described a process in which cellulose was modified using plant triglycerides, which are clearly non-toxic, plant-based materials. So this published procedure received a "+" rating in the "Green origin of treatment" column. Likewise, Gaiolas *et al.* (2009) used the natural products myrcene and limonene as the treatment agents. Natural products also were used by Liu *et al.* (2010b) and Shang *et al.* (2013) as treatment agents. Lackinger *et al.* (2012) showed that it was possible to make paper hydrophobic through use of a special type of alkenylsuccinic anhydride (ASA) that was derived from vegetable oils; conventional ASA is prepared from petroleum fractions. Work by Lee and Wang (2006) was given an intermediate rating of "0" in this category because even though they started with a bio-based material lysine, they prepared a diisocyanate component from that material, requiring the usage of non-renewable chemicals.

Avoidance of harmful solvents

Judging from various examples that appear in the book *Green Chemistry* (Anastas and Warner 1998), one of the most promising ways to improve the environmental compatibility of an industrial process is to decrease or eliminate the use of organic solvents. Such a concept is embodied in Principle 5 of Green Chemistry which states "minimize the use of auxiliary substances and wherever possible make them innocuous when used." Even if one takes effective measures to avoid release of solvents or their vapors, many of them would be classed as non-renewable resources. Furthermore, energy must be expended to separate the solvent from the given cellulosic material after its modification.

In assigning scores relative to solvent use, the authors considered such factors as the type and amount of respective solvent. Processes requiring the dispersion of cellulosic fibers in an organic solvent would be regarded as less desirable, especially when one considers the volume-ratios that are required to achieve good mixing in such a dispersion. In typical cases, and due to the high length-to-thickness ratio of typical cellulosic fibers (50 to 200), a ratio of 100 parts liquid to one part of cellulosic fiber solids may be needed to achieve good mixing. As in the dry-cleaning of laundry, the process can be relatively expensive in comparison to aqueous treatments. Quantitative recovery of the solvent after completion of the treatment is likely to be expensive. It follows that treatment procedures requiring the use of a solvent would have to be restricted to high-price applications, such as those involving molecular recognition, nano-technology, temperature-responsive or pH-responsive systems, sensors, and other high-tech applications and devices.

Certain types of chemical derivatizing reactions are often carried out in organic media, especially in cases where the reagents either are insoluble with water or would react with water (Missoum *et al.* 2013a). Thus, Blachechen *et al.* (2013) described the use of acid chlorides to esterify the surfaces of cellulose nanocrystals. These authors showed that the choice of solvent played a major role in determining the results of the treatment. Trialkoxysilanes are another class of compounds that are commonly applied from organic solvents due to their high reactivity with water. However, as noted by Castellano *et al.* (2004), a trace amount of moisture must be present to convert the siloxane to a reactive silanol intermediate, which can then react with the fiber surface. The grafting of polyolefins is another type of reaction that typically requires the use of solvents; however Kalia *et al.* (2013) noted that microwave-induced grafting can be carried out with less usage of solvent. Alternatively, as shown by Littunen *et al.* (2011), acrylic monomers can be graft copolymerized onto nanofibrillated cellulose in aqueous media with the use of a redox-initiated free radical system. Another way to avoid “solvents” is by applying the reagent in its neat form as the solvent medium (Goodrich and Winter 2009; Hu *et al.* 2011; Khoshkava and Kamal 2013; Ashori *et al.* 2014). Thus, Ashori *et al.* (2014) used full strength acetic anhydride in the presence of pyridine as a catalyst to esterify the surface of cellulose nanofibers. A negative score (“-”) was assigned in this case, for the category of solvent use, due to the use of pyridine.

Vapor-phase treatment, where applicable, appears to be an effective way to address concerns not only about solvents, but also about the use of energy (see next). Examples of molecules that can be effective when applied from the vapor phase include tri-alkoxysilanes (Cunha and Gandini 2010), trichloromethylsilane (Cunha *et al.* 2010b), acid chlorides (Berlioz *et al.* 2009; Fumagalli *et al.* 2013), and alkenylsuccinic anhydride (Zhang *et al.* 2007; Khoshkava and Kamal 2013). The cited work of Zhang *et al.* (2007) was assigned a high score in Table A (see later) in light of the energy-efficiency and effectiveness of the approach used.

As a closely-related approach, surfaces also may be treated by various types of plasma (Vesel and Mozetic 2009; Alf *et al.* 2010). For instance, an oxygen plasma can be expected to increase the hydrophilic nature of cellulosic surfaces (Vesel and Mozetic 2009). Alternatively, the high-energy species present during plasma treatment of a surface can be utilized to initiate free-radical polymerization of organic molecules so that they become grafted to a cellulosic surface (Alf *et al.* 2010).

Avoidance of toxic materials

The category of toxicity, though it partly overlaps the topic of solvents, is especially concerned with the nature of the substances used for treatment. The use of a toxic material for treatment has potential to cause harm both during manufacture and during use of a modified cellulosic product, depending on the details of the treatment. A negative score was assigned by the authors in various cases where the reaction was carried out in the presence of toxic solvents such as pyridine, dichloromethane, or toluene (Goussé *et al.* 2004; Cunha *et al.* 2006, 2007a; Carrales *et al.* 2007). Such assignment is based on a risk of release of the solvent to the air or water, either during the processing or later due to residual solvent left in the treated cellulosic material.

The use of ionic liquids often has been proposed as a potential way to avoid the use of volatile organic solvents. For example, Missoum *et al.* (2012a) used various anhydrides dissolved in ionic liquids as a means of esterifying nanofibrillated cellulose. Positive features of such approaches can include the absence of vapor emission, opportunity to use the system at ATP (ambient conditions), thus displaying low energy demands for the reaction, and the stated ability to recover and reuse almost all of the ionic liquid in many cases. However, depending on the case, the expense and possible toxicity of ionic liquids can be counted as disadvantages.

Minimization of energy use

The energy usage during a manufacturing process is important because non-renewable resources, such as coal or petroleum, often make up a major portion of electrical power. Thus, environmental benefits generally can be achieved by implementing process changes that allow goals to be met with less energy consumption. The energy required to procure a given amount of wood material is about 4 to 15 MJ/kg, which is much lower than many other materials used in manufacturing (Shah 2013). However, substantial additional energy is required to implement many of the surface treatment processes listed in Table A.

Drying is often one of the most energy-intensive steps in the processing of cellulose-based materials. From this perspective, treatments that require immersion in aqueous solutions may involve greater input of energy compared to gas-phase treatments. Let us assume, for instance, that after an aqueous-based treatment the cellulosic material can be filtered and pressed to reduce the water content to just 50%. To evaporate most of the remaining water (achieving a moisture content of 10%), would require input of at least about 1800 MJ/kg of solids (heat of vaporization times the ratio of water to solids).

The need to evaporate water (or other liquid) can be avoided in some cases by carrying out surface modification reactions in the gas phase. For example, vapor-phase modification with a silane coupling agent has been achieved by just heating the dry material briefly to 110 °C (Abdelmouleh *et al.* 2002), a process that avoids the need to overcome the heat capacity of a liquid medium. One should bear in mind, however, that different amounts of energy might be expended in other parts of a life cycle; the authors' ratings in Table A relative to energy are generally limited to the treatment step and subsequent drying of the modified cellulosic surface.

Another factor that tends to increase the amount of energy expended during manufacturing involves the number of separation stages the material must pass through. In other words, if the surface is treated with a solution, then the spent solution after treatment will generally require processing to recover the byproducts and to isolate the solvent for reuse. So a rating of "-" was generally assigned for "minimizes energy use" for those modification approaches that require many treatment steps and separation operations.

Biodegradability

Different chemical treatments can change the biodegradability of cellulosic materials (Simoncic *et al.* 2010). For instance, the acetylation of cellulose makes it more difficult for organisms to break down the material (Puls *et al.* 2011). The cited authors noted that a different set of enzymes may be needed to cleave the acetyl groups before the usual cellulases and other enzymes can degrade the rest of the material. As noted by El Seoud and Heinze (2005), the esters of cellulose can be regarded as among the more biodegradable of the cellulose derivatives. Ly *et al.* (2010) showed that treatment of cellulosic substrates with isocyanate-terminated oligoethers to form corresponding carbamates by reaction with surface –OH groups resulted in a delay in biodegradation. On the basis of the cited articles, surfaces that are lightly treated to form a monolayer or submonolayer bound by ester or ether groups were given a "0" rating in terms of biodegradability, whereas thick layers of synthetic polymers generally were assigned a rating of "-".

Avoidance of waste materials

The generation of waste materials during a manufacturing process can be regarded as undesirable from the standpoint of sustainability (Anastas and Warner 1998). Either the efficiency of each step needs to be high (Matlack 2010), or any byproducts that are generated need to have valuable uses. For example, Lackinger *et al.* (2012) called their hydrophobizing agent "green" partly on account of the high yield of the reaction involved in its preparation. Thus, the high efficiency of reaction was emphasized in several articles dealing with modification of cellulosic surfaces (Lönnberg *et al.* 2006; Nishio 2006; Berlioz *et al.* 2009; Cunha *et al.* 2010b; Li *et al.* 2010b; Koga *et al.* 2011; Littunen *et al.* 2011; Filpponen *et al.* 2012; Fumagalli *et al.* 2013). Negative ratings were assigned to processes listed in Table A that either had low yields or generated low-value byproducts as a result of the treatment.

Minimization of petrochemicals

Chemicals derived from fossil sources, such as petroleum and coal, are essentially non-renewable, at least within a time scale consistent with human activity (Lior 2012). So, rather than deplete this resource, there is an ecological advantage of employing cellulosic materials, which are products of photosynthesis. Thus, the authors applied a "+" score for those processes that avoided the use of petrochemicals altogether. A "0" score was applied to systems that avoided the use of petrochemicals to a major extent.

Recyclability and likelihood or recycling

An unfortunate type of wastage occurs when a manufactured product reaches the end of its usefulness and when its embodied material is not suitable for recycling (Matlack 2010; Cabeza *et al.* 2013). In this regard, the author assigned a "+" rating to processes leading to high recyclability, as in the case of typical paper products (Hubbe *et al.* 2007c). As noted by Mantia and Morreale (2011), the intimate mixing of two components, even if both can be separately regarded as recyclable, can render recycling much more difficult. Another aspect of recyclability involves how common the material is; a pervasive and rather unusual treatment of a cellulosic material would render the treated material as a very unlikely candidate for later recycling after its first use.

Avoiding damage to the cellulosic material

Based on the descriptions of the many different chemical treatments that were considered in the course of preparing this review article, hardly any discussion was found regarding damage to the physical or chemical nature of the cellulosic material. As an exception to this rule, Pasquini *et al.* (2008) reported substantial damage to sugarcane bagasse fibers after treatment with octadecanoyl and dodecanoyl acid chlorides. The degree of polymerization of the cellulose was apparently decreased, leading to a decrease in zero-span tensile strength. The effect was attributed to the release of HCl during the treatment and the consequent acid hydrolysis of the polysaccharides. Accordingly, a negative rating was assigned in cases where treatments involved exposure of the cellulosic material to strong acids or oxidizing agents, *etc.*

Achieving an important change of properties

Regardless of how eco-friendly a surface treatment may be, the treatment cannot be regarded as having been successful unless there was an important change in the surface properties. One might argue that "insignificant change" implies a need to apply additional steps at modification – which can hardly be viewed as being an eco-friendly result. Various advanced grafting procedures offer the inherent advantage of being able to achieve a very wide range of specific chemical functionalities on cellulosic surfaces (Bergenstrahle *et al.* 2008). However, for most common purposes, such as for achieving a hydrophobic surfaces, more eco-friendly approaches such as esterification or even treatment with a cationic surfactant may achieve satisfactory results. Two important categories of "changes of properties" that merit special attention are wettability and superhydrophobicity.

Wettability: Cellulosic materials are generally regarded as being hydrophilic, though in some cases their character is affected by natural waxes, triglycerides, resin acids, as well as lignin, all of which are more hydrophobic than either hemicellulose or cellulose (Heng *et al.* 2007). Wang and Piao (2011) reviewed methods for rendering the surfaces more hydrophobic. Studies aimed at increasing the hydrophobic nature of cellulosic surfaces were carried out by Seto *et al.* (1999), Lindström and Larsson (2008), Bourbonnais and Marchessault (2010), Li *et al.* (2011b), Lackinger *et al.* (2012), Pan *et al.* (2013), Samyn *et al.* (2013), and Ahsori *et al.* (2014). As a further extension of the same theme, studies have been carried out to render cellulosic surfaces resistant to wetting by oils (Bongiovanni *et al.* 2011). Very rarely have studies been carried out with the aim of modifying cellulosic fibers to make them more hydrophilic; such a study was carried out by Henriksson and Gatenholm (2002), who adsorbed xylans onto chemithermomechanical pulp fibers at high temperature and high pH.

Superhydrophobicity: A surface can be regarded as being "superhydrophobic" when droplets of water "bead up" on the surface, having contact angles of 150° or higher (Freire and Gandini 2006; Samyn 2013; Song and Rojas 2013). There have been many reports of treatments achieving superhydrophobic effects on cellulosic surfaces (Andresen *et al.* 2006; Balu *et al.* 2008; Erasmus and Barkhuysen 2009; Li *et al.* 2010a). Based on the articles considered in preparation of this review, it appears that the first essential step taken in most of these studies was to render the surface rough on a nano scale, either by etching (Sahin *et al.* 2002; Balu *et al.* 2008), by deposition of polymeric material (Li *et al.* 2007, 2008; Nyström *et al.* 2009; Obeso *et al.* 2013), or by deposition of nanoparticles (Ogawa *et al.* 2007; Yang and Deng 2008; Xue *et al.* 2008; Bayer *et al.* 2009; Gonçalves *et al.* 2009; Hu *et al.* 2009c; Khalil-Abad and Yazdanshenas 2010; Xu *et al.* 2010; Nypelö *et al.* 2011; Chen and Yan 2012; Shang *et al.* 2012; Wang *et al.* 2012; Liang *et al.* 2013). Alternatively, the hydrophobic material itself may be applied in very fine particulate form (Zhang *et al.* 2007; Cunha and Gandini 2010; Werner *et al.* 2010; Samyn *et al.* 2013; Soboyejo and Oki 2013). The mechanism underlying superhydrophobicity appears to be closely related to that governing contact angle hysteresis (Nurmi *et al.* 2010). In either case, the initial wetting of a dry surface is impeded by the presence of submicroscopic roughness or porosity, coupled with low surface energy. The effect of the low surface energy becomes amplified because of the fact that the wetting liquid may be in contact with more air than solid material due to the very rough morphologies at a nano scale (Song and Rojas 2013; Samyn 2013).

Scoring of Modification Options Relative to Eco-Friendliness

The numerical column towards the right-hand side of Table A presents an overall score based on the criteria just described. Table 2 provides a few selected examples from Table A, showing some of the treatments achieving the highest or the lowest scores.

Table 2. Selected Examples from Table A, Emphasizing Treatments Receiving Very High or Very Low Overall Ratings Relative to Eco-friendliness

Treatment System	Green origin of treatment	Avoids harmful solvents	Avoids toxic materials	Minimizes energy use	Biodegradable	Avoids material waste	Avoids petrochemicals	Product can be recycled	Does not hurt cellulose	Scale-up-friendly	Durable surface changes	Big effect on wettability	Overall score	Citation
Alkylketene dimer	+	+	+	+	0	+	+	+	+	+	+	+	23	Lindström and Larsson 2008
Alkenylsuccinic anhydride	+	+	+	+	0	+	+	+	+	+	+	+	23	Lackinger *et al.* 2012
Crystallizing wax	+	+	+	+	0	+	+	0	+	0	0	++	22	Werner *et al.* 2010
$CaCO_3$ and fatty acid	+	+	+	0	+	0	+	+	+	+	-	++	22	Hu *et al.* 2009c
Esterification	+	+	+	+	0	+	+	+	0	+	+	+	22	Bourbonnais & Marchess 2010
CMC & nano-PCC	+	+	+	+	+	+	+	+	+	+	0	0	22	Nypelö *et al.* 2012
Nano-$CaCO_3$, pectin, ASA	0	+	+	+	0	+	+	+	+	+	0	+	21	Nypelö *et al.* 2011
Cat. surfactant after TEMPO oxidation	0	+	+	+	0	+	+	+	+	+	0	+	21	Alila *et al.* 2007
Triglycerides transesterification	+	+	+	0	0	+	+	0	0	+	+	+	20	Dankovich and Hsieh 2007
Alkenylsuccinic anhydride	-	+	+	+	0	+	0	+	0	+	+	+	19	Zhang *et al.* 2007
PTFE- penetrated	-	-	0	-	-	-	-	-	+	-	0	+	6	Mori *et al.* 2008
Titanate	-	-	-	-	0	-	-	0	0	-	+	0	5	Hill & Abdul Khalil 2000
3D polymer grafting	-	-	-	-	-	-	-	-	0	-	+	+	5	Kuroki *et al.* 2013
Pentafluoro-benzoylation	-	-	-	-	-	-	-	-	0	-	+	+	5	Cunha *et al.* 2007a

In Table 2 each "++" rating (of which very few were assigned) was equated with four points, each "+" was assigned two points, each "0" earned one point, and each "-" received no points. Totals ranged from a low of 5 up to a high of 23. Some of the processes receiving particularly high scores according to this rating system happened to be technologies presently in high-tonnage use within the paper industry. Such instances will be discussed further in subsequent sections dealing with specific modification processes and approaches.

MODIFICATION METHODS

In the subsections that follow, surface modifications involving covalent linkages will be considered first. It makes sense when one is aiming to achieve significant, long-lasting changes to cellulosic surfaces to consider such bonding strategies as esterification, etherification, silanation, urethane formation, and amidation. As an extension of such approaches, grafting methods, in which a polymeric chain is formed on (grafting from) or attached to (grafting to) the surface will be reviewed. This will be followed by discussion of surface treatments that oxidize or otherwise chemically convert, erode, or purify the original material present at a cellulosic surface.

Although chemical reactions at cellulosic surfaces can yield significant, relatively permanent changes to the surfaces, one of the important questions to consider is whether or not corresponding changes can be achieved by less energy-intensive or more eco-friendly routes, with special consideration given to strategies that involve adsorption, nano-scale deposition strategies, rinsing treatments, mechanical treatments, or heating.

Chemical Modifications that Attach Groups

The subject of chemical modification of cellulosic surface by creating linkages such as ester bonds has been reviewed from various perspectives (Hill and Abdul Khalil 2000; Lu *et al.* 2000; George *et al.* 2001; Mohanty *et al.* 2001; Belgacem and Gandini 2005; Freire and Gandini 2006; Cunha and Gandini 2010; Xie *et al.* 2010b; Cheng *et al.* 2012; Kabir *et al.* 2012; Albinante *et al.* 2013; Habibi 2014). A general theme that emerges from the cited work centers on the fact that the hydroxyl groups, which are so prominent at the surfaces of cellulosic materials, allow advantageous transformations. These reactions can be grouped in a number of categories, which are described below.

Esterification

Esterification is a classical approach to coupling hydroxyl groups with carboxylic acid and related chemical species. It is perhaps the most common chemical or biochemical transformation in nature as well as in chemical synthesis. Chemical routes to forming ester bonds with surface hydroxyl groups (mainly associated with cellulose and hemicelluloses) are summarized in Fig. 1. There are many examples in the literature in which such reactions have been implemented (Table A). Although not the first to discover the process, Haskins (1932) received the first patent for the production of cellulose esters, particularly with respect to the production of the acetate product. Its importance cannot be overemphasized because of the ubiquity of cellulose acetate in so many products, ranging from films to dialysis membranes, LCD television screens, toothbrushes, coatings, and composites.

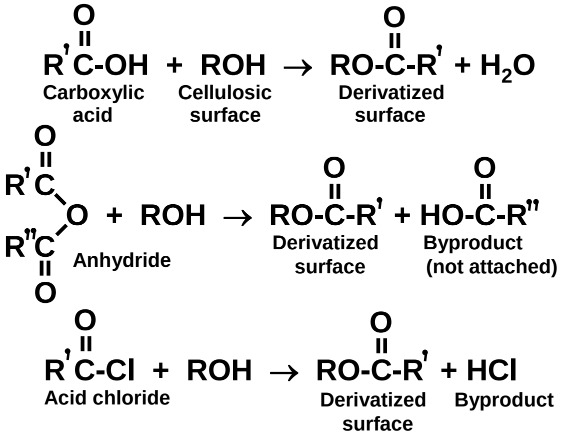


Fig. 1. Common reactions leading to esterification of cellulosic surfaces. The R symbol without primes corresponds to cellulose or hemicellulose. The symbols R' or R'' indicate reagent species.

Carboxylic acids: The most straightforward approach to forming an ester linkage at the cellulosic surface involves the heating of a mixture containing the protonated form of a carboxylic acid (Braun and Dorgan 2009; La Mantia and Morreale 2011; Yang *et al.* 2013). For instance, it is known that the introduction of acetyl groups onto the hydroxyls can be achieved by treatment in glacial acetic acid or other carboxylic acids, followed by heating (La Mantia and Morreale 2011; Yang *et al.* 2013). Using a green chemistry approach (the application of Principle 5 – Reducing use of solvents/auxiliaries), Peydecastaing *et al.* (2006) heated mixtures of cellulose and fatty acids to 195 °C in the absence of solvent; the reaction was catalyzed, and degradation was minimized by carrying out such reactions in the presence of fatty acid salts or small amounts of NaOH. In fact, an efficient gas-phase-based synthetic method was recently developed for surface esterification of cellulosic substrates displaying high crystallinity (Berlioz *et al.* 2009). The reaction was based on gas-phase action of palmitoyl chloride and demonstrated an evolving growth of ester from the shell to the crystalline core. The reaction also can be carried out in the presence of cellulose solvent systems. For instance, work by Vaca-Garcia *et al.* (1998) showed that fatty acids and anhydrides can be used to esterify cellulosic surfaces in the presence of lithium chloride and N,N-dimethylacetamide.

Xue *et al.* (2008) employed 110 °C curing to promote reaction with stearic acid in the presence of silica nanoparticles. Lee *et al.* (2011) and Lee and Bismarck (2012) showed that such surface-specific reactions could be carried out effectively in an equimolar pyridine medium. Braun and Dorgan (2009) hydrolyzed and esterified cellulose to form surface-esterified nanocrystals by treatment with acetic or butyric acid in the presence of hydrochloric acid. Overnight treatment, followed by heating to 105 °C, achieved both liberation of the nanocrystals and the surface modification. Dai and Fan (2013) showed evidence that ester bonds were formed between carboxylate groups on an unsaturated polyester matrix and the –OH groups of cellulose in the course of heating at 80 °C.

Anhydrides for esterification: The relatively intense conditions or catalysts required to promote esterification of carboxylic acids can be regarded as a disadvantage in some cases, for instance during the manufacture of paper or when the treatment conditions result in degradation of the material to be treated. In such cases it can be advantageous to employ the corresponding anhydrides of the carboxylic acids. In principle, anhydrides are formed by heating up two molar units of the source carboxylic acid sufficiently to drive off one molar unit of water. The resulting species are generally more reactive and capable of forming esters at lower temperature compared to the starting carboxylic acid. The greater reactivity can be attributed mainly to entropic considerations (Tafipolsky and Schmid 2007) and the steric (torsional) strain associated with the cyclic anhydride form.

Acetic anhydride has been widely employed as a means of acetylating cellulosic surfaces (Kim *et al.* 2002; Wang *et al.* 2006a; Ifuku *et al.* 2007; Jonoobi *et al.* 2010; Rampinelli *et al.* 2010; Hu *et al.* 2011; Rodionova *et al.* 2011; Yan *et al.* 2013; Ashori *et al.* 2014). As shown by Hu *et al.* 2011, one of the ways to promote the reaction is by use of iodine as a catalyst. Interestingly, Li *et al.* (2009) showed that the reaction could be expedited without the use of a solvent under microwave conditions (with iodine). Jonoobi *et al.* (2010) added pyridine to undiluted acetic anhydride and carried out the reaction at 100 °C. Yan *et al.* (2013) carried out esterification of nanocrystalline cellulose by treatment with acetic anhydride in a phosphoric acid medium. Rampinelli *et al.* (2010) used pure acetic anhydride without catalyst, with a temperature of 120 °C for 10 h. Rodionova *et al.* (2011) carried out the acetylation in a toluene medium at 70 °C. Yuan *et al.* (2005) and Cunha *et al.* (2006) achieved very low values of surface free energy by treating cellulose fibers with an analogous reagent, trifluoroacetic anhydride. Cunha *et al.* (2006) did the reactions from toluene, and both the temperature and time of treatment were varied over wide ranges. The most significant finding of the cited work was that the trifluorinated ester was quite susceptible to hydrolysis upon exposure to water (Cunha *et al.* 2006, 2007b). Yuan *et al.* (2005) employed vapor-phase treatment using the same reagent.

Missoum *et al.* (2012a) carried out esterification of nanofibrillated cellulose with a series of different carboxylic acid anhydrides. An ionic liquid was used as the medium for suspension of the solids and of dissolution of the anhydrides. Similar degrees of substitution (0.2 to 0.3) were found for acetic, butyric, iso-butyric, and hexanoic anhydrides. Sehaqui *et al.* (2014) carried out esterification of cellulose nanofibers from acetone solution; in this work the degree of substitution decreased from about 0.4 to about 0.1 with increasing alkyl chain length in the range from 2 to 16. Oil-repellent surfaces have been achieved by treatment with trifluoroacetic anhydride (Cunha *et al.* 2007b).

Esterification by means of a carboxylic anhydride appears to play a key role in the use of maleated polyolefins, one of the most popular types of coupling agents employed during the compounding of cellulosic-fiber-reinforced plastic composites (Mohanty *et al.* 2001; Park *et al.* 2004; Renneckar *et al.* 2006; Bledski *et al.* 2008; La Mantia and Morreale 2011). One of the uncertainties when using a coupling agent having an anhydride group is whether (a) the anhydride becomes hydrolyzed to a di-acid prior to its use, and (b) whether such a di-acid species revert to an anhydride form, as an intermediate state, in the course of compounding at high temperature (Moad 1999).

The reagent alkenylsuccinic anhydride (ASA), in which the alkenyl group is typically between about 18 and 22 carbons in length, is widely employed for hydrophobic sizing during the manufacture of paper (Hubbe 2007; Nypelö *et al.* 2011; Lackinger *et al.* 2012). Figure 2 shows the reaction of ASA with –OH groups at cellulosic surfaces. The most common way of applying the reagent in those cases is as a cationic-starch-stabilized oil-in-water emulsion. Yuan *et al.* (2006) employed a similar approach for hydrophobic treatment of cellulose nanocrystals. Experience has shown that ASA can almost fully react with a cellulose surface during the ordinary drying of paper, which takes place within minutes at temperatures generally below the boiling point of water. Studies have shown that ASA can be applied by heating the reagent sufficiently to induce vapor-phase transfer to the cellulosic surface (Zhang *et al.* 2007; Cunha and Gandini 2010). Khoshkava and Kamal (2013) likewise heated ASA to 145 °C as a means of treating a dry pellet of cellulose nanocrystals by vapor-phase transfer and esterification.

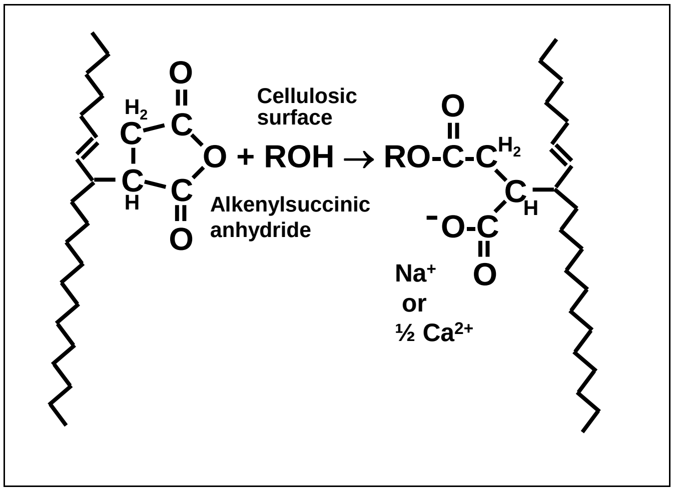


Fig. 2. Reaction of alkenylsuccinic anhydride (ASA) with the –OH groups of cellulosic surfaces

Regarding efforts to minimize environmental impacts, an honorable mention can be accorded to the work of Lackinger *et al.* (2012). Whereas the ASA products most often used in papermaking are derived from petroleum products, the cited authors used mono-unsaturated fatty acids from vegetable oil as their starting material. According to Table A, an overall score of 23 was assigned, matching the outstanding score assigned for treatment of papermaking furnish with alkylketene dimer (see next subsection).

To provide perspective, some of the lowest scores in Table A were assigned for work related to similar reactions as just discussed, but with other substituent groups (Cunha 2006, 2007a). The different outcome, in terms of the environment-oriented rating system used here, can be partly attributed to the use of a highly fluorinated reagent, thus rendering the modified surface less suitable for recycling (see earlier discussion). Also, the treatment employed solvents, toxic materials, and multiple processing steps. On the other hand, some similar treatments have been shown to result in labile structures that are susceptible to biodegradation (Cunha 2007b). Such modified materials may be suitable for recycling of the fibers.

Most of the aforementioned articles were concerned with treatments that rendered the cellulosic surfaces more hydrophobic. Stendstad *et al.* (2008) found that the opposite effect could be achieved by reacting cellulosic surfaces with unsubstituted maleic or succinic anhydrides. Likewise, Hubbe *et al.* (1999) showed that treatment of cellulosic fibers with maleic anhydride in the dry phase within an optimum temperature range rendered the carboxylated fibers more capable of inter-fiber bonding during preparation of paper, leading to higher dry-strength characteristics.

Alkylketene dimer: Though the detailed chemistry is different, alkylketene dimer (AKD) can be regarded as being similar to an anhydride in many respects (Hubbe 2007; Lindström and Larsson 2008; Cunha and Gandini 2010). Like an anhydride, AKD can react with –OH groups when suitably heated. But unlike ASA, AKD cannot be used effectively for vapor-phase treatment (Zhang *et al.* 2007; Lindström and Larsson 2008) due to its chemical instability on heating. An attractive feature of AKD is that the main raw material use in its production is a fatty acid, a relatively low-cost, renewable material.

AKD has been considered in various studies as a way to modify cellulosic surface properties (Werner *et al.* 2010). The most prominent use of AKD is in the preparation of water-resistant paper. For example, most milk cartons are made with AKD treatment. No extra energy is expended during the AKD curing, since the reaction takes place during the usual drying of the paper. AKD also has been used to hydrophobize nanocellulose. Missoum *et al.* (2013b) employed emulsified AKD to treat nanofibrillated cellulose; the resulting nano-paper sheets were dried at 80 °C, which apparently was sufficient to cure the AKD. Benkaddour *et al.* (2014) found that AKD could be used to derivatize cellulose even after TEMPO-mediated oxidation (see later sections), a treatment that results in extensive formation of aldehyde and/or carboxylate groups on the cellulosic surface.

Acid chlorides for ester formation: To go one step further to render carboxylic acid species reactive towards –OH groups for the formation of ester bonds, one may first convert them to the corresponding acid chlorides (Belgacem and Gandini 2005). Treatment with tosyl chloride provides a convenient way to convert the carboxylic acid (Freire *et al.* 2006; Dankovich and Hsieh 2007). Uschanov *et al.* (2011) used the alternative approach of treating the cellulosic materials with a mixture of 4-toluenesulfonyl chloride and fatty acid. As a general rule, the acid chlorides are more reactive even than the corresponding anhydrides. The downside is that HCl is formed in the course of the reaction with cellulosic materials, and the resulting acidic conditions can be damaging to the material in some cases. Thus, Pasquini *et al.* (2008) found a substantial drop in degree of polymerization of microcrystalline cellulose after treatment with octadecanoyl or dodecanoyl chloride.

Organic solvent systems have been used most often in published work concerning acid chloride esterification of cellulosic surfaces. Mukherjee *et al.* (2013) used acetoyl chloride in such a system. Pasquini *et al.* (2008) used refluxing in a toluene solution of the long-chain alkanoyl chlorides. Blachechen *et al.* (2013) used methyl adipoyl chloride in different non-aqueous solvents to modify the surface of cellulose nanocrystals. Freire *et al.* (2006) observed a greater degree of substitution when using a solvent having greater swelling ability for the cellulose. Corrales *et al.* (2007) applied oleoyl chloride to jute fibers from swelling solvents and non-swelling solvents. Again, a higher degree of reaction was found in the case of a swelling solvent (pyridine), which is consistent with greater accessibility to the esterifying reagent. Dixon *et al.* (1979) found that phenoxyacetyl esters were more stable to hydrolysis compared to esters formed from more water-soluble reagents. Acylation of cellulose was pursued by Barthel and Heinze (2006) in ionic liquids. Ionic liquids (ILs), *viz.*, 1-N-butyl-3-methylimidazolium chloride ([C4mim]+Cl−), 1-N-ethyl-3-methylimidazolium chloride ([C2mim]+Cl−), 1-N-butyldimethylimidazolium chloride ([C4dmim]+Cl−), and 1-N-allyl-2,3-dimethylimidazolium bromide ([Admim]+Br−), were the solvents for a homogeneous acylation of cellulose. Cellulose acetates with a degree of substitution from 2.5 to 3.0 were obtained within 2 h at 80 °C.

Gas-phase treatment has been used in several studies involving acid chloride treatment of cellulosic materials (Berlioz *et al.* 2009; Fumagalli *et al.* 2013). The surface-specific nature of the resulting esterification was established (Berlioz *et al.* 2009). Fumagalli *et al.* (2013) judged the vapor-phase treatment to be superior to the use of solvent systems to hydrophobize aerogels formed from cellulose nanocrystals. Comparable accessibility and reactivity were observed, and the use of solvent could be avoided.

Acid chlorides have also been used as a way to achieve oil-resistant properties of cellulosic surfaces. Cunha *et al.* (2007a) used pentafluorobenzoylation to esterify bacterial cellulose, while the same strategy was employed by Salam *et al.* (2015) to impart both hydrophobic and oleophobic characteristics to cellulose nanocrystals.

Transesterification: Another potentially advantageous route to the esterification of cellulosic surfaces is to employ a suitable ester as the reagent (Cunha and Gandini 2010). For example, one can use triglycerides of fatty acids, *i.e.* vegetable oils (Dankovich and Hsieh 2007). A treatment temperature of 110 to 120 °C was found to be sufficient. The cited work received a high score of 20 in Table A, since durable effects were achieved just by heating of the natural products. Dong *et al.* (2013) heated an ethanolic mixture of soybean oil and microcrystalline cellulose to 100 °C. The treated MCC continued to show the same degree of crystallinity, but it was rendered highly compatible with low-polarity solvents.

Azetidinium, wet-strength chemistry: Esterification also can be achieved by treatment with reagents or copolymers containing azetidinium groups; this is an approach that is widely used in papermaking for the development of wet-strength character (Holik 2013). However, unlike the other esterification systems considered thus far, this approach has potential to form esters with carboxylic acid groups at the cellulosic surface (Hagiopol and Johnston 2012; Holik 2013). Ahola *et al.* (2008a) studied the adsorption of such reagents onto cellulose nanofibrils, using a quartz crystal microbalance. A potential advantage of using azetidinium-type chemistry for cellulose surface modification is that the reaction can be achieved during ordinary conditions of drying, *e.g.* at a temperature near to the boiling point of water. A disadvantage, at least in some cases, is that the cellulosic surface may need to be oxidized before the esterification in order to achieve a satisfactory degree of substitution.

Etherification

Etherification of cellulosic surfaces can be achieved under highly alkaline conditions by treatment with suitable organic epoxides or chlorides (Belgacem and Gandini 2005; Habibi 2014). One of the most important applications of such reactions, from the standpoint of paper manufacture, is in the preparation of cationic starch products, which are often used as dry-strength additives (Roberts 1991). The same type of reaction has been used to cationically treat cellulose (Hubbe *et al.* 2007a; Hasani *et al.* 2008; Ho *et al.* 2011; Zaman *et al.* 2012; Soboyejo and Oki 2013). The main reactions are shown in Fig. 3. Similarly, cationic cellulose surfaces can be achieved by treatments involving epihalohydrins (Patiño *et al.* 2011). By treatment with propylene oxide, it is possible to hydroxyethylate or hydroxypropylate the cellulose surface (Wang *et al.* 2006a). Etherification also can be used for cross-linking of cellulosic materials, for instance as a means of modifying the behavior of cotton-based textiles (Ibrahim *et al.* 2013a). Another variant is cyanoethylation, using acrylonitrile under alkaline conditions (Mohanty *et al.* 2001).

Etherification also has been used as a means of attaching alkyne groups to cellulosic surfaces, thus preparing the surface to accept a wide variety of tailor-made functions groups *via* "click chemistry" (see Click Chemistry subsection) (Pahimanolis *et al.* 2011; Mangiante *et al.* 2013). An exciting recent development (Fox *et al.* 2011) opens the window to control regioselectivity of etherification as well as esterification for cellulose.

This work clearly demonstrated that simple solvent systems allowed for precise regioselective substituent reactions.

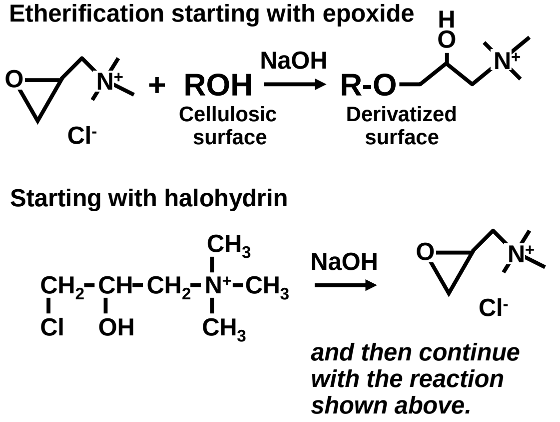


Fig. 3. Examples of etherification reaction (to impart cationic charge) starting with epoxide (scheme from Hasani *et al.* 2008) or from the halohydrin (scheme from Patiño *et al.* 2011)

By treatment of cellulose with monochloroacetic acid one can carboxymethylate the surface of cellulose, thus increasing the inter-fiber bonding potential in the preparation of paper (Gandini and Pasquini 2012). Carboxymethylation of nanocelluloses is a useful approach to achieving a higher negative charge, as well as high dispersability in water (Lundqvist and Ödberg 1997; Laine *et al.* 2003; Habibi 2014). As an alternative, carboxymethylcellulose (CMC) can be adsorbed onto cellulosic surfaces (Laine *et al.* 2000; Nypelö *et al.* 2012)

Li *et al.* (2010b) employed the unusual approach of preparing a copolymer of poly-(lactic acid) and gylcidyl methacrylate having terminal epoxy groups and then reacting this with bacterial cellulose by drying from a xylene solution at room temperature and then curing at 105 °C for 2 h. A high degree of hydrophobicity was achieved by this "grafting onto" treatment.

Silanization

Silane treatment is a popular approach used for modifying cellulosic material, especially in regards to the reinforcement of composites (Cunha and Gandini 2010; Wang and Piao 2011). Figure 4 shows the main reactions involved in the most widely used type of treatment, which starts with the hydrolysis of a trialkoxysilane compound (Xie *et al.* 2010b). Although the reaction clearly requires some water in order to generate the reactive hydrolyzed species, there is often sufficient moisture either in the air or in the substrate to be treated. Thus, the reactions are commonly carried out either in a non-aqueous solvent or in air.

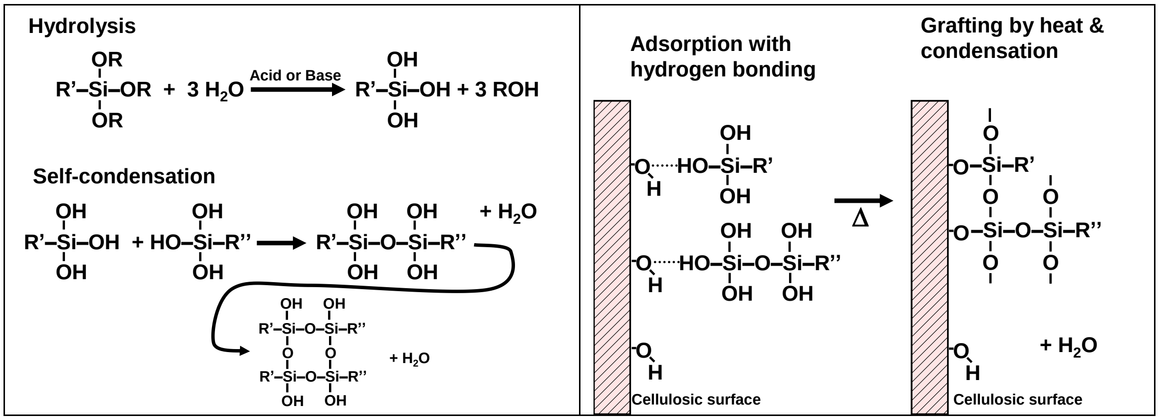
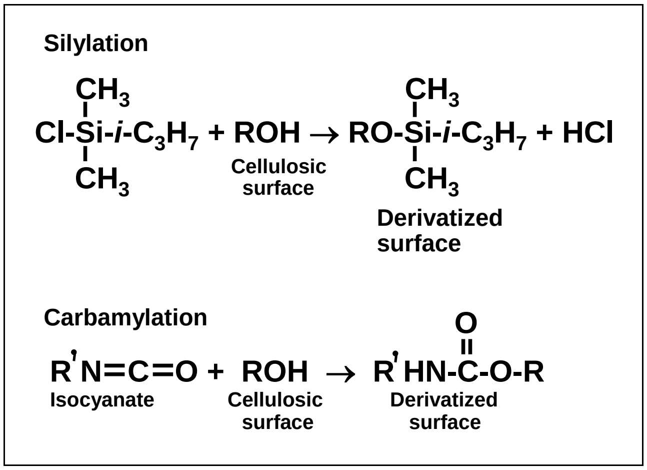


Fig. 4. Silane treatment scheme based on hydrolysis of a trialkoxysilane, followed by possible initial condensation (left), hydrogen bonding with a cellulosic surface (right), and subsequent curing (right). Figure concept based on Xie *et al.* (2010b).

An alternative reaction scheme, based on a chlorosilane species, is shown in Fig. 5 (Andresen *et al.* 2006). The following articles provide background regarding silane-based coupling agents that are designed to react with the surface of cellulosic material and to provide functional groups or extended chains that are compatible with the matrix polymer under consideration (Maldas *et al.* 1988; Valadez-Gonzalez *et al.* 1999; Hill and Abdul Khalil 2000; Abdelmouleh *et al.* 2002; Pickering *et al.* 2003; Park *et al.* 2004; Renneckar *et al.* 2006; Lu *et al.* 2008; Ly *et al.* 2009; Xie *et al.* 2010b; La Mantia and Morreale 2011; Qu *et al.* 2012; Zhang *et al.* 2012; Taipina *et al.* 2013).



$$Cl\text{-}Si(CH_3)_2\text{-}i\text{-}C_3H_7 + ROH \rightarrow RO\text{-}Si(CH_3)_2\text{-}i\text{-}C_3H_7 + HCl$$

$$R'N{=}C{=}O + ROH \rightarrow R'HN\text{-}C({=}O)\text{-}O\text{-}R$$

Fig. 5. Top: Reaction during treatment of a cellulosic surface with a substituted chlorosilane derivative and related reagents in the absence of water; scheme based on Andresen *et al.* (2006). Bottom: Carbamylation reaction of isocyanates to form urethanes at surfaces having –OH groups, based on scheme from George *et al.* (2001)

Examples of silane treatments can be cited. Goussé *et al.* (2004) silylated cellulose microfibrils and observed their rheological properties in methyl oleate systems. Koga *et al.* (2011) used a silane compound to decorate cellulosic surfaces with amine groups. Rouabhia *et al.* (2014) used aminosilane treatment as the first step in preparing antibacterial surfaces. The peptides arginine, glycine, aspartic acid, and cysteine were grafted onto the 3-aminopropyltriethoxysilane, which was then reacted with bacterial cellulose. Boufi *et* *al.* (2008) employed silanization as an intermediate step in the preparation of ultra-thin cellulose films that had been functionalized with porphyrin groups. The silylated cellulose was spin-coated from a tetrahydrofuran solution, followed by evaporation of the solvent. The cellulose was then regenerated by hydrolysis of the silane groups. Thus, depending on what is attached to the other end of a triethoxysilane (or related chemical), a wide variety of functional groups can be attached to a cellulosic surface.

Silanization also has been used as a final step in the preparation of superhydrophobic or highly hydrophobic cellulose-based surfaces (Navarro *et al.* 2003; Andresen *et al.* 2006; Li *et al.* 2007, 2008; Ogawa *et al.* 2007; Balu *et al.* 2008; Gonçalves *et al.* 2008, 2009; Tomšič *et al.* 2008; Yang and Deng 2008; Bayer *et al.* 2009; Erasmus and Barkhuysen 2009; Cunha *et al.* 2010a,b; Li *et al.* 2010a; Xu *et al.* 2010; Jin *et al.* 2012a; Wang *et al.* 2012; Liang *et al.* 2013). Such treatments will be considered in a later section dealing with the deposition of nanoparticles.

The question of when and to what extent silane coupling agents actually react with the cellulosic surfaces has been examined in several studies. According to Castellano *et al.* (2004) the trialkoxysilane species does not itself react with the hydroxyl groups of cellulose, even at high temperature. Rather, it condenses only with phenolic groups, such as those of lignin. Reactivity toward cellulosic surfaces is induced by partial hydrolysis of the siloxane moieties. The idea of silanizing cellulosic nanocrystals was recently successfully demonstrated within the context of nanofiller technology (Raquez *et al.* 2012). In this effort, surface functionalization was investigated using methacryloxy-based trialkoxysilane treatment of the nanocrystals, which were then successfully incorporated into poly-lactic acid by melt extrusion without the need of any solvent or loss of any of the physical or chemical characteristics of the nanocrystals.

Isocyanates: Carbamylation (urethane)

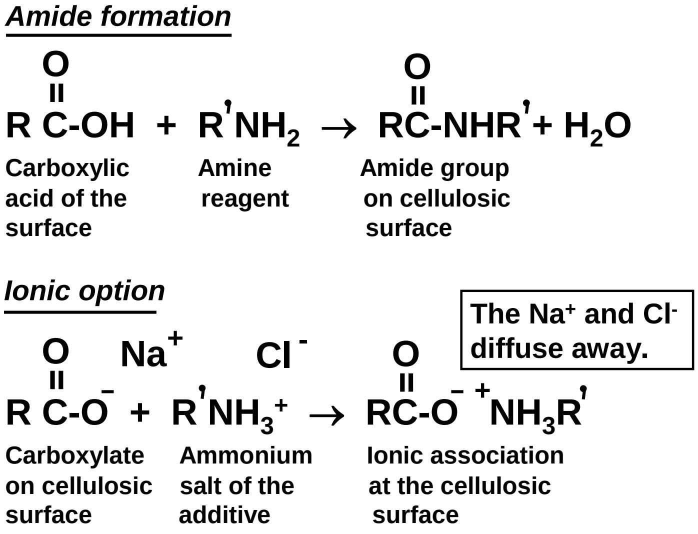
The isocyanate group is another highly reactive function that can be employed to create covalent linkages with the –OH groups of cellulosic surfaces under relatively mild conditions (George *et al.* 2001; Mohanty *et al.* 2001; Renneckar *et al.* 2006; La Mantia and Morreale 2011; Dufresne and Belgacem 2013; Habibi 2014). The reaction is generally carried out in an organic solvent such as toluene, and dibutyl dilaurate can be used as a catalyst (La Mantia and Morreale 2011). The main reaction is shown in Fig. 5 (bottom scheme). Missoum *et al.* (2012b) showed that although the reaction took place mainly at the surface of nanofibrillated cellulose, there was also some degree of reaction in the bulk phase of the material, which is not surprising given the fact that cellulose nanocrystals are known to have differing surface reactivities and morphologies as a result of how they are processed prior to surface grafting (Tian *et al.* 2014).

Isocyanate-based coupling agents including toluene di-isocyanate (TDI) are often used to promote good adhesion within cellulose fiber-plastic composites (Maldas *et al.* 1988; Lee and Wang 2006; Shang *et al.* 2013). Lee and Wang (2006) employed lysine-based diisocyanate (LDI) to render bamboo fibers more compatible with poly-(lactic acid) (PLA). Shang *et al.* (2013) used isocyanate-terminated castor oil (a vegetable oil derivative) to modify cellulose nanocrystals. Similar work was reported by Taipina *et al.* (2013), who verified that the reaction occurred mainly on the cellulose crystal surfaces. Siqueira *et al.* (2010) likewise treated sisal fibers with *n*-octadecyl isocyanate. The reaction was carried out at 110 °C in a toluene medium, followed by rinsing to remove the amine formed in the reaction.

Because of their high reactivity, isocyanates are sometimes preferred as a route to achieve polymer grafting onto or from cellulosic surfaces (Dufresne and Belgacem 2013). Yu and Qin (2014) grafted 3-hydroxybutyrate-co-3-hydroxyvalerate onto cellulose nanocrystals by an acylation reaction with N,N-dimethyl formamide (DMF). Toluene diisocyanate (TDI) served as the coupling agent, and dibutyltin dilaurate was used as a catalyst. Gregorova *et al.* (2009) used isocyanate treatment in a different way to promote compatibility with silane-treated cellulosic fibers. Rather than treat the cellulosic component, they used 4,4-methylene diphenyl diisocyanate to treat the poly(lactic acid) matrix.

Amidation (after oxidation)

Cellulosic surfaces that are rich in carboxylic acid groups have the potential to react with amine functions, thereby forming amide linkages (Habibi 2014). The main reaction is shown in Fig. 6 (top part). The reaction is not unlike esterification except that amide linkages are universally recognized as being less susceptible to hydrolysis.



$$\mathrm{R\overset{O}{\overset{\|}{C}}\text{-}OH + R'NH_2 \rightarrow R\overset{O}{\overset{\|}{C}}\text{-}NHR' + H_2O}$$

$$\mathrm{R\overset{O}{\overset{\|}{C}}\text{-}O^- + R'NH_3^+ \rightarrow R\overset{O}{\overset{\|}{C}}\text{-}O^-\,{}^+NH_3R'}$$

Fig. 6. Reaction of carboxylic acid and amine to form an amide

Benkaddour *et al.* (2014) reacted stearylamine with the carboxylated surface of a cellulose gel using carbodiimide as catalyst and hydroxysuccimide as the amidation agent. Johnson *et al.* (2011) employed octadecylamine to modify the surface of oxidized cellulose nanocrystals. These authors compared two different approaches: the covalent amidation reaction *vs.* charge-induced association between a cationic amine function and an anionic carboxylate function. The latter option is represented by the lower part of Fig. 6. The amidation reaction was carried out in dimethylformamide (DMF) at 50 °C for 4 h. Both strategies led to comparable hydrophobization, and the cellulose crystal structure was not adversely affected by either approach. Yang *et al.* (2014) treated cellulose nanofiber composite membranes with N-hydroxysuccinimide, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride, and cysteine in aqueous solution at room temperature for 24 h to achieve amidation. Sadeghifar *et al.* (2011) employed a related approach to decorate cellulose nanocrystals with alkyne groups as a preparatory step for subsequent "click chemistry".

In a related chemical approach, Boufi *et al.* (2011) used N,N'-carbonyldiimidazole (CDI) in an ionic liquid solution of cellulose to convert the –OH groups to a reactive form suitable for amidation with various species having multiple amine functions, *e.g.* diaminobutane. In this manner, amine groups were established on the resulting cellulosic films. The amine-functionalized cellulose served as a suitable platform for *in-situ* formation of gold nanoparticles.

Other

Titanates have been mentioned as a potentially important means of modifying cellulosic surfaces (Liao *et al.* 1997; Hill *et al.* 2000; Lu *et al.* 2008). Such treatments have been found effective for converting hydrophilic cellulosic surfaces, making them more hydrophobic, and improving their compatibility with various plastic matrix materials. Chen *et al.* (2010) used NaOH to catalyze reaction of acrylonitrile with the surface –OH groups of cellulose. Benzylation of cellulosic surfaces can be brought about by reaction of benzyl chloride in a 10% NaOH medium (La Mantia and Morreale 2011). An approach related to melamine wet-strength treatment (Landes and Maxwell 1945) has been used by Xie *et al.* (2010a) as a means to imparting shape memory behavior to fabrics. As is the case for this type of wet-strength treatment, it is not certain whether or not such treatment involves covalent reaction with the cellulosic material. Rather, it is likely that the effects can be attributed at least partly to a cross-linking effect within the resin.

Polymer Grafting

The word "grafting" will be used here to emphasize the covalent attachment or unit-by-unit polymerization of an oligomeric or polymeric chain connected to the cellulosic surface. In general, two broad approaches have been well documented in the literature (Carlmark 2013; Kalia *et al.* 2013): "grafting from" and "grafting to." The grafting of a polymer to a surface is colorfully described as resulting in brushes attached to a solid surface, and it is a very versatile tool for surface functionalization. Both grafting to and grafting from processes result in a thin polymer brush layer on the solid surface. The general topic has been the subject of several reviews (Bhattacharya and Misra 2004; Belgacem and Gandini 2005; Freire and Gandini 2006; Nishio 2006; Dufresne 2011; Kalia *et al.* 2013; Missoum *et al.* 2013a; Samyn 2013; Habibi 2014). Addition-type polymers can be generated by free-radical initiation, using such approaches as redox initiators, ultraviolet light, microwave energy, and plasma generation of free radicals. Recently there has been a great deal of attention given to controlled radical polymerizations (Hansson *et al.* 2009), which allow efficient and well-controlled attachment of a great variety of functional groups under relatively mild non-aqueous conditions. To complete the picture, enzymatic systems also have become increasingly considered as a way to graft polymeric groups onto cellulosic surfaces (Kudanga *et al.* 2011; Saastamoinen *et al.* 2012; Garcia-Ubasart *et al.* 2013; Cusola *et al.* 2014).

Grafting to, from

In general, the "grafting from" approach tends to result in a denser population of attached chains, consistent with a relatively easy accessibility of the surface to monomeric reagent molecules (Harrisson *et al.* 2011). Though steric and kinetic constraints may limit "grafting to" strategies, a potential advantage is that the molecular mass distribution or other factors concerning the chains can be determined before the reaction with the surface. For example, Paquet *et al.* (2010) were able to graft polycaprolactone chains having different molecular weights onto cellulose; they used phenyl isocyanate to block one end of the chain, then they used 2,4-toluene diisocyanate to connect the other end to an –OH group at the surface of microcrystalline cellulose.

Vinyl grafting

Vinyl grafting involves polymers formed by unsaturated –C=C– groups. For instance, Liao *et al.* (1997) grafted wood fibers with acrylonitrile to improve their compatibility with a polyethylene matrix. Grafting of such substances at cellulosic surfaces has been initiated in a variety of ways, as will be described in the subsections that follow.

Free-radical induced: One of the most straightforward means of starting a chain reaction involving compounds having –C=C– double bonds or rings is to add a monomeric species having an odd electron, *i.e.* a free radical (Moad 2006). For instance, Mori *et al.* (2008) employed perfluorinated benzoyl peroxide as an initiator for polymerization of tetrafluoroethylene in a supercritical fluoroform medium. Notably, the approach used in the cited work received a low score in Table A. This is partly a reflection of the use of toxic materials and solvents, plus the generation of a relatively thick layer of non-biodegradable, non-recyclable polytetrafluoroethylene.

Redox systems: Some widely used initiator systems fall under the category of redox systems (Sarac 1999). For example, Littunen *et al.* (2011) used cerium ammonium nitrate as an initiator for graft polymerization of acrylonitrile onto nanofibrillated cellulose. Singha and Rana (2012) likewise used the same redox system to induce polymerization of acrylonitrile onto *Cannabis indica* fiber. Stenstad *et al.* (2008) employed cerium (IV) to pretreat microfibrillated cellulose as a precondition for grafting with glycidyl methacrylate. Mohanty *et al.* (2001) recommended the use of a $CuSO_4$-$NaIO_4$ initiator system in order to minimize degradation of the cellulosic substrate. Such a system was used by Ghosh and Ganguly (1994) to graft polyacrylonitrile from jute fibers. Thackur *et al.* (2013a,b) used free-radical initiation to induce grafting of methyl acrylate or butyl acrylate polymer chains from cellulose.

The Fenton oxidative system (iron ionic species Fe^{3+} and Fe^{2+} in combination with free radicals ·OH and ·OOH) has been used to initiate grafting from cellulosic surfaces (Liu *et al.* 2010b; Kalia *et al.* 2013). Liu *et al.* (2010b) used such an approach to form guaiacol oligomers that were uniformly self-assembled as nanoparticles on the surface of cellulose fibers. Kalia and Vashistha (2012) used the same system to induce grafting of methyl methacrylate onto sisal fibers.

Photo-induced: Light-induced activation is another way to promote vinyl grafting (Bhattacharya and Misra 2004; Kalia *et al.* 2013). A particular attraction of this technique is its inherent selectivity in activating specific chemical reactions to the exclusion of others; however, most studies have simply used photoinitiated radical-induced reactions, which do not display any inherent selectivity relative to thermal or chemical reactions. For example, Woo *et al.* (2006) employed UV light and photoinitiators to induce polymerization of methyl methacrylate in a multilayered assembly of cellulose derivatives. Bongiovanni *et al.* (2011) used ultraviolet light to induce grafting of a highly fluorinated acrylic monomer onto cellulose sheets. The outermost treated surface was found to have a composition corresponding to the pure monomer.

Gamma irradiation also can be used to initiate polymerization (Kalia *et al.* 2013). Lacroix *et al.* (2014) showed that such an approach could be used to prepare biodegradable films with a wide range of composition.

Microwave-induced: Microwave treatment is said to provide a means of inducing homogenous polymerization in the absence of solvents (Kalia *et al.* 2013). It can be considered a type of radiation-based mechanical refinement because of its inherent ability for exciting water molecules to high vibrational energies. Thus, Kalia and Vashitha (2012) employed microwave irradiation to induce grafting of methylmethacrylate onto sisal fibers. Microwave energy also can be used with certain controlled radical polymerization schemes to be discussed later (Lin *et al.* 2009).

Plasma-induced: A plasma can be defined as a high-energy gas-like mixture that contains ionic or radical species, usually as a mixture that is rich in neutral, non-radical species. Plasmas can be generated by electrical discharge between electrodes. For most practical treatments, “cold plasma” conditions are used (Gaiolas *et al.* 2009; Cunha and Gandini 2010; Song *et al.* 2013), meaning that only a small proportion of the molecules are ionized. Depending on the nature of the medium subjected to plasma creation, the resulting reactions with cellulosic surfaces can give rise to either hydrophobic or hydrophilic conditions of the surface (Samyn 2013). For instance, Graupner *et al.* (2013) employed mixtures of ammonia and ethylene as input for plasma treatment of Lyocell regenerated cellulose fibers; the treated fibers had much stronger adhesion to a polylactic acid matrix when formed into a composite.

When cellulosic surfaces are exposed to plasmas in the presence of unsaturated or ring-form organic compounds, polymerization can be induced either from the cellulosic surfaces or in the bulk. Kong *et al.* (1992) used plasma treatment to induce polymerization of octafluorocyclobutane. Conditions were adjusted to be as mild as practical to avoid damage to a cellulosic membrane material. Samanta *et al.* (2012) treated rayon fabric with an atmospheric pressure glow plasma of He and 1,3-butadiene and achieved a high level of hydrophobicity. Song *et al.* (2013) hydrophobized paper surfaces by exposure to cold plasma formed from butyl acrylate and 2-ethyl-hexyl acrylate. Gaiolas *et al.* (2009) used a green chemistry approach in which the natural oil compounds myrcene and limonene were subjected to cold plasma conditions and used to hydrophobize paper surfaces.

Highly hydrophobic effects can be achieved when using fluorochemicals as a component in plasma treatment (Balu *et al.* 2008). Sahin *et al.* (2002) and Sahin (2007) used a CF_4 plasma to induce surface fluorination of paper. In contrast to various other reports of plasma treatments, the fluorination appeared to be rather evenly distributed on both sides of the paper. Similarly, Mirvakili *et al.* (2013) used treatment with a fluorocarbon plasma to induce highly hydrophobic character to paper-like samples. Navarro *et al.* (2003) used radio-frequency plasma treatment to enhance treatment of sisal paper surfaces with fluorotrimethylsilane. Zhang *et al.* (2003) treated a cotton fabric surface with a fluorocarbon plasma, which manifested itself as a nanoparticulate hydrophobic film. Siro *et al.* (2013) were able to adjust the extent of hydrophobic character by adjusting the gas ratio of CF_4 and O_2 in plasma treatment of cellulose films.

Controlled radical polymerization

The subject of controlled radical polymerization has been reviewed recently by several groups (Hansson *et al.* 2009; Tizzotti *et al.* 2010; Carlmark *et al.* 2012; Carlmark 2013). Such reaction schemes are characterized by providing a reaction pathway in which the growing polymer chain can remain in a dormant, but still triggerable state. Such an approach has been shown to be effective in the preparation of grafted surfaces with a large range of molecular mass and grafting density of the attached chains. The major reaction schemes, which have become known by their acronyms ATRP, RAFT, ROP, and ROMP, are summarized below with reference to the grafting of polymer chains from cellulosic surfaces (Figs. 7 and 8). Such polymerization schemes tend to be highly favored in the polymer community because they display "living" characteristics. Living polymerization is a type of chain growth polymerization in which the capacity of a growing polymer chain to self-terminate is avoided. The polymer chain propagates at a much more constant rate than observed in traditional chain polymerization; moreover, the chain lengths are very similar (low polydispersity indices). It is a currently popular method for synthesizing block copolymers because they can be synthesized in stages. Each stage has a different monomer with an overall polymer displaying predetermined molar mass and control over end groups. Living polymerization techniques tend to achieve a high degree of control over polymer chain architecture. Examples of the type of polymers that can be synthesized include block copolymers, comb-shaped polymers, multi-armed polymers, ladder polymers, and cyclic polymers. This control of structure, in turn, results in polymers with widely diverse physical properties, even though they are made from readily available low-cost monomers.

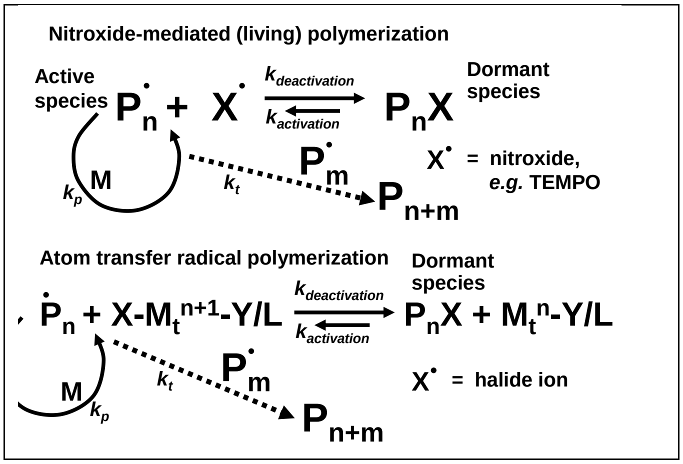


Fig. 7. Reaction schemes for the "living" polymerizations: nitroxide-mediated polymerization (NMP) and atom transfer radical polymerization (ATRP). Schemes shown as reported by Tizzotti *et al.* (2010).

ATRP: Atom transfer radical polymerization (ATRP) can be regarded as a "living" polymerization scheme in which free radical sites can be generated on dormant ends of polymer chains (Braunecker and Matyjaszewski 2007; Malmström and Carlmark 2012; Kalia *et al.* 2013). As in the work reported by Morandi *et al.* (2009) and Morsi *et al.* (2011), ATRP can be induced by treating a cellulosic surface with 2-bromoisobutyryl bromide. Then an unsaturated monomer can be polymerized in the presence of a CuBr/ N,N,N',N',N"-pentamethyldiethylenetriamine catalyst system and a sacrificial initiator (Morandi *et al.* 2009). Singh *et al.* (2008) used ATRP to grow copolymer chains of ethylene glycol and methacrylate from cellulose ultrafiltration membranes; the treated membranes were resistant to fouling. Wandera *et al.* (2011, 2012) likewise used ATRP as a means of preparing block copolymer layers on cellulose ultrafiltration membranes. Yu *et al.* (2014a) used ATRP to prepare hydrophobic bamboo flour. In further work by the same authors, ATRP was used to graft rosin-derived chains from ethylcellulose in solution. An ATRP system was used with perfluorinated monomers to prepare superhydrophobic cellulosic surfaces (Nyström *et al.* 2009). Zhou *et al.* (2005, 2007) showed that ATRP could be used to derivatize xyloglucan polymers, which then could be used to modify cellulosic surfaces by their adsorption. Hansson *et al.* (2009) introduced the term “activators regenerated by electron transfer” (ARGET) for ATRP carried out in the presence of a sacrificial initiator. Both grafting from the surface and propagation of polymers in the free solution were quantified.

Cellulose nanocrystals were functionalized with thermoresponsive poly(N-isopropylacrylamide) brushes via surface-initiated single-electron transfer living radical polymerization under various conditions at room temperature to prepare stimuli-responsive cellulose nanomaterials (Zoppe *et al.* 2010, 2011). Similarly, bioactive films based on cellulose nanofibrils were produced by conjugation of a short peptide onto a hydrophilic copolymer, poly(2-aminoethyl methacrylate hydrochloride-co-2-hydroxyethylmeth-acrylate) (poly(AMA-co-HEMA)), that was grafted on cellulose via surface initiated polymerization from an initiator coupled to the cellulosic substrate (Zhang *et al.* 2013).

RAFT: Reversible addition fragmentation chain-transfer (RAFT) can be regarded as another version of living polymer grafting in which the –OH groups at the fiber surfaces can be reacted with 2-chloro-2-phenylacetyl chloride (CPAC), which then can be converted to S-methoxycarbonylphenylmethyl dithiobenzoate, which is a known RAFT group (Favier and Charreyre 2006; Roy 2006; Malmström and Carlmark 2012). Figure 8 shows a reaction scheme (Tizzotti *et al.* 2010).

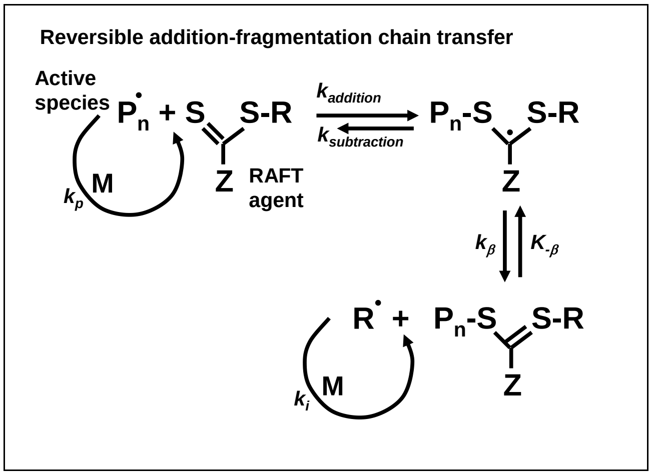


Fig. 8. Reaction scheme for reversible addition-fragmentation chain transfer (RAFT), as reported by Tizzotti *et al.* (2010)

As has been noted by Roy (2006) it is possible to use this approach in two ways, either with the leaving and reinitiating (“R”) group attached to the polymer backbone or the stabilizing (“Z”) group attached to the backbone. The former approach permits grafting from a cellulosic surface and generally yields high grafting densities. The “Z” group approach, by contrast, is essentially a “grafting onto” approach, and it can suffer from steric and kinetic difficulties. Yuan *et al.* (2013) employed a surface-induced RAFT procedure to functionalize 2-bromoisobutyryl-functionalized ethylcellulose with resin acid compounds. The technology is amenable to control under a number of conditions; for example, it has found particular appeal within ionic liquids for cellulose. Lin *et al*. (2013) were able to show for the first time that MMA could be grafted onto cellulose in 1-N-butyl-3-methylimidazolium chloride or BMIMCl.

ROP: Ring-opening polymerization (ROP) is a living polymer scheme in which reaction of lactides such as *ε*-caprolactam is initiated by tin octoate to react with –OH groups, such as those on cellulosic surfaces (Nishio 2006; Carlmark *et al.* 2012). ROP has been employed in numerous studies involving modification of cellulosic surfaces (Lönnberg *et al.* 2006; Chen *et al.* 2009; Goodrich and Winter 2009; Lin *et al.* 2009; Paquet *et al.* 2010; Labet and Thielemans 2011; Lönnberg *et al.* 2011; Tehrani and Neysi 2013). The basic reaction is shown in Fig. 9.

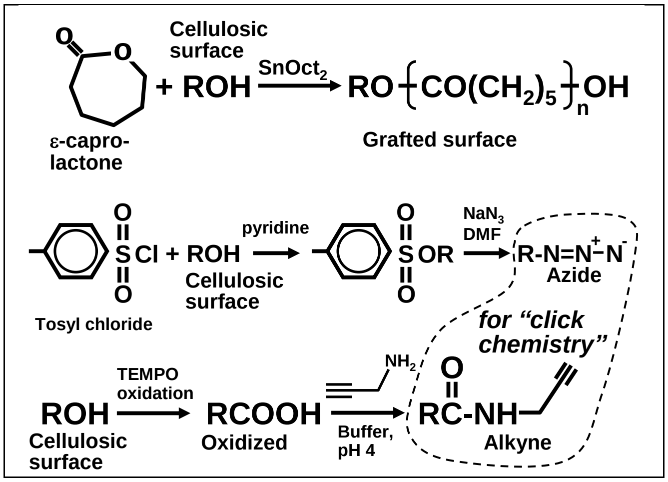


Fig. 9. Reactions for ring-opening polymerization (ROP) with ε-caprolactone, and click chemistry by way of tosyl chloride and azide derivatization or TEMPO oxidation and amidation to obtain an alkyne. The latter two reactions lead to species suitable for "click chemistry". Schemes according to Nishio (2006, top) and Sadeghifar *et al.* (2011, middle & bottom)

Click chemistry

The term "click chemistry" was first coined by K. Barry Sharpless to denote an approach of chemical synthesis that is characterized by rapidity and reliability of reaction. The overall nature of an archetypical "click reaction" is very much akin to the principles endorsed by green chemistry (mainly atom economy), but it does not fall within a single category of reaction. For example, [3+2] reactions (or so called Huisgen Reactions) are commonly referred to as "click reactions," in addition to thiol-ene reactions, Diels-Alder, and [4+1] cycloadditions. In another incarnation, it denotes a two-step process whereby the surface is first derivatized by means of isocyanate chemistry to attach an azide group, and thereafter it can be connected under mild conditions to a tailor-made functional group or chain having matching functionality at one end (Dufresne and Belgacem 2013; Habibi 2014). The approach has been demonstrated in several studies involving cellulosic surfaces (Pahimanolis *et al.* 2011; Sadeghifar *et al.* 2011; Eyley *et al.* 2012; Xu *et al.* 2012). In related work, Filpponen *et al.* (2012) and Junka *et al.* (2014a) used click chemistry to functionalize carboxymethylcellulose (CMC), which then could be adsorbed onto cellulosic surfaces under environmentally friendly conditions. The lower part of Fig. 9 shows the reaction at the cellulosic surface used to establish the covalent attachment of the reactive groups. Two types of reactive groups suitable for click chemistry are shown in Fig. 10, after covalent bonding to a cellulosic surface.

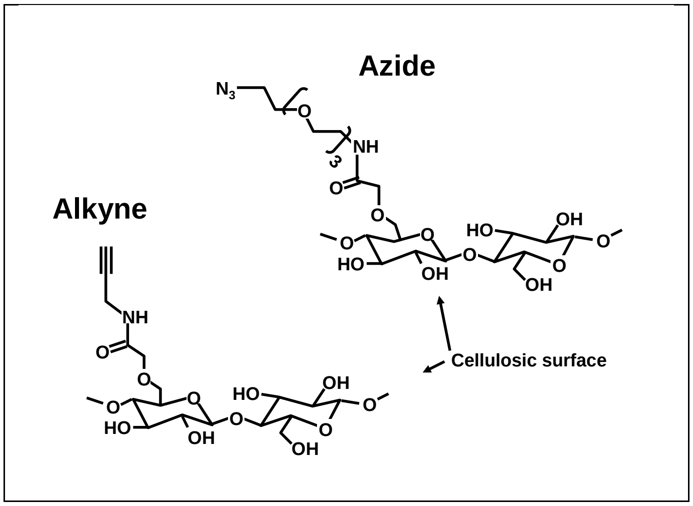


Fig. 10. Reactive groups suitable for click chemistry shown covalently attached to a cellulosic surface. Figure based on a scheme shown by Filpponen *et al.* (2012)

Enzyme-catalyzed coupling

To complete the section on creating covalent attachments to or from cellulosic surfaces, an elegant approach that deserves much more attention in the future involves enzymatic activation. Saastamoinen *et al.* (2012) showed that the laccase enzyme was able to catalyze the polymerization of the hydrophobic compound dodecyl gallate (DAGA) in unbleached nanofibrillated cellulose. The system was found to be reactive with lignin species. Laccase, an oxidative enzyme contributing to the breaking down of lignin structures, also has been found to catalyze certain grafting reactions (Kudanga *et al.* 2011). Likewise, a laccase–based biocatalytic method was used to couple short nonpolar chains containing aromatic groups onto flax fibers and nanofibrillated cellulose and to produce materials with different levels of hydrophobicity (Garcia-Ubasart *et al.* 2013). Similarly, a multicomponent colloidal system for the hydrophobization of cellulose nanofibrils was presented (Cusola *et al.* 2014).

Chemical Modifications that Convert Functionalities

As an alternative to covalently attaching molecular moieties in order to modify the surface behavior of cellulosic material, another approach is to modify the groups already present. In particular, the cellulosic surface can be oxidized, roughened, or selectively degraded. Such treatments will be considered in this section. Emphasis will be placed, once again, on treatments affecting the outer surface of the material being treated.

Oxidation

It has been known for a long time that oxidation of wood surfaces can render the material more suitable for bonding with certain adhesives (Back 1991). In addition to creating high-energy functional groups such as carboxyl and aldehyde functions, oxidative treatments can have the effect of removing low-energy substances such as fatty acids and waxes. This can help in the spreading of glues on such surfaces, especially in the case of aqueous-based glues that have relatively high interfacial tension with air. The subsections that follow consider several different main approaches that have been used to oxidize cellulosic materials.

Bleaching

Because they are so widely applied in industrial practice, it is important to consider treatments involving oxidative bleaching agents such as chlorine dioxide, sodium hypochlorite, ozone, and hydrogen peroxide. The action of such agents has been well reviewed with reference in their usage for the preparation of papermaking pulps (Hart and Santos 2013). It is well known that, rather than just affecting the fiber surface, conventional bleaching treatments tend to decolorize and/or remove chromophores, such as lignin-related compounds, throughout the cellulosic material. An example of typical mechanistic steps is shown in Fig. 11 for the widely used chlorine dioxide oxidative bleaching agent (Kolar *et al.* 1983). As noted in the figure, when the bleaching treatment is followed by alkaline extraction and washing, as in conventional preparation of papermaking pulp, the net effect generally can be described as a purification of the carbohydrate component of the material.

Although the oxidation reaction tends to create carboxyl groups, the byproducts associated with those groups are to a large extent removed from the pulp during washing because the muconic acid/ester end products are typically water soluble. This effect is evident when comparing the negative charge content of cellulosic fibers before and after application of different sequences of bleaching treatments (Herrington and Petzold 1992b; Laine 1997).

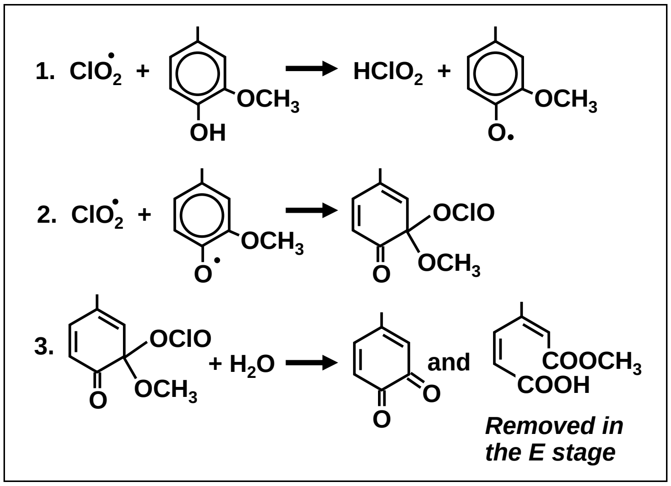


Fig. 11. Reaction of a guaiacyl group from lignin with chlorine dioxide. Scheme as reported by Kolar *et al.* 1983

TEMPO-mediated oxidation

A highly specific oxidation of the C6 groups of cellulose to carboxylic acids can be achieved when oxidation is brought about by the 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) in the presence of a suitable oxidizing agent such as sodium hypochlorite or hydrobromic acid (Saito *et al.* 2005; Isogai *et al.* 2011; Johnson *et al.* 2011; Sadeghifar *et al.* 2011; Orelma *et al.* 2012a,b; Habibi 2014). The mechanism is diagrammed in Fig. 12 (Isogai *et al.* 2011). As described in the cited articles, a key advantage of TEMPO-mediated oxidation is that only the C6 –OH groups are significantly oxidized to aldehyde or carboxyl forms. That means that the macromolecular chain remains largely intact.

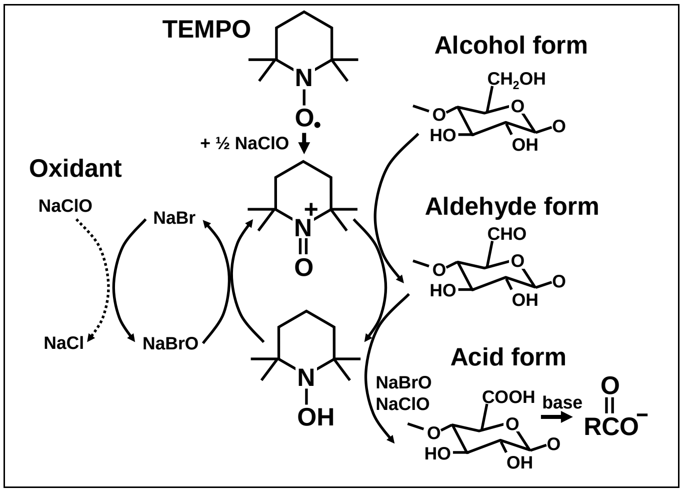


Fig. 12. Mediated oxidation of polysaccharides (*e.g.* cellulose, hemicellulose, or starch) by the combination of the 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) accompanied by an oxidizing agent

Pelton *et al.* (2011) reported a different approach to TEMPO-mediated oxidation in which the TEMPO groups were tethered to polyvinylamine, a polyelectrolyte with a high propensity for adsorption onto cellulosic surfaces. The authors found that reactions resulting from treatment with such an agent were restricted to the outer surface of cellulosic fibers, *i.e.* to locations accessible to the large polyelectrolyte molecules. The reagent also was judged to be highly efficient. One can speculate that reaction with the cellulosic surface is promoted by a system that keeps the active domain of the agent near to the surface that it is supposed to attack.

Periodate oxidation

Periodate oxidation is known to be an alternative way to produce aldehyde groups at cellulosic surfaces. However, compared to the TEMPO-mediated systems just described, periodate oxidation is much less specific and tends to favor the C2 and C3 positions of cellulose (Larsson *et al.* 2008). Also there is more breakdown of the cellulose macromolecular chains. Sirviö *et al.* (2011) showed that such oxidation could be combined with mechanical milling for the production of microfibrillated cellulose.

Sulfate and phosphate groups and others

It is known that intensive treatment of cellulose with sulfuric acid not only can convert the material to cellulose nanocrystals, but that the resulting crystals will be substituted protonated sulfate half-ester groups, providing the surface with a large net negative charge (Peng *et al.* 2011; Habibi 2014). Gu *et al.* (2013) quantified the level of substitution. They also found that it was difficult to completely remove the sulfate groups either by solvolysis or by a catalytic approach.

Phosphorylation of cellulose can be brought about by treatment with phosphoric acid in the presence of dimethylformamide and urea (Oshima *et al.* 2008).

Brief treatment with potassium permanganate in an acetone medium provides another way to oxidize cellulosic surfaces (La Mantia and Morreale 2011).

Corona discharge and plasma treatments

The electrical spark resulting from high voltage and a gap in a circuit can be used to create transient ionic species in the air, *i.e.* the generation of a plasma. The term “corona discharge” has been used to denote the use of such systems when ionization of air is used for the oxidative treatment for solid material (Back 1991; George *et al.* 2001; Belgacem and Gandini 2005; Mukhopadhyay and Fangueiro 2009; Cunha and Gandini 2010). In general, corona treatment tends to render cellulosic surfaces more wettable by aqueous fluids (Cunha and Gandini 2010; Kramar *et al.* 2013). One of the characteristic features of such treatment is that the oxidative effect tends to be one-sided, affecting mainly the front side of the treated material facing the applicator (Mukhopadhyay and Fangueiro 2009). La Mantia and Morreale (2011) described the typical results as “heterogeneous”. From an ecological standpoint, the process has some potential advantages: The reaction can take place without solvent, using ordinary air and ambient pressures (Vesel and Mozetic 2009). Though some potentially toxic molecular species may be created, most of them revert to unreactive forms within seconds or minutes. Patiño *et al.* (2011) showed that plasma treatment could be used in combination with cationization of cotton fabrics by means of epihalohydrin treatment, giving additive effects relative to the dyeability of the fabric. Kramar *et al.* (2013) showed that corona treatment with ambient air could enhance the antimicrobial effect of silver and copper ions in rayon fabric. It has been found that when cellulosic fibers are treated with an atmospheric cold plasma provided by a dielectric-barrier discharge, improvements in wet-strength and wet-stiffness can be obtained (Vander Wielen *et al.* 2006). In the cited work it was found that fiber water wettability increases with low dielectric-barrier discharge treatment, but drops with increased treatment intensity, which is likely due to changes in the polar and dispersive components.

Plasma treatments involving different input gas composition can yield a variety of changes to cellulosic substrates (Gorjanc and Gorensek 2010a,b). The cited authors noted that different plasma treatments can change cotton fabrics to become either more hydrophilic or more hydrophobic. They can be used to improve the action of adhesives, as well as for bleaching and for cleaning. Various hydrophobizing treatments involving plasma-induced polymer grafting were mentioned in an earlier section (see, for instance, Gaiolas *et al.* 2009; Cunha and Gandini 2010; Song *et al.* 2013). Such treatments go well beyond simple oxidation; rather, as described earlier, a polymer grafted to a cellulosic surface is obtained.

Adsorption of Surfactants

All of the modification methods discussed so far in this article involve some form of chemical reaction, either to create covalent bonds with cellulosic surfaces or to change their existing chemical nature, *e.g.* through oxidation. Each such reaction entails some cost, both in terms of the economy of the process or the adverse environmental effects involved. This section introduces another general approach – the direct addition of surface-active compounds. Rather than using covalent reactions with cellulosic materials, this approach involves only physical effects, which in the present context include such things as charge-charge interactions, association of hydrophilic groups in aqueous media, hydrophobic effects, and hydrogen bonding. A great advantage of using such an approach is that any chemical synthesis steps involving the treatment agent can be carried out under well-known, highly optimized synthesis conditions, completely separately from any process related to the cellulosic materials.

A surfactant can be defined as a molecule having two parts having different affinities, leading to affinities toward polar and non-polar media. Thus, it makes sense that through the use of surfactants there may be an opportunity to easily modify surfaces, even at an industrial scale, and thus to affect the behavior of cellulose to make it suitable to practical applications. On the other hand, since there is no covalent attachment involved, one needs to be concerned about the relative permanence and robustness of the effects imparted by the used surfactants. Also, as mentioned by Missoum *et al.* (2013a), a surfactant has the potential to migrate away from its point of application. Cases of adsorption of cationic, anionic, and nonionic surfactants are reviewed below.

Cationic surfactants

Surfactants that bear a positive charge have a potential advantage for practical modification of cellulosic surfaces due to the characteristic negative charge of such materials (Biswas and Chattoraj 1997). Indeed, strong adsorption tendencies and other features of such systems have been reported (Alila *et al.* 2007). A characteristic feature of surfactants in contact with cellulosic surfaces is their tendency to cluster together as adsorbed aggregates (forming bilayers, patchy bilayers, and so-called hemimicelles), rather than adsorbing as individual molecules occupying single sites on the surface (Boufi and Gandini 2001; Alila *et al.* 2005; 2007; Penfold *et al.* 2007). This tendency is illustrated schematically in Fig. 13.

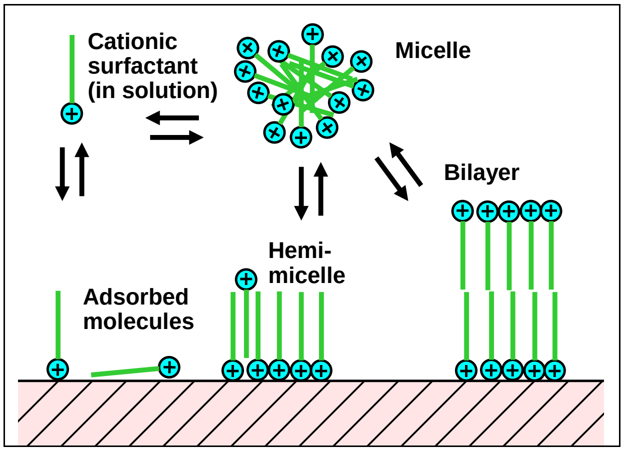


Fig. 13. Schematic illustration of cationic surfactant in solution, associated as micelles, and adsorbed onto a cellulosic surface in different molecular orientations, as hemimicelles, or as bilayers

A potential effect of adsorption of oppositely charged surfactants on cellulosic fibers is improved adhesion, which can result when they are processed with a polymeric, often hydrophobic, matrix material (Dai and Fan 2013). For instance, dioctadecyldimethylammonium bromide (DODA), a cationic surfactant that has been used in Langmuir films, has been used to form monolayers of DODA-cellulose nanoparticles at the air/water interface, followed by their deposition on hydrophobized substrates. This process takes advantage of the expected strong electrostatic interactions between the cationic DODA surfactant and anionic cellulose nanocrystals (Habibi *et al.* 2010).

TEMPO-enhancement of cationic surfactant adsorption

As might be expected, the strength of interaction of a cationic surfactant can be increased by pre-treatments that increase the density of negative charges at the cellulosic surfaces in aqueous solution. For instance, adsorption of cationic surfactants is enhanced in cases where the cellulose has been TEMPO-oxidized (Alila *et al.* 2005, 2007; Syverud *et al.* 2011). The system described by Alila *et al.* (2007) received a high score in Table A, reflective of the fact that a durable effect was achieved even without covalently attaching the hydrophobic substance to the cellulosic surface.

As noted in an earlier discussion, Johnson *et al.* (2011) compared results for cationic surfactants used in the manner discussed here, or alternatively after reaction to form amide linkages with cellulosic surfaces; notably, the practical results were similar in terms of rendering the surfaces hydrophobic in a durable manner. Because the non-reacting system is much easier to achieve in practice, the implications of the study are clear: The option involving use of cationic surfactants – and the enhancement of such systems by oxidation of cellulosic surfaces, ought to be evaluated as a high priority for various applications.

Yang *et al.* (2014) carried out related work in which TEMPO-oxidized cellulose nanocrystals served as a substrate for amidation reactions with suitable amine species. Salajkova *et al.* (2012) compared results for the adsorption of four different cationic surfactants onto TEMPO-oxidized cellulose. These systems were all dispersible in toluene, thus demonstrating high compatibility with a hydrophobic medium despite a lack of covalent bonding. In summary, cationic amines can bind sufficiently strongly to highly negative cellulosic surfaces, so that it may not be critically important whether or not formation of amide linkages takes place.

Nonionic surfactants

Although nonionic surfactants are very widely used in industry and in academic research, few reports exist in which a cellulosic surface was deliberately modified with uncharged surfactants. Since nonionic surfactants are in general less expensive than their cationic counterparts, it makes sense that many efforts to disperse cellulosic materials in aqueous medium will rely on nonionic surfactants. The use of a surfactant as a dispersant is based on the assumption that the hydrophilic group(s) of the surfactant adsorbs on the cellulosic surface, whereas its hydrophobic group(s) finds proper solvency conditions in the solvent or matrix. This arrangement deters aggregation of the cellulose inclusions via steric stabilization. In order to improve the adhesion of cellulose fibrils to a surrounding matrix, a non-ionic surfactant, a sorbitan monostearate, was used to stabilize cellulose nanoparticles (Kim *et al.* 2009) and later used in producing nanocomposites with polystyrene (Rojas *et al.* 2009).

Key attributes affecting the behavior of surfactants include the relative size of the constituent blocks on adsorption, the structure of the adsorbed layer relative to the length of the hydrophilic and hydrophobic blocks of the macromolecule, and the interfacial properties. Some structural aspects and effects of triblock copolymer surfactants are represented in Fig. 14.

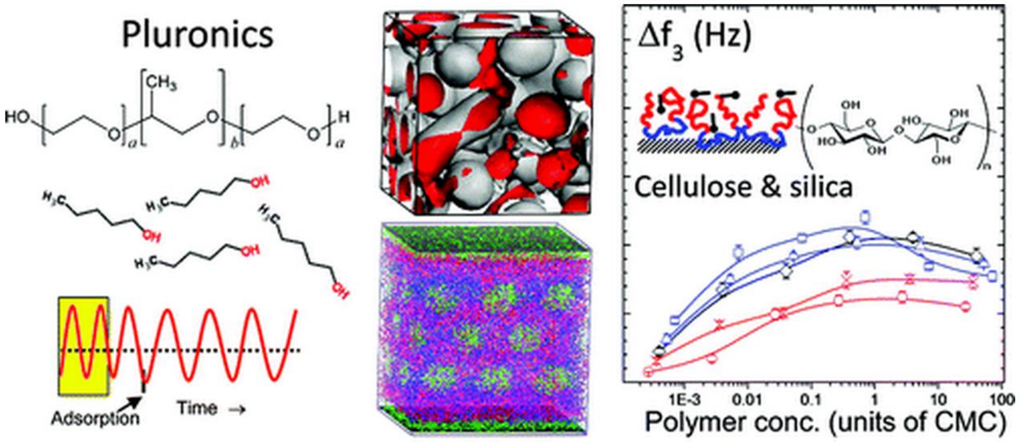


Fig. 14. Representation of adsorption of nonionic triblock polymer surfactant (Pluronic) onto cellulose or silica surfaces as sensed by quartz crystal microbalance (QCM) method. Different curves correspond to aqueous media or mixtures with ethanol or pentanol. The lower (red) curves were obtained after rinsing. Figure reprinted with permission from (Liu 2012b). Copyright 2012 American Chemical Society.

The effect of aqueous polymer concentration on the extent and dynamics of adsorption and desorption on cellulose has been elucidated (Liu *et al.* 2010a, 2011b, 2012b). The cloud point, surface tension, critical micelle concentration (CMC), and maximum packing at the air–water interface were determined, and the latter was compared to the amount of the same polymer that adsorbed onto cellulose surfaces from aqueous solutions with different solvency. Further, the effect of the adsorbed nonionic polymeric surfactants on lubrication and friction between cellulose was determined (Li *et al.* 2011c, 2012c), and the results were supported by theoretical and computational studies (Liu 2012a,b). These amphiphilic macromolecules form self-assembled structures in solution. Moreover, upon adsorption at the cellulose/fluid interface and upon confinement and shear, it was found that the self-assembly occurs very fast. As a result, surface damage under frictional forces can be prevented, thus demonstrating that these surfactants can act as a protection layer (Liu 2012a). Finally, the affinity with cellulose of the nonionic polymeric surfactants was enhanced by installing cationic end-caps on the polymer, as demonstrated by experiments that used quarternized poly(2-dimethylaminoethyl methacrylate). Solvency and electrostatic forces were found to be primary factors influencing the adsorption (Liu *et al.* 2011b)

Gradwell *et al.* (2004) prepared a pullulan abietate, which was essentially a linear sugar-type polymer having rosin-type substituent groups (degree of substitution 0.027). The surfactant was shown to adsorb essentially irreversibly, rendering the surfaces suitable for bonding with plastic matrix materials. Cherian *et al.* (2012) employed saponins, which are natural surfactants comprised of a hydrophobic triterpene unit attached to a sugar-type hydrophilic unit. These were used as a strategy to compatibilize banana nanofibers for use in composites. In both of these cited cases, the molecules were relatively large, potentially enabling them to adsorb strongly even without the advantages of having an opposite charge relative to that of the surface.

Adsorption of Macromolecules

To extend a theme just introduced, macromolecules often display high adsorption affinity with substrates (Fleer *et al.* 1993; Wågberg 2000). Such behavior is consistent with their generally large molecular size and the possibility of multiple points of contact. Thus it makes sense to consider the adsorption of macromolecules for the modification of cellulosic surfaces. In particular, high adsorption affinity can be expected for macromolecules having ionic charge, *i.e.* polyelectrolytes, since such molecules are more likely not only to be soluble in water, but also they can benefit from various charge-related mechanisms that favor adsorption. This section also will consider the use of polyampholytes (in which ionic groups having both signs of charge are present), block copolymers, polyelectrolyte complexes, layer-by-layer deposition of polyelectrolytes, and the use of enzymatic binding modules. The general subject of macromolecular adsorption onto cellulosic surfaces has been reviewed (Wågberg 2000; Habibi 2014).

Polyelectrolyte adsorption has been used extensively by the paper manufacturing industry for many years as a means of increasing the inter-fiber bonding strength that develops during the drying process (Hubbe 2006, 2014). Dufresne (2010) has reviewed related research targeted for the processing and use of cellulosic nanomaterials. The subsection that follow consider reports of several kinds of polyelectrolytes that have been used to modify cellulosic surfaces.

Heteropolysaccharides (anionic polyelectrolytes, e.g. hemicelluloses)

Because hemicellulose is already understood to function as a bonding agent when naturally present in cellulosic fibers (Oksanen *et al*. 1997; Al-Dajani and Tschirner 2008; Yoon and van Heiningen 2008), as well as in the making of paper (Lima *et al.* 2003; Hubbe 2014; Song and Hubbe 2014a,b), it is natural to consider using it to treat cellulosic surfaces. For example, the adsorption of guar gum and starch derivatives and their interactions with cellulosic fiber and fines, as well as soluble and colloidal carbohydrates, present in cellulosic fiber suspensions were investigated by employing HPLC and spectrophotometry (Rojas and Neuman 1999). These additives are known to improve the physicomechanical properties of paper by regulating the state of flocculation in the cellulosic fiber suspension during the sheet-forming process. The effect of the nature (charge type and degree of substitution) of the hemicellulose additives and other variables strongly influences the outcome of the process on account of their adsorption behavior. Henriksson and Gatenholm (2002) treated suspensions of chemithermomechanical pulp with xylans (a variety of hemicellulose) at high pH and temperature. The resulting layer of xylan was observed to have microparticulate topography, and the fibers were much more readily wetted by water after the treatment. Eronen *et al.* (2011) used quartz crystal microbalance tests to demonstrate affinity between hemicelluloses and cellulose nanofibrils.

Beyond the work described above, with practical consequences, adsorption of hemicellulose onto cellulosic surfaces has been employed as a highly unusual but effective strategy to endow the material with specialized chemical functionalities. Thus, Zhou *et al.* (2005, 2007) used the already-described ATRP method of grafting to attach a variety of chemical features to xylan macromolecular chains, which could be subsequently adsorbed onto cellulose.

Carboxymethyl cellulose (CMC), a derivative of cellulose, is negatively charged in aqueous solutions due to its anionic carboxyl groups (pK_a of ~4.5). In the presence of salt CMC adsorbs irreversibly on cellulose, and therefore it can be used to increase the negative charges of cellulosic materials. Moreover, because CMC shares exactly the same backbone structure as ordinary cellulose, there is reason to expect unique possibilities for adsorption interactions involving these two materials. Indeed, research work has shown that it is possible to modify the surface of cellulose by exposure to CMC solutions under suitably high ionic strength, temperature, and/or time conditions (Laine *et al.* 2002; Duker and Lindström 2008; Duker *et al.* 2008; Gandini and Pasquini 2012). Also, the degree of adsorption can be optimized by selecting a degree of substitution of CMC that is just high enough to enable its solubilization in water (Laine *et al.* 2000).

The carboxylic groups on cellulose can mediate in a number of further functionalizations. For example, CMC adsorption from aqueous solution has been found to enhance the physisorption of biomolecules at acidic and neutral conditions (Orelma *et al.* 2011). Filpponen *et al.* (2012) and Junka *et al.* (2014a) took further advantage of CMC adsorption onto cellulosic surfaces to achieve a unique form of surface treatment. Click chemistry was used to attach a variety of functions to CMC, and then the derivatized CMC was adsorbed onto the cellulose. A great potential advantage of such an approach is that the challenging chemical steps are carried out in homogeneous solution, away from the papermaking system itself. Also, such an approach to treatment does not require there to be any covalent reaction with the fiber surface.

Cationic polyelectrolytes

Due to a combination of electrostatic attractions, multi-point attachment, and the increased entropy resulting from the release of counter-ions when a cationic polyelectrolyte adsorbs onto a negatively charged cellulosic surface, strong and essentially irreversible adsorption can be expected in such cases (Rojas *et al.* 2000; Wågberg 2000; Orelma *et al.* 2011; Toivonen *et al.* 2015). Adsorption of a sufficient amount of cationic polyelectrolyte onto cellulosic surfaces also can reverse the sign of charge from negative to positive (Lvov *et al.* 2006), which can be seen as evidence of their potential to modify cellulosic surfaces in a variety of applications.

Cationic polyelectrolytes of low charge density adsorb onto cellulose to an extent that depends on the charge density and the number density. However, it is the combination of electrostatic and non-electrostatic interactions that are to be considered as contributors to the adsorption of low charge density cationic polyelectrolytes on cellulose. Since such polymers are commonly used in charge determination (polyelectrolyte titration), it is expected that the use of adsorbed amounts of polyelectrolytes to determine the surface charge of cellulose surfaces needs to be considered carefully, since the assumption of stoichiometric charge neutralization does not hold necessarily (Rojas *et al.* 2000). Also, there can be much uncertainty due to a time-dependent and molecular mass-dependent tendency of cationic polyelectrolytes to diffuse into the mesopore structure of fiber cell walls (Hubbe *et al.* 2007a).

In paper manufacture some of the most prominent uses of cationic polyelectrolytes are as dry-strength (Hubbe 2006) and wet-strength (Espy 1995) agents. Cationic starch products (Howard and Jowsey 1989; Ulbrich *et al.* 2012), as well as acrylamide copolymers (Sakaemura and Yamauchi 2011) are the most widely used dry-strength agents for paper. Poly-(amidoamine-epichlorohidrin) products, which are cationic as well as capable of undergoing curing reactions during the drying of paper, are presently the most widely utilized type of wet-strength agent.

Chitosan, which is a cationic polysaccharide derived from chitin, is known to adsorb irreversibly from aqueous solution on cellulose, most likely by virtue of their opposite charges. Such adsorption is known to influence the swelling of cellulosic fibers.

This phenomenon depends on the balance of charges and thus on the pH of the medium. A simple change in the environmental conditions (*i.e.* an increase of pH) reduces the hydration of chitosan, promoting multivalent physical interactions between cellulose nanofibrils (CNF) and chitosan over those with water, resulting effectively in physical crosslinking (Fig. 15). For example, Toivonen *et al*. (2015) showed a concept based on such a phenomenon for modification of nanofibrillated or microfibrillated cellulose with chitosan upon adsorption from aqueous dispersion and the preparation of films, showing high mechanical strength in the dry and wet state. Transparency (~70 to 90% in the wavelength range 400 to 800 nm) was achieved by suppressing aggregation and carefully controlling the mixing conditions. Chitosan can be dissolved in aqueous medium at low pH, leading to CNF/chitosan mixtures that form easily processable hydrogels. In the water-soaked state, films of CNF/chitosan 80/20 w/w showed excellent mechanical properties, with an ultimate wet strength of 100 MPa (with corresponding maximum strain of 28%), and a tensile modulus of 4 and 14 GPa at low (0.5 %) and large (16 %) strains, respectively (Toivonen *et al.* 2015).

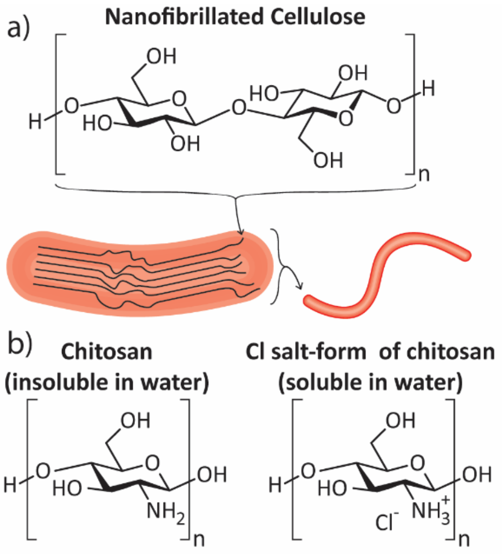


Fig. 15. a) Molecular structure of cellulose and illustration of cellulose chains forming cellulose nanofibrils (CNF) with the crystalline and amorphous domains. The surface-bound residual heteropolysaccharides are not shown. **b)** Molecular structure of chitosan in the neutral and charged forms (Reprinted with permission from (Toivonen et al. 2015). Copyright 2015 American Chemical Society).

The extent and tenacity of adsorption of cationic polymers can be enhanced by prior modification of the solids to increase the negative surface charge density. This was found to be useful in the development of dry strength agents for papermaking applications (Arboleda 2014a,b)

Fujisawa *et al.* (2013) used an amine-terminated polyethylene glycol oligomer (2182 Daltons) to stabilize TEMPO-oxidized cellulose nanomaterials in organic media. Although the cited authors used the term “grafting”, it is clear from the description that the beneficial effects on the dispersion of the nanocellulose were due to ionic effects, *i.e.* attraction between the cationic amine groups and the anionic carboxylate groups.

Polyampholytes

Polyelectrolytes that have both positive and negative ionic groups, *i.e.* polyampholytes or amphoteric polymers, are known to have some interesting characteristics relative to adsorption onto cellulosic surfaces. In the case of weak polyelectrolytes, such interactions can be expected to depend on the pH. Adsorption is often maximized at a pH that approximately corresponds to the iso-electric condition, in which the material has a net-neutral charge (Sezaki *et al.* 2006; Song *et al.* 2006; Hubbe *et al.* 2007b) (Fig. 16). The cited research showed that polyampholyte-treated cellulosic surfaces can display favorable bonding ability upon drying, often exceeding what can be achieved by adsorption of a similar cationic polyelectrolyte (Song *et al.* 2006; Wang *et al.* 2006b, 2007a,b). The advantage has been attributed to the somewhat water-swollen, three-dimensional nature of the polyampholytes in the adsorbed condition, as well as the hydrogen bonding ability of the systems used for such purposes (Silva *et al.* 2009; Song *et al.* 2010).

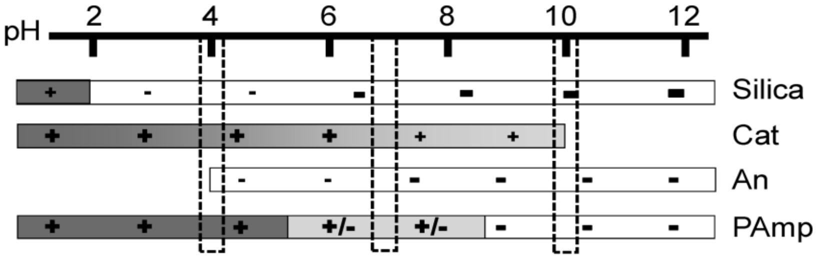


Fig. 16. Illustrative chart with the net charge of a surface (silica, taken here as an example) and cationic (Cat), anionic (An) and amphoteric (PAmp) polymers applied at different pH (2 to 12)

A relative indication of dominant charge at pH 4, 7, and 10 is given in the figure with "+" or "-" signs. The state of "charge symmetry" would occur for an amphoteric polymer with an isoelectric pH around 7. Such amphoteric polymer would adsorb to a largest extent at intermediate pH. Also, a cationic polymer would be expected to adsorb best at intermediate pH, in consideration of electrostatic effects. For example, in such condition the cationic substance would not have to compete with protons for adsorption sites. At high pH, depending on the nature of a cationic polymer, cationicity would fall (due to deprotonation of ammonium groups, hydrolysis of aluminum species, *etc.*), but that would not be true in the case of polymers containing (permanent) quaternary ammonium groups. Adsorption of anionic polymer on negatively charged surfaces is expected to be minimal unless interactions different than electrostatic are present. It is worth noting that adsorption on a surface depends not only on the electrostatic charges but the type and density of charged groups (polymer and surface), polymer molecular size, solvency and electrolyte content. Therefore, it is difficult to establish generic rules to determine adsorption unless all effects are considered.

Proteins

Because proteins contain both amine and carboxyl groups, they can be regarded as a special subclass of polyampholytes. The adsorption of proteins onto cellulosic and other surfaces has been studied (Jin *et al.* 2012b; Salas *et al.* 2012; Arboleda *et al.* 2014a,b). Due to their interesting properties, soybean proteins have found uses in different nonfood applications. The use of proteins is closely related to their solubility, hydration properties, gelation, and interfacial activity, which, in turn, are governed by the structure and charge balance of the macromolecule. The effect of pH, ionic strength, and chemical modification on the functional properties of proteins has been studied extensively, especially in food applications. The kinetics and extent of adsorption on cellulose surfaces of glycinin and β-conglycinin, the main proteins present in soy, were studied in detail as a function of solution ionic strength, pH, and denaturation (Salas *et al.* 2012). This and other related work has triggered interest for papermaking applications. For example, various soy protein products, either alone or as polyelectrolyte complexes with cationic starch, were shown to be effective as bonding agents for paper (Arboleda *et al.* 2014b).

Another widely available protein, gelatin, has been used in related processes. As was the case of polyampholytes and other proteins, it was found that the highest adsorption of gelatin onto cellulose occurred at the isoelectric pH of the protein. Based on this and other results, a gelatin loading has been proposed to facilitate molecular and surface interactions and, thus to improve the formability of cellulose-based materials in paper molding (Khakalo *et al.* 2014; Vishtal *et al.* 2015). The cited work used aqueous gelatin solutions, which were sprayed on the surface of wet webs composed of wood fibers. Upon gelatin treatment, the elongation and tensile strength of paper under unrestrained drying was increased by 50% (from 10% to 14%) and by 30% (from 59 to 78 N m/g), respectively. The mechanical performance of gelatin-treated fibers was further improved by glutaraldehyde-assisted cross-linking. This approach based on inexpensive proteins represents cost-effective and facile methods to improve the plasticity of fiber networks, which otherwise cannot be processed in the production of packaging materials by direct thermoforming.

The role of surface spatial and population heterogeneity on proteins adsorption has been studied by single-molecule tracking of protein dynamics on a cellulose surface (Langdon *et al.* 2015), revealing interesting conclusions related to the role of cellulose's surface characteristics. Besides this work using sophisticated tools, other work with proteins has covered the field of bioactive cellulose. For example, Orelma *et al.* (2014) attached anti-human serum albumin (anti-HSA) antibody ligands on bacterial cellulose (BC) by physical adsorption, demonstrating their application for biofiltration of blood proteins. Another example is provided by Hierrezuelo *et al.* (2104), who adsorbed an adenosine receptor antagonist onto regenerated cellulose; then streptavidin was immobilized onto the treated surface.

Enzyme adsorption

Enzymes may be regarded as a specialized type of polyampholyte molecule characterized by a specific folded structure. Due to their biological origin, enzymes are generally regarded as offering eco-friendly options for future technology. Efforts in this area have been concerned mainly with research to produce the so-called second generation biofuels, that is, ethanol derived from cellulosic feedstock (Hu *et al.* 2008). Some reports involve observations made by *in-situ*, on-line monitoring *via* quartz crystal microgravimetry and surface plasmon resonance (Turon *et al.* 2008; Ahola *et al.* 2008b;

Hu *et al.* 2008, 2009a,b). Findings relevant to the issue of adsorption of enzymes on cellulose can be found in the report of Hoeger *et al.* (2012) and Martín-Sampedro *et al.* (2013). The cited authors found preferential adsorption and activity of mono and multi-component cellulases on lignocellulose films.

In principle, highly specific attachment to cellulosic surfaces can be achieved by use of the cellulosic binding domains (CBDs), which are tethered to the hydrolytic part of many types of cellulase enzyme (Yokota *et al.* 2008). Studies have shown that CBDs can be used as a means of attaching specific functionalities to cellulosic surfaces (Yokota *et al.* 2009, 2012; Sato *et al.* 2012). However, as demonstrated by Sato *et al.* (2012), sometimes the binding cannot be completely differentiated from that of the adsorption of ordinary proteins derived from non-enzymatic nucleotide sequences.

Enzymatic treatments of cellulosic surfaces hold the potential to enable highly specific interactions with selected biomaterials. For example, Orelma *et al.* (2012a) treated thin films composed of TEMPO-oxidized cellulose nanofibrils with N-hydroxy-succinimide and 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride. The resulting cationic surfaces were able to bind proteins including bovine serum albumin. Specific interactions with antihuman IgG were demonstrated. In further work, Orelma *et al.* (2012b) adsorbed Avidin and NeutrAvidin on cellulose films. TEMPO oxidation was shown to favor such adsorption. Again, immunospecific effects were demonstrated.

A related approach has been used to bind TiO_2 nanoparticles to cellulosic surfaces (Ye *et al.* 2009). The cited authors employed bioconjugation, meaning that the cellulose fiber was modified with an immunospecific protein bound to cellulose binding domain. The TiO_2, which had been prepared with biotin, was then bound to the surface with the intermediation of a streptavidin from *Streptomyces avidinii*.

Block copolymers having ionic charge

Strong adsorption and various targeted effects can be achieved by use of ionically charged block copolymers. In principle this might be a way to achieve an eco-advantage by avoiding the need for covalent attachment of a modifying agent. Adsorption on cellulose of nonionic block copolymers can be enhanced by end-capping the polymer with small cationic chains (Liu *et al.* 2011b). Likewise, Nurmi *et al.* (2010) adsorbed block copolymers having a cationic segment and a fluorochemical segment onto mica and cellulose fiber surfaces. The very strong hydrophobic effects observed were attributed partly to the nanoparticulate nature of the fluorochemical segments in their adsorbed condition.

Strong hydrophobization of cellulosic packaging was achieved by Pan *et al.* (2013) through the use of a block copolymer between a cationic segment and a hydrophobic segment. The additive was described as a core-shell material in which the hydrophobic part was stabilized by the cationic portion. The cationic groups favored a high degree of adsorption onto cellulosic fibers during papermaking. The treatment contributed to good barrier properties as well as paper strength.

Polyelectrolyte complexes

Studies have shown that polyelectrolyte complexes provide a means of effectively adsorbing relatively large quantities of bond-promoting hydrophilic agents onto cellulosic materials, potentially leading to very large relative increases in paper strength (Lofton *et al.* 2005). Although substantial energy and procedural steps will be required for chemical synthesis of a polyelectrolyte, such steps take place before the agents are brought into contact with the cellulosic surface to be treated. Adsorption of polyelectrolyte complexes tends to be maximized near to the point of charge neutrality (Hubbe 2005; Hubbe *et al.* 2005), or at point that the charge of the complexes is relatively low but positive, thus providing an electrostatic attraction to typical cellulosic surfaces. The molecular process is illustrated in Fig. 17. The terms "ladder" and "scrambled egg" were first used by Michaels (1965) to describe the two models by which polyelectrolyte chains might arrange themselves in order to maximize the electrostatic interaction.

The mutual neutralization of polyelectrolytes is known to greatly decrease their solubility, an effect that can favor adsorption (Ström *et al.* 1981, 1985; Philipp *et al.* 1989). The formation of ion pairs between the two interacting polyelectrolytes makes it possible for the counterions (such as sodium and chloride ions) to diffuse into the bulk of solution; the resulting increase in degrees of freedom of the system provides a thermodynamic driving force in favor formation of such complexes. Tests with papermaking systems showed by far the best results when the respective polyelectrolytes were added sequentially *in situ* to an agitated suspension of cellulosic fibers (Hubbe 2005). Such results are tentatively attributed to the formation of non-equilibrium trapped states (Claesson *et al.* 2005) of complexation of polyelectrolytes in the agitated fiber suspension.

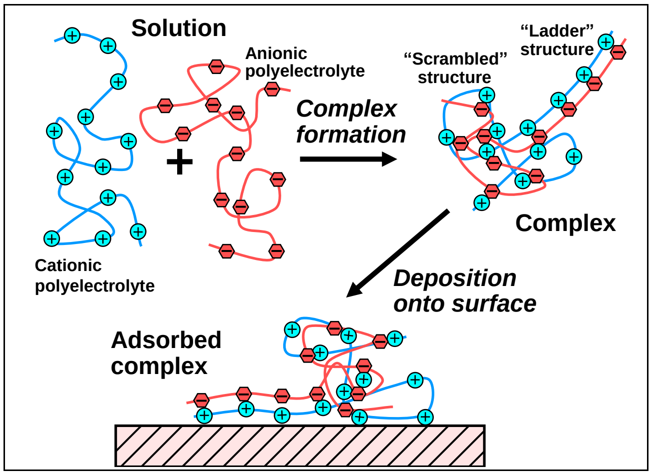


Fig. 17. Schematic illustration of polyelectrolyte complexation as a means of treating cellulosic surfaces with combinations of polyelectrolytes having opposite charge

Polyelectrolyte complexes (PEC) are even more relevant in systems where not only cellulose fibers but also mineral particles are present. As such, PECs composed of polyacrylamides carrying opposite charges (A-PAM and C-PAM) were investigated in terms of precipitated calcium carbonate (PCC) floc shear resistance and re-flocculation effects (Korhonen *et al.* 2015). Light transmission was used in real time to monitor the dynamics of flocculation under shear fields. Compared to the single polyelectrolytes, PECs greatly enhanced particle re-flocculation, while minor differences in shear resistance were observed. Shear resistance and re-flocculation depended strongly on the molecular weight and charge ratio of the PEC components. In order to achieve floc stability and re-flocculation conditions, a minimum concentration of charge-asymmetric PEC may be required (Korhonen *et al.* 2015)

Layer-by-layer adsorption

Perhaps due to the elegance of being able to achieve highly reproducible thickness of the applied films, there has been a great deal of study of layer-by-layer deposition of polyelectrolytes. Some notable studies involving cellulosic substrates can be cited (Wågberg *et al.* 2002; Lvov *et al.* 2006; Zheng *et al.* 2006; Lingström *et al.* 2007; Salmi *et al.* 2009; Buck and Lynn 2010; Lin and Renneckar 2011a,b; Li *et al.* 2012a; Junka *et al.* 2014c). The general approach is highly flexible, allowing for instance alternating layers of a cationic polyelectrolyte and oppositely charged nanoparticles such as titanium dioxide (Ogawa *et al.* 2007), silica (Yang and Deng 2008), or montmorillonite clay (Lin and Renneckar 2011a,b). By suitable choice of the composition of one of the layers, such an approach also can be used to render the treated cellulosic surfaces moderately hydrophobic (Lingström *et al.* 2007; Lin and Rennackar 2011a). Li *et al.* (2011b) achieved hydrophobization by self-assembly of lignosulfonates, alternating with Cu^{2+} layer applications. Also, by depositing relatively large amounts of polyelectrolyte onto cellulosic fibers in the course of multiple layer application, the strength of the resulting paper can be increased substantially (Lvov *et al.* 2006; Zheng *et al.* 2006; Li *et al.* 2012a). Illergard *et al.* (2012) used such an approach to bind relatively large amounts of polyamines, alternating with an anionic polyelectrolyte. The combination was shown to be effective for resisting bacterial growth on the treated surface.

Although electrostatic assembly in the form of multilayers has been investigated extensively, still many features relevant to the nature of such a process are not fully understood. For the most part, highly charged, strong polyelectrolytes have been the focus of studies related to layer-by-layer adsorption (Kato *et al.* 2002). In the case of weak polyelectrolytes, it has been found that pH adjustments can be used as a tool to fine-tune the composition and rate of buildup of successive layers (Eriksson *et al.* 2005; Renneckar and Zhou 2009; Lin and Renneckar 2011b). By adjusting the pH such that a given polyelectrolyte has a lower density of ionic charge, a larger proportion can be taken up by an oppositely charged substrate. In such manner, it is possible to form thicker polyelectrolyte multilayers. In a similar manner, high molecular mass, low charge density polyacrylamides can be used to impart strong inter-fiber adhesion and bonding in papermaking (Liu *et al.* 2011a, Wang *et al.* 2011).

From an environmental standpoint, layer-by-layer applications suffer from the disadvantage of requiring relatively large amounts of pure water (or pure saline solution) for rinsing between each stage of deposition. In many cases the preferred method also entails heat-curing of the treated cellulosic surface after depositing of each successive layer, and thus there is a substantial energy requirement, either for clarifying water or for heating the solid material.

In-situ polymerization

Even in the absence of a chemical reaction with the cellulose, when a polymer is synthesized in the presence of a cellulosic surfaces, it may be possible for there to be strong anchoring, possibly due to mechanical intertwining of the reacted material with fibrils at the surface (Sasso *et al.* 2011). Such an approach was used by Shang *et al.* (2012), who polymerized fluorinated polybenzoxazine with silica nanoparticles and electrospun cellulose acetate. The resulting material was highly hydrophobic. As another example, Merlini *et al.* (2014) carried out *in-situ* polymerization of polyaniline in the presence of coconut fibers. The resulting coated fibers were highly electrically conductive.

Nano-scale Film Application

Up to this point, modification methods considered in this article have mainly involved molecular interactions. But additional interesting effects become better explained when one considers the next higher size range of organization, namely nano-scale effects. This type of modification of cellulosic surfaces has been discussed in certain earlier review articles (Nishio 2006; Wang and Piao 2011; Samyn 2013).

Due to the diverse nature of approaches involving deposition of nano-scale layers of materials onto cellulose surfaces, it is hard to generalize regarding environmental implications. Readers are encouraged to check the ratings given in Table A regarding studies to be cited in the subsections below.

Cellulose thin films

If one's goal is to enhance the cellulosic nature of a surface, then a possible strategy would be to deposit an ultra-thin film of cellulose on that surface. There are numerous accounts on the formation of ultrathin films of cellulose (Song *et al.* 2009a,b; Taajamaa *et al.* 2011; Hoeger *et al.* 2011, 2012, 2014; Csoka *et al*. 2011, 2012; Martín-Sampedro *et al.* 2013). The reader is referred to a critical review on the subject, including the methodology of preparation, as well as the applications of the films for fundamental research (Kontturi *et al.* 2006). Much progress has been achieved in recent years in the preparation and deposition of nano-scale cellulosic films (Roman 2013). Dai and Fan (2013) employed nanocellulose to modify cellulose fibers in two ways. The nanocellulose, which was prepared by oxidation and ultrasonification, was able to fill spaces within the roughness (stria) at the surfaces of individual hemp fibers. Also, nanocellulose helped to bridge the spaces between adjacent fibers. The crystallinity of the material as a whole was increased due to the treatment.

Lignin deposition

Solubilized lignin-based materials are known to redeposit onto cellulosic surfaces in cases where aqueous conditions are suitably changed, resulting in decreased solubility (deJong *et al.* 1997; Selig *et al.* 2007; Liu *et al.* 2015). Thus, lignin products can be regarded as means to create "thin film" modifications of cellulosic surfaces. While lignin is naturally present in lignocellulosic fibers, it is typically removed during pulping to allow for the production of white (bleached) fiber grades. By re-introducing lignin or its byproducts to the cellulosic surface there is an opportunity to endow the fibers with some interesting properties. This is especially the case of nanomaterials derived from biomass. For example, it was found that upon microfluidization of fibers with increased residual lignin concentration the resultant lignocellulose nanofibrils presented a smaller width, consistent with the radical scavenging ability of the lignin that results in better cell wall deconstruction (Ferrer *et al*. 2012a,b). When nanopapers were produced with such lignocellulose nanofibers, it was noted that the stiff nature of the lignin-containing fibrils made them conform to each other less well on the supporting screen used for dewatering and therefore, they produced a more open structure that enhanced the filtration rate. Later, during hot pressing, the softening of the lignin in the nanopapers and its amorphous nature enabled a "fusing" effect on the fibrils, filling the voids in the structure and making the surface of the nanopapers smoother (Rojo *et al.* 2015). The interfacial free energy of interaction changes drastically with the increased lignin content, revealing the increase in hydrophobicity. Together with the significantly less porous structure, lower water absorbency was observed with increased lignin content. Lignin also reduced the oxygen permeability by up to 200-fold. Whilst it might be expected that lignin interferes with hydrogen bonding between fibrils, this is apparently counteracted by the uniform distribution of lignin, seemingly aiding stress-transfer between fibrils and thus preserving mechanical properties (Rojo *et al.* 2015). A word of caution is given here; these conclusions are not to be generalized, since a broad spectrum of lignin types exists, depending on the process used for separation or fractionation from the lignocellulosic fibers.

Latex deposition

A latex might be defined as a suspension of nano-scale, spheroidal particles composed of groups of copolymer chains. Styrene, butadiene, vinyl, and acrylic monomeric units are common in such products. As noted by Dufresne (2010), typical latex materials have sufficient water-loving character to be compatible with cellulosic surfaces, including cellulose nanocrystals. As shown by Alince (1999), a cationic latex can be used very effectively to cover the surfaces and to modify the properties of cellulosic fibers. Benefits of such treatment can include an increase in paper strength, resistance to moisture, and the retention of mineral additives during papermaking. Pan *et al.* (2013) showed that when cationic latex includes a substantial proportion of a hydrophobic co-monomer, which is presumed to involve a core-shell structure of the latex particle, the adsorption onto cellulosic surfaces can impart hydrophobicity. Likewise, Aarne *et al.* (2013) showed that diblock copolymers, in which a predominant hydrophobic co-monomer was stabilized in suspension by means of short chains having a cationic character, were very effective for preparation of hydrophobic paper.

Langmuir-Blodgett and Langmuir-Schaefer films

The Langmuir-Blodgett (LB) method provides a means for preparing molecularly-thin films at a water-air interface and then transferring such films to various surfaces (Schaub *et al.* 1993; Holmberg *et al.* 1997; Hoeger *et al.* 2014). Roman (2013) has reviewed studies in which the LB method, or a closely-related Langmuir-Schaefer technique (Habibi *et al*. 2010), was used to transfer nano-scale films of cellulose nanocrystals. The advantage of this method is that well-ordered monolayers can be transferred with high precision, often yielding contiguous monolayer films. The method can be readily repeated as a means of building up films to a selected number of layers. Disadvantages include the length time required and the need for specialized equipment. Perhaps these disadvantages can help to explain a declining interest in the LB method in recent years (Ariga *et al.* 2013). Also, in many cases, one needs to be concerned about whether or not there is sufficient compatibility of the deposited material with the cellulosic surface so that it has sufficient durability to be useful in a selected application. Woo *et al.* (2006) carried out related work in which cellulose nanocrystals were treated with flexible isopentyl side chains, then organized into LB films that were applied to a surface.

Chemical vapor deposition

As noted by Alf *et al.* (2010), the chemical vapor deposition (CVD) method can be used to deposit thin films having a wide variety of composition onto suitable solid surfaces. Advantages can include relatively low energy input, moderate vacuum requirements, and room-temperature conditions. Cellulosic materials are among the substrates to which the CVD method has been applied. The method is closely related to the plasma-induced grafting methods discussed earlier, where reactions with the cellulosic surfaces were emphasized. The CVD approach can be used, for instance, to increase the fine-scale roughness of a cellulosic surface (Li *et al.* 2007; Balu *et al.* 2008). Kettunen *et al.* (2011) used a CVD method to coat a thin TiO_2 film on lightweight native nanocellulose aerogels to offer a novel type of functional material that shows photo-switching between water superabsorbent and water-repellent states.

Nanoparticle deposition

Silver nanoparticles have often been reported for functionalization of cellulose (Nypelö *et al.* 2012; Arcot *et al.* 2014a,b). Non-metal nanoparticles have also been reported, such as quantum and carbon dots (Junka *et al.* 2014b). Though deposition of nanoparticles clearly could be used as a means of surface modification, one needs to be concerned regarding the durability of attachment. Numerous studies have reported the deposition of nanoparticles onto cellulosic surfaces (Seto *et al.* 1999; Ogawa *et al.* 2007; Tomšič *et al.* 2008; Bayer *et al.* 2009; Gonçalves *et al.* 2009; Benavente *et al.* 2010; Bourbonnais and Marchessault 2010; Li *et al.* 2010a; Xu *et al.* 2010; Nypelö *et al.* 2011, 2012; Katayama *et al.* 2012; Lam *et al.* 2012; Shang *et al.* 2012; Obeso *et al.* 2013; Samyn *et al.* 2013; Soboyejo and Oki 2013; Yin *et al.* 2013). In some cases such treatments can be justified in terms of antimicrobial effects (Lam *et al.* 2012; Kramar *et al.* 2013). An unusual approach was taken by Lindström *et al.* (2008), who used a nanoclay coating on cellulosic fibers as a means of reducing inter-fiber flocculation during the preparation of fiber-reinforced polymer composites. The cited authors attributed the easy separation between the fibers to the easy separation of the montmorillonite clay layers.

Work reported by Werner *et al.* (2010) deserves special note, since these authors achieved a high score of 22 in Table A. The rapid expansion of supercritical CO_2 was used as a means of dividing crystalline wax into extremely small particles. A paper surface was thereby rendered highly hydrophobic by use of relatively cheap materials and a modest input of energy. The same high score was assigned for the work reported by Hu *et al.* (2009c), who coated $CaCO_3$ particles with fatty acid, taking advantage of the relative stability of calcium carboxylates. Nypelö *et al.* (2011), who received a high score of 21 for the cited work, derivatized nano-$CaCO_3$ with ASA, thus achieving effects closely related to those reported by Hu *et al.* (2009c).

Nanoparticle in-situ generation: In-situ generation can be regarded as a promising strategy for fixing nanoparticles to various surfaces. In the case of metal nanoparticles this is often accomplished by metal ion reduction, nucleation, and growth into particles (Uddin *et al.* 2014; Arcot *et al.* 2014b; Nypelö *et al.* 2014). The idea is that mechanical interlocking or chemical fusing might occur as a solid material is being formed in contact with a surface. Several studies have been published in which such an approach has been employed so that nanoparticles are affixed to cellulosic surfaces (Son *et al.* 2006; Shin *et al.* 2007, 2008; Khalil-Abad and Yazdanshenas 2010; Liu *et al.* 2010b; Mulinari *et al.* 2010; Boufi *et al.* 2011; Wang and Piao 2011; Klemencic *et al.* 2012; Martins *et al.* 2012; Wang *et al.* 2012; Costa *et al.* 2013; Martins *et al.* 2013). For instance, noble metal nanoparticles can be formed in place on cellulosic surfaces, with possible applications in promoting electrical conductance or resistance to bacteria (Son *et al.* 2006; Shin *et al.* 2008; Boufi *et al.* 2011; Klemencic *et al.* 2012; Martins *et al.* 2012). Though such *in-situ* generation might be viewed as an effective strategy to place nanoparticles onto cellulosic surfaces, none of the cited works clearly addressed the question of whether equivalent result might have been achieved by separate generation of the nanoparticles followed by their deposition. There is a need for definitive studies to follow up on this kind of work.

Laser ablation

Chitnis and Ziaie (2012) described a strategy by which laser light energy is used to create patterns of hydrophobicity on wax paper. The laser ablation method was used to selectively etch and dissipate wax from fiber surface in certain areas of the paper surface, rendering them hydrophilic. A resolution of about 100 μm was demonstrated. In a second step the paper was treated with a suspension of ferromagnetic particles, which exclusively became distributed to hydrophilic areas.

Atomic layer deposition

Hyde *et al.* (2009) demonstrated an approach in which tetrakis(dimethylamido) titanium (TDMAT) was vapor-deposited onto a cotton fabric surface at 100 °C, under which conditions there was a chemical reaction to form a nano-scale coating of titanium nitride. This so-called "atomic layer deposition" procedure was used to control the adhesion tendencies of biological cells, with possible application for medical implant devices.

Superhydrophobic effects

A surface can be defined as "superhydrophobic" if a droplet of water placed on it assumes an acute contact angle greater than 150° and the sliding angle is less than 10°. An extensive review on the subject can be found in Song and Rojas (2013). Based on publications in this area, the most convenient strategies to achieve superhydrophobicity generally involve two steps (Wang and Piao 2011). The first step involves creation of nano-scale roughness. For instance, such roughness can be established by deposition of nanoparticles (Li *et al.* 2008; Xue *et al.* 2008; Yang and Deng 2008; Gonçalves *et al.* 2009; Hu *et al.* 2009c; Khalil-Abad and Yazdanshenas 2010; Xu *et al.* 2010; Nypelö *et al.* 2011; Shang *et al.* 2012; Wang *et al.* 2012; Liang *et al.* 2013; Samyn *et al.* 2013), by etching (Sahin *et al.* 2002; Balu *et al.* 2008), or by combinations involving polyelectrolyte multilayer deposition (Ogawa *et al.* 2007; Gonçalves *et al.* 2008; Yang and Deng 2008). The second step involves derivatization of the surface with a hydrophobic substance such as a triethoxy-perfluorosilane (Gonçalves *et al.* 2008; Song and Rojas 2013).

Alternatively, the two steps can be combined, as in the work of Aarne *et al.* (2013), who allowed hydrophobic diblock copolymers to deposit as nanoparticles on natural fiber surfaces. In related work, Bayer *et al.* (2009) employed Pickering emulsions, which were prepared by dispersing cyclosiloxanes in water through use of layered silicate particles and a zinc oxide suspension. Chen and Yan (2010) were able to achieve very high levels of hydrophobicity just by deposition of montmorillonite clay that had been hydrophobically treated with alkyl-ammonium surfactant. Hu *et al.* (2009c) employed stearic acid in combination with fine calcium carbonate particles to achieve contact angles greater than 150° on paper surfaces. In the systems just described, rather than adsorbing the hydrophobic substance (*e.g.* stearic acid) onto cellulose directly, these procedures allow hydrophobized particles to become spread over the cellulosic surfaces. Alternatively, hydrophobic material can be deposited onto paper in particulate form. Thus, Werner *et al.* (2010) used the rapid expansion of supercritical CO_2 to achieve a nano-scale distribution of AKD wax particles on paper surfaces to reach water contact angles in the range of 150 to 160°.

Cunha *et al.* (2010a) subjected cellulose fibers to silane treatment, followed by acid hydrolysis in the presence of fluoro-silane moieties. The resulting combination of nano-scale roughness and low-energy surface chemistry resulted in high resistance to both water and non-aqueous fluid. Related work was reported by Li *et al.* (2007).

Effects that Can Be Achieved by Rinsing

Up to this point in the article, attention has been focused on chemical reactions and chemical additives. But there are also many studies that have been carried out in which cellulosic materials were rinsed, washed, or extracted as a means of bringing about changes in surface characteristics. The common feature is that no chemicals are being added to the surface of such systems. Thus, in terms of Table 1, one may anticipate that environmental issues can be minimized. Such research will be briefly reviewed here, with emphasis being placed on the question of whether or not significant changes in surface characteristics were obtained.

Removal of extractives

The presence of extractable materials on cellulosic surfaces can have an adverse effect on bonding with hydrophilic adhesives (Back 1991). Belgacem and Gandini (2005) and Heng *et al.* (2007) reviewed work up to that point dealing with solvent rinsing treatments to remove such extractives. For instance, Bismarck *et al.* (2002) observed that washing with 2% NaOH increased the hydrophilic nature of flax fiber surfaces. Based on changes in zeta potential, one can conclude that the alkaline rinsing resulted in removal of negatively charged species from the fiber. Removal of alkali-soluble materials, including lignin, has been shown to favor the subsequent reaction of such surfaces with other agents, such as silane treatments (Valadez-Gonzalez *et al.* 1999). Figure 18 gives a schematic illustration of how extraction of hydrophobic substances such as fatty and resin acids can be expected to uncover the more hydrophilic hemicellulose and cellulose.

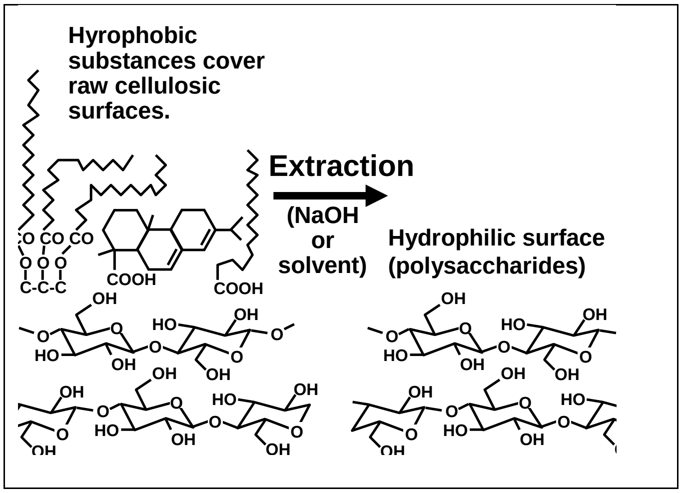


Fig. 18. Schematic illustration of change in surface composition when raw cellulosic material is extracted with alkaline solution or solvent to remove such hydrophobic materials as triglyceride fats, resin acids, and fatty acids

Mercerization

Mercerization can be defined as treatment of cellulosic materials with 10% NaOH while heating to about 80 °C for several hours, followed by rinsing and drying (La Mantia and Morreale 2011). Some indications related to effects of mercerization already might be anticipated from the already-cited work of Bismarck *et al.* (2002), who found that the surface area of fibers generally decreases following treatment with increasing NaOH concentrations, up to 10%. Such treatments tend to disrupt the crystalline nature of cellulose, thus increasing the relative amount of amorphous cellulose, while also making the surface rougher (Albinante *et al.* 2013). As noted by Mohanty *et al.* (2001), hemicellulose can be largely solubilized and removed by such treatment. At the same time, the microfibrils may become more closely aligned to the fiber axis, thus increasing the Young's modulus of the fiber and decreasing its compliance (Kim and Netravali 2010). The same authors also found that mercerization yielded better adhesion of sisal fibers to a soy protein matrix. In summary, although the effects of mercerization clearly involve the whole of the treated material, the surface is profoundly affected both in terms of increased roughness and in terms of composition.

Effects that Can Be Achieved by Mechanical Treatments

Mechanical treatments of cellulosic materials have been considered in other review articles (Htun and Salmén 1996; Li *et al.* 2011a; Naylor and Hackney 2013). With respect to the ratings in Table A, such approaches offer a way to avoid the need to chemically treat a cellulosic surface. Here the focus will be on ways in which mechanical treatments can be expected to affect the chemical nature of the outer surfaces.

Machining

The water-wettability of wood surfaces often can be improved by removing some of the material, for instance by sanding (Gindl *et al.* 2004; Sinn *et al.* 2004; Qin *et al.* 2015). The effect generally has been attributed to the gradual diffusion of hydrophobic monomeric substances from the bulk of natural cellulosic substances to the surface (Swanson and Cordingly 1959). On the other hand, the weathering of wood in the course of its exposure to ultraviolet light often has the reverse effect of depleting the relatively hydrophobic lignin from the surface regions (Teacă *et al.* 2013). In either case, machining can be expected to restore the surface properties to more closely agree with the bulk composition of the wood. Whether or not a beneficial result is achieved can be expected to depend on the chemical composition of the bulk material.

Refining

When wood chips pass between the patterned surfaces of refiner plates, one rotating and the other stationary, the usual objective is to separate the fibers from one another while at the same time minimizing breakage or other damage to individual fibers. Studies have shown that somewhat easier separation can be achieved, along with less reduction in fiber length, if refining is carried out under pressure so that the temperature can be raised above the softening point for lignin (Back and Salmén 1982). It has been shown that the distribution of lignin within the cell wall is highly non-uniform, with the greatest concentration present in the middle lamella, *i.e.* the crust at the outside of fibers that serves to bind them together (Donaldson 2001). This is the principle of thermomechanical pulping (TMP), which is widely employed in preparing fibers for use in newspapers and magazines

(Li *et al.* 2011a). A pressurized system is used during TMP processing so that the temperature can be raised to about 160 to 180 °C (Fernando *et al.* 2011). Another consequence of employing high temperatures during mechanical pulping is that separation between the fibers tends to occur within the lignin phase (Fernando and Daniel 2008), and thus the outer surfaces of TMP fibers tend to be coated with lignin, which is relatively hydrophobic. For example, Fig. 19 shows the relative distributions of cellulose and lignin in beech wood, when viewing the corner region between two adjacent fibers (Röder *et al.* 2004). After cooling, the lignin tends to resist deformation, so that the inter-fiber bonding potential is generally inferior to that of delignified pulps, *e.g.* kraft fibers. Although the effects just described are well known, there does not seem to have been a good way to avoid this situation and still be able to benefit from the relatively high fiber length achieved by high-temperature mechanical processing.

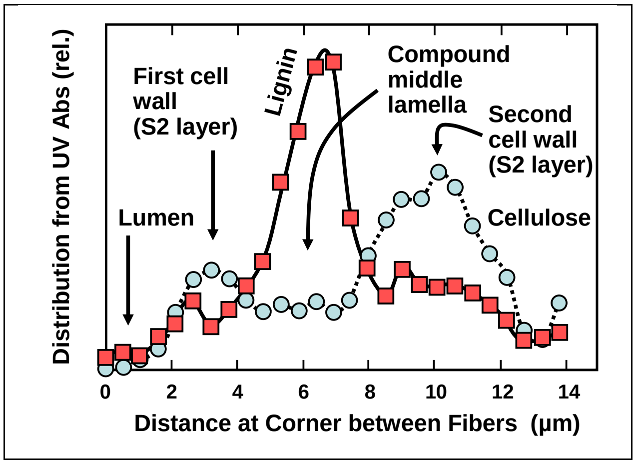


Fig. 19. Relative concentrations of cellulose and lignin *vs.* distance at the corner region between adjacent beech wood fibers, based on ultraviolet light absorption (Röder *et al.* 2004).

Steam explosion

Steam explosion treatment of cellulosic materials involves pressurization in the presence of superheated steam, followed by abrupt depressurization (Mukhopadhyay and Fangueiro 2009). Although some of the conditions are similar, in terms of temperature and moisture, the steam explosion method can be expected to have a different effect on the surface properties of cellulosic material, in comparison to the TMP process just described. That is because steam pressure, rather than a shearing action, is responsible for the creation of the freshly exposed surfaces. The moisture and pressurized steam can be expected to be present especially within fiber lumens. As a consequence, the explosion process can be expected to tear some of the fibers apart from the inside, exposing parts of the biomass that are relatively high in carbohydrate content. Perhaps it is for this reason that steam explosion is often regarded as a beneficial approach to facilitating digestion of biomass by cellulases (Mukhopadhyay and Fangueiro 2009).

Renneckar *et al.* (2006), reported on a novel steam explosion treatment carried out in the presence of polyolefins, *i.e.* a reactive steam-explosion process. The fibers became coated with a polyolefin layer, presumably due to a combination of acid-catalyzed depolymerization of wood components, incipient oxidation of the polyolefin, and mobilization of polymer segments.

Katayama *et al.* (2012) described a related method in which cotton fibers were first immersed in water, then pressurized with supercritical CO_2. Abrupt reduction of pressure to ambient conditions imparted a wrinkled morphology to the fibers.

Effects that Can Be Achieved by Heating

Yet another class of treatments that has potential to change the nature of the surface of cellulosic materials involves heating, which can range all the way from mere drying, to torrefaction, to carbonization, or to hydrothermal treatment or melting. Again, the general effects of heating of cellulosic materials are well known (Esteves and Pereira 2009; Pelaez-Samaniego *et al.* 2013), but attention here will be focused on surface effects. From the standpoint of the green nature of surface modification, any strategy that calls for heat treatment will require the input of energy, which can be regarded as an adverse contribution to the environment. But the presumption here is that such impacts often will be less significant in comparison to more aggressive, chemical-based modification means.

Heat application during drying

Studies have shown many cases in which the drying of cellulosic materials at moderate temperatures gives rise to measurable increases in hydrophobicity (Ibrahim *et al.* 2013b). A common explanation for such changes is that monomeric components become redistributed. In particular, lipophilic materials such as wood resins can become enriched at the air-solid interface, yielding an increase in hydrophobic character as a consequence of heating (Swanson and Cordingly 1959). Greater hydrophobicity has been observed, especially if the cellulosic material is heated to the range of about 200 to 300 °C, *i.e.* torrefaction (Stelte *et al.* 2012). A decrease in solid mass during torrefaction (Stelte *et al.* 2012) suggests that such changes in surface behavior may be attributed to the volatilization and loss of byproducts from hemicellulose, which is the most water-loving of the main components of cellulosic materials.

The strong capillary forces at work during the drying of cellulosic materials, in combination with the plasticization provided by moisture at elevated temperatures, can bring about some essentially irreversible changes in the material (Stone and Scallan 1966; Weise 1998). In particular, mesopores within the cell walls of delignified fibers tend to close up during drying, and not all of them re-open when the system is placed back into water (Weise 1998). The hard-to-reopen nature of such effects has been attributed to the coalescence between adjacent crystalline cellulose surfaces, *i.e.* a “healing” effect at the interface between crystallites so that larger crystallites are formed (Pönni *et al.* 2012). Thus, a cellulose-rich surface that has been subjected to drying can be expected to be less swellable in water, possibly affecting its interactions with aqueous glues or coatings.

Carbonization

Though sufficiently strong heating to convert cellulosic material to carbon form is clearly not just a surface treatment, the effects of such processing on surface properties are obvious. The hydrophobic nature and high surface area of carbonized materials – especially in the case of activated carbon products – have been reviewed elsewhere (Marsh 2006; Chowdhury *et al.* 2013). Briefly stated, biochar materials are dominated by multi-ring, aromatic carbon structures, which tend to be hydrophobic. Ali *et al.* (1990) showed that pyrolysis of Douglas fir bark at increased temperatures above 575 °C resulted in increasing crystalline content, although the nature of the crystal was not identified.

Melt processing

Different effects of heating can be achieved in cases where a thermoplastic laminate or coating layer has been applied to a cellulosic material. The plastic material can become tightly attached to the base material, presumably because of mechanical interlocking. For instance, Seto *et al.* (1999) employed a melting process to affix poly(ethylene glycol)-coated polystyrene nanospheres to cellulose film. The coated film was highly hydrophobic. The subject of laminations using plastic materials has been reviewed (Mangaraj *et al.* 2009).

PRACTICAL IMPACTS OF SURFACE MODIFICATIONS

Cellulosic materials continually face competition from various plastic or metal alternatives. Even though it may be possible to alter the surface characteristics of a given cellulosic material to make it suitable for a selected application, not all such strategies will be cost-effective. Those that are too expensive, too difficult to implement, or inadequate in their effects are likely to be ignored, since they will not be able to gain market share relative to other competing materials. This section will explore three different general approaches to dealing with such competition. The first approach takes advantage of the eco-friendly nature of cellulosic materials. By employing modification procedures that are likewise eco-friendly, there is potential to strengthen a marketing advantage. Secondly, the competition against other materials can be handled by addressing a specific area in which some of the most eco-friendly surface modification methods are most vulnerable, *i.e.* the issue of durability. The challenge is to achieve greater durability of changes induced by surface treatment without abandoning either the cost-effectiveness or the environmentally friendliness of a particular approach. Thirdly, there will be product categories in which surface-modified cellulosic materials can successfully compete against over-engineered and overly expensive alternatives – cases in which the properties of materials currently being used for some application exceed what the user really needs. Such situations are ripe for implementation of disruptive innovations (Evans 2003), a strategy in which a cheaper alternative, even if it has lower performance in key aspects, has potential to gain market share.

Strategies to Reduce Environmental Impact

As was already shown in Table A, published strategies for modifying cellulosic surfaces show great diversity with respect to their environmental favorability. The criteria that can be used to form a preliminary judgment regarding different treatment procedures are the same as those that are used in formal life cycle assessment studies (Ciambrone 1997; Bauman and Tillman 2004). As noted by Anastas and Warner (1998), considerable improvements relative to “green chemistry” can be achieved by avoiding the use or generation of hazardous substances and by minimizing the number of processing steps – especially in procedures that require usage of toxic or non-renewable materials.

Minimizing solvent use and toxicity

Based on the rating scale used in preparing Table A, some of the most advantageous systems for modification of cellulosic surfaces involve either aqueous media or gas-phase applications. Though aqueous systems are clearly effective for certain of the treatments shown in the table, there are countless chemical reactions that require non-aqueous conditions. Suppose, for instance, that one's goal is to achieve some highly controlled grafting effects – the type that ordinarily require the use of non-aqueous media such as toluene solutions (Tizzotti *et al.* 2010). For potential high-tonnage applications it may be simply too expensive to place cellulosic materials into such media, since one then needs to carry out further processing to thoroughly remove the solvent. A way to get around this dilemma may be to carry out key parts of the treatment – those requiring the use of solvents – in preparation of intermediate treatment agents that can be applied in aqueous media. An excellent example of such an approach is the previously mentioned derivatization of carboxymethylcellulose (CMC) with an azide function (Filpponen *et al.* 2012). The use of solvents in such a treatment is of lesser concern, since the amount of CMC is typically only 1% or less of the amount of cellulosic material to be treated. Under suitable aqueous conditions the derivatized CMC can be made to adsorb strongly to cellulosic surfaces. Then, in a subsequent reaction, the azide functionality will undergo azide-alkyne cycloaddition click reactions, which can be carried out under relatively benign aqueous conditions.

Reactions not requiring a catalyst sometimes can be carried out in the vapor phase, and as shown by the rating results in Table A, some gas-phase treatments received very favorable overall ratings. Some particularly notable treatments, in this regard, are the esterifications by means of anhydrides (Yuan *et al.* 2005). Inherent advantages of anhydrides, relative to some other approaches of creating ester attachments to cellulosic surfaces, include moderate temperatures of reaction (compared to using the corresponding fatty acids), the avoidance of HCl off-gasing (compared to the use of acid chlorides), and the achievement of covalent bonding to surfaces rich in –OH groups. Tri-ethoxysilanes also seem to be especially well suited for gas-phase treatments (Taipina *et al.* 2013).

Assuring biodegradability

In principle, if one derivatizes a biodegradable material with a non-biodegradable substituent, then the product will be more difficult to be digested by natural enzymes (Simoncic *et al.* 2010). A rating of "-" was assigned, for instance, when applying a relatively thick layer of tetrafluoroethylene (Daoud *et al.* 2006). However, as can be seen from Table A, relatively few of the treatments described in the literature were assigned unfavorable ratings of "-" for the criterion of biodegradability. Rather, the neutral rating of "0" was assigned in a great many cases. The reasoning for such a tolerant approach to rating in such cases was based on the results of composting studies. Notably, it has been found that even a rather thick and highly non-biodegradable layer such as polyethylene sheeting merely slows down the biodegradation of an adjacent cellulosic material under composting conditions (Sridach *et al.* 2006, 2007). Also, as noted earlier, esterification of surface groups of cellulosic materials causes only a moderate delay in biodegradation (El Seoud and Heinze 2005; Ly *et al.* 2010; Puls *et al.* 2011). In summary, in typical cases, modifying the surface of cellulosic material is not expected to render the whole of the material to be completely biodegradable.

What happens if one mixes a moderate amount of surface-modified cellulosic material into a non-biodegradable matrix such as recycled polyethylene? Does such mixing render the whole of the material degradable? Consider, for instance, the filled plastic composite materials that are increasingly being used for patio decking, park benches, and playground equipment (George *et al.* 2010). Some decomposition of the cellulosic reinforcing elements in such composites has been reported (Darabi *et al.* 2012; Moya-Villablanca *et al.* 2014), which lowers the quality of such items. However, composting generally is not a viable option at the end of the useful life of composites that are primarily composed of a non-biodegradable plastic. A better option, from an environmental standpoint, may be to use an effective treatment with a coupling agent so that water permeation is minimized and the useful life of the composite material is extended.

Waste avoidance

As has been pointed out by Anastas and Warner (1998), many manufacturing schemes that have been used for many years to manufacture chemical products result in large proportions of waste byproducts. The good news, from the perspective of modifying the surfaces of cellulosic materials, is that the desired chemical structures are often much simpler than, say, the pharmaceutical products that are emphasized in the cited book. However, as can be appreciated from the ratings assigned to waste avoidance in Table A, there is definitely potential to select less waste-producing manufacturing schemes for surface treatment of cellulosic materials. For instance, several authors have proposed using a layer-by-layer adsorption of polyelectrolytes having alternate signs of charge (Decher 1997; Lvov *et al.* 2006; Lingström *et al.* 2007; Renneckar and Zhou 2009; Li *et al.* 2011b, 2012; Lin and Renneckar 2011a,b; Illergard *et al.* 2012). The laboratory procedures for most such treatments call for rinsing with pure water or fresh saline solution between each macromolecular layer – which would potentially result in huge volumes of wastewater that need treatment if the system were scaled up to commercial production. Short-cuts, such as skipping of rinsing stages, would be expected to reduce the purity of the successive polyelectrolyte layers. There is a need for research to determine when such impurity of successive layers is likely to interfere with the mechanism of layer-by-layer deposition.

Recyclability

Many cellulosic products are inherently recyclable. For example, once a paper product is no longer needed, most of its content usually can be recovered and used for the production of a new generation of paper. The proportion of used paper in the US that becomes recycled now exceeds 65% (Riebel 2013). Likewise, used wood material from construction and demolition wastes can be used again, especially for such applications as particleboard (Hubbe 2015). By contrast, the cellulosic material is much less likely to be recycled if it has been finely divided and then modified to render it hydrophobic. Hydrophobic fibers would be poorly suited for papermaking applications due to their poor inter-fiber bonding ability. On the other hand, the incorporation of hydrophobized cellulosic material as a reinforcement in a plastic matrix (a composite application) makes it less likely that the plastic will be recycled. Though it may be theoretically possible to melt and re-form certain thermoplastic materials, it would be difficult to know the optimum processing conditions for each scrap of waste material. If the reprocessing temperature is set high enough to be able to melt most plastics, including polyamide-6, one could then expect thermal degradation of any cellulosic reinforcing materials (Li *et al.* 2012b). So, in at least one application, hydrophobic surface modifications are likely to be unfavorable relative to the likelihood of reuse of cellulosic materials.

Not damaging the cellulose

Certain kinds of treatments have potential to seriously diminish the strength of cellulosic materials. Examples include cellulase enzymes and strong acid solutions. Ideally, when one’s goal is to modify a cellulosic surface, it is important to avoid changes to the bulk material. In other words, surface-specific effects are sought. This can be achieved, for example, by tethering the reactive function to a relatively large molecular structure, thus limiting the reactions to near the outer surface of the material being treated (Pelton *et al.* 2011). By contrast, damaging effects have been observed when esterifying cellulosic surfaces by means of acid chlorides (Pasquini *et al.* 2008), an effect that was attributed to the release of HCl during the reaction. Fortunately, as can be seen from Table A, there appear to be a great many treatment options that do not tend to damage the bulk cellulosic material.

Strategies to Improve Robustness

For a variety of reasons various treatment systems listed in Table A were classified as having low ("-") or intermediate ("0") degrees of durability. Reasons for lack of durability can include inherently labile covalent bonds (Wilson *et al.* 2014). In addition, many of the modification procedures evaluated in published works involve mere physical adsorption of the treatment agent onto a cellulosic surfaces; in other words, there are no covalent bonds attaching the agent to the cellulosic surfaces in such cases. This section will consider strategies to render such systems more durable, meaning that modifications to the surface properties are more likely to withstand rinsing and other challenges associated with their intended usage.

Selection based on resistance to hydrolysis

As shown by Abdelmouleh *et al.* (2002), adsorbed material that is not covalently bonded to a cellulosic surface often can be easily removed. In the cited case, a highly durable modification was achieved upon heat-curing of the agent, a prehydrolyzed alkoxysilane. However, certain ester-type bonds are known to be more susceptible to hydrolysis than others (Cunha and Gandini 2010). For instance, Cunha *et al.* (2006) employed trifluoroacetic anhydride to esterify the surface of cellulosic fibers. They found that the original hydrophilic nature of the fibers could be restored by exposure to neutral water at room temperature for 1 to 7 days. One way to address such vulnerability involves modifications in the chemical structure of the esterifying agent (Cunha and Gandini 2010).

Ways to enhance durability of physical adsorption

When employing physical adsorption as a means of modifying a cellulosic surface, ionic attractions provide an initial approach to improving the durability. Already, in earlier sections, it was noted that cationic surfactants have a relatively high affinity for cellulosic surfaces (Biswas and Chattoraj 1997; Alila *et al.* 2005). This affinity can be attributed to the generally negative charge of cellulosic surfaces in their untreated state (Herrington and Petzold 1992a,b). As has been shown, such affinity can be further enhanced by increasing the density of negative charges on the cellulosic surface (Alila *et al.* 2007; Salajkova *et al.* 2012; Johnson *et al.* 2011; Syverud *et al.* 2011). This can be achieved by oxidation, *e.g.* by use of the TEMPO-mediated oxidation system (Saito *et al.* 2005). Another approach would be to employ a cationic polyelectrolyte, such that the treatment agent has multiple points of contact between opposite charges (Wågberg 2000).

One potential enhancement in the case of treatment with certain cationic surfactants is the possible formation of amide groups; for instance Benkaddour *et al.* (2014) used amidation to attach stearylamine molecules to carboxyl groups on a TEMPO-oxidized cellulosic surface. Similar approaches were reported by Johnson *et al.* (2011) and Yang *et al.* (2014).

Self-association

As a way to account for the moderate durability even in the case of mere adsorption of cationic surfactants, it has been proposed that the adsorbed surfactant molecules can interact with each other such as to reinforce the stability of the monolayer film (Alila *et al.* 2007; Renneckar 2013). In particular, the adsorbed surfactant molecules are expected to line up such that the hydrophobic groups pack together in a thermodynamically stable arrangement (Penfold *et al.* 2007). For instance, surfactant molecules having sufficiently long alkyl tails are known to adsorb in the form of hemi-micelles or densely-packed contiguous monolayers (Alila *et al.* 2007). Such arrangements of molecules have the potential to decrease the chance that an individual molecule will desorb from the surface.

Three-dimensional linkages within surface layers

To achieve an even more permanent fixation of adsorbed molecules onto a cellulosic surface, another option is to somehow crosslink the adsorbed molecules together. For instance, Boufi and Gandini (2001) first adsorbed cationic surfactants having unsaturated groups, *i.e.* alkenyl functions. Then, free-radical polymerization was induced to connect the surfactant molecules together. The polymerization among the surface groups not only increased the durability of the modification, but also the hydrophobic nature of the treated surface was enhanced. Results reported by Dankovich and Hsieh (2007) suggest that similar enhancement can be achieved by heat-curing of certain surfactants; it is not certain whether the reported effects were due mainly to enhanced ester formation with surface groups or whether some form of polymerization also took place. Effects described by Gaiolas *et al.* (2009), involving treatment of cellulosic fibers with the unsaturated compounds myrcene and limonene with use of cold plasma, may have a similar explanation.

As noted by Alf *et al.* (2010), the durability of certain layers applied by chemical vapor deposition can be enhanced by use of grafting reactions. In principle, such reactions can take place either among the deposited materials or with cellulosic surface groups. Kuroki *et al.* (2013) employed 3-dimensional grafting to achieve a durable and self-healing surface layer of polymer brushes on various surfaces.

Xie *et al.* (2010b) noted that silane coupling agents interact in such a way as to form a “grid” of condensed material on cellulosic surfaces. Even though the initial Si-O-C bonds linking the silane moieties to the cellulosic surface are unstable to hydrolysis, the condensed structures can be suitably durable. There is opportunity to consider analogous strategies to achieve durable fixation of other agents that lack strong covalent attachments to the cellulose surface.

Disruptive Innovations

Sometimes as a consequence of surface modification, a cellulosic material can be rendered capable of playing a role that usually would have been limited to other kinds of materials, such as plastics. Such circumstances raise the possibility that cellulosic materials might be able to replace those materials in some applications. In other words, there can be opportunities for disruptive innovations (Christensen 2003).

Overqualified materials

Though plastic materials often display outstanding suitability for various challenging applications, there are many situations in which the properties of plastics may exceed what is actually required for the situation. For instance, there are many practical applications in which the effects of surface modification do not need to persist for more than a short time. One of the most striking examples of this is air-plasma treatments aimed at increasing the surface energy of cellulosic material, usually for purposes of achieving better adhesion to another surface (Back 1991; Mukhopadhyay and Fangueiro 2009; Vesel and Mozetic 2009). It is a common practice to apply such "corona" treatments immediately before such operations as lamination in order to benefit from the presence of activated groups before the cellulosic surface reverts back to its initial condition (Vesel and Mozetic 2009). Presumably, if the surface properties of a material need only to remain in their optimal condition for a few seconds, during a critical phase of the processing, then it may be wasteful to use a material that retains those properties in the long term. So the main point may not be to achieve long-term durability, but merely an effect that lasts long enough to be useful during a processing step.

An argument can be made that during the preparation of a cellulose fiber-reinforced thermoplastic composite the initial wetting of the cellulosic surfaces is more critical than issues related to the chemical stability of covalent bonding of coupling agents or compatibilizers that were used to enhance wetting and adhesion. The reason for this assertion is that successful wetting of the surface during preparation of the composite is necessary in order to achieve molecular-scale contact between the phases (Baldan 2012). Soon after the wetting of the cellulosic surfaces by the melted plastic takes place, the temperature is reduced, thus essentially freezing the composite into a fixed structure. Even if the original covalent bonds at phase boundaries are somewhat labile or reversible, the system is likely to remain intact and strong, due to such factors as mechanical interlocking, van der Waals forces, acid-base forces, and various transient or remnant covalent bonding effects (Leite *et al.* 2012).

Efforts to increase the tear strength of paper provide a further example in which a seemingly less satisfactory surface effect can sometimes lead to a better outcome. It is well known that the addition of bonding agents such as cationic starch before the formation of paper can increase such strength properties as the tensile force required for rupture (Formento *et al.* 1994). But results discussed in the cited work also provide an example in which refining strengthened the bonding between fibers and simultaneously caused a decrease in the tear strength of the paper. Salam *et al.* (2013) likewise observed decreased tearing strength when adding chitosan-complexed starch nanoparticles as a bonding agent in paper. This type of effect can be attributed to an increased tendency toward brittle failure in cases where the fibers are more strongly bonded to each other. In such cases the breakage event is restricted to a narrow zone or crack. By contrast, a suitably low degree of bonding between fibers in a paper structure will allow the failure event to be spread out over a wider zone, thus consuming more energy before breakage occurs (Karenlampi 1996).

Water resistance

Another application in which relatively short-term modification of cellulosic surfaces may be well suited is in the manufacture of paper. To consider one illustrative example, the hydrophobic sizing agent alkenylsuccinic anhydride (ASA) is widely employed when manufacturing paper products intended for the exclusive use on laser printers (McCarthy and Stratton 1987). Since laser printers operate based on the principles of xerography, which literally means "dry writing," there is no apparent need for a hydrophobic character of the paper surface during its main application. Rather, many papermakers like to use ASA sizing during manufacture of such products as a way to improve the operating efficiency of the papermaking process and to limit permeation of starch solution into the paper during size-press treatments (Aloi *et al.* 2001). Although ASA treatment involves formation of covalent bonds with the paper surface, the treatment is somewhat vulnerable due to the presence of C=C double bonds in the hydrophobic part of the attached molecule, a situation that has potential to lead to loss of hydrophobicity when paper is exposed to air-borne oxidants.

Inkjet printing provides a well-known example in which modification of a cellulosic surface needs to remain in a modified state only for a brief period of time, often a minute or two after the paper comes out of a package. Delayed wetting of a paper surface is important in such applications to avoid a feathered appearance of the printed image and in order to achieve a suitably high print density by keeping the ink near to the surface of the paper (Barker *et al.* 1994). In this regard, the ASA sizing system, which is most often employed in manufacturing such paper products, may be somewhat over-engineered, providing a hydrophobic character that is more persistent than needed. Such circumstances raise prospects that another disruptive innovation will come along that is sufficient to achieve useful effects at a lower cost.

A papermaking approach

The emphasis of this review article up to this point has been on ways to modify the surfaces of cellulosic materials. But it is important to point out that the need for surface modification sometimes can be rendered unnecessary by employing processes and materials that are well-suited to the untreated surfaces of cellulosic source materials or their somewhat purified forms, *e.g.* kraft fibers, microcrystalline cellulose, and the like. Papermaking technology provides numerous examples of situations in which the hydrophilic nature of cellulosic surfaces is well suited for achieving such goals as strong inter-fiber bonding, good adhesion to printing inks, and ability to absorb water.

Even from the perspective of the papermaking process, one encounters many situations in which it can be advantageous to either modify the charged nature of the surface or to cover the cellulosic fibers with something that will enable yet stronger bonding to occur (Hubbe 2006, 2014). Such considerations bring reminders of some key themes that have been brought out in this review article, such as the importance of adsorption by polyelectrolytes (Wågberg 2000). It has been shown that high levels of polyelectrolyte adsorption can be achieved, leading to very high increases in paper strength, when forming polyelectrolyte complexes *in situ* during agitation of a fiber suspension (Lofton *et al.* 2005). But in addition, papermakers rely to a great extent on the transient effects of adsorption of multivalent inorganic ions, such as those associated with aluminum sulfate (Arnson and Stratton 1983). The stagewise hydrolysis and adsorption of the aluminum ions, resulting in changes in the electrical charge of a cellulosic surface, is illustrated in Fig. 20 (see Guide 1959; Strazdins 1989; Bi *et al.* 2004). The effects of such treatment are not durable, but they allow processes such as the deposition of colloidal mater onto cellulosic fibers to occur in the last seconds before formation of a paper sheet.

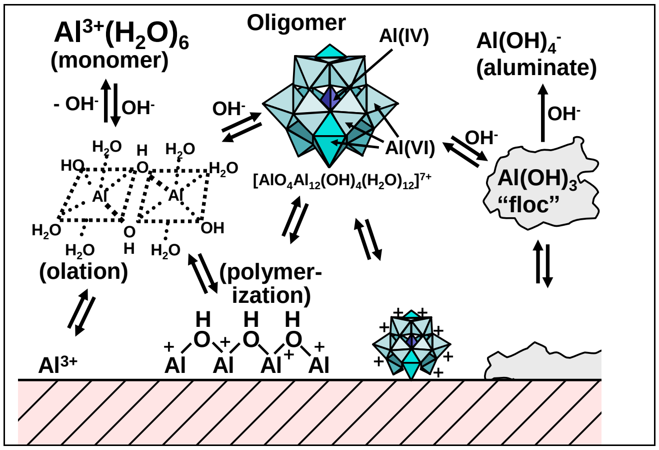


Fig. 20. Schematic illustration of species of aluminum present in solution, as a function of interaction with OH^- ions and adsorption or deposition onto a cellulosic surface

Two kinds of innovation seem especially promising. On the one hand, papermaking technology teaches that many highly promising goals can be achieved by surface modifications that are completed in fractions of seconds. Such "on the fly" transient modifications, which enable processing to occur effectively, have the potential to be adopted in other industries. Secondly, there may be opportunities for the traditional cellulosic product industries to branch out into various advanced product niches by employing some of the more exotic surface treatment approaches that have been discussed in this article. Living polymerization methods (Roy 2006; Tizzotti *et al.* 2010; Kalia *et al.* 2013) have potential to enable cellulosic materials to serve as the platform for various high-tech applications, such as in sensing technology (Lam *et al.* 2012). So, whatever is one's perspective regarding the modification of cellulosic surfaces, there is more than enough research work to keep researchers busy for many years to come.

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APPENDIX

TABLE A – Modification Procedures for Cellulosic Surfaces and their Environmental Implications

(++ = highly favorable; + = favorable; 0 = neutral or unknown; - = unfavorable; -- = very unfavorable)

Substrate	Modification system	Green origin of treatment	Avoids harmful solvents	Avoids toxic materials	Minimizes energy use	Biodegradable	Avoids material waste	Avoids petrochemicals	Product can be recycled	Does not hurt cellulose	Scale-up-friendly	Durable surface changes	Big effect on wettability	Overall score	Research highlights	Citation (year)
Cellulose	Silane coupling	-	0	-	-	0	-	-	0	0	0	0	+	8	Prehydrolyzed alkoxysilanes were adsorbed onto cellulose fibers in ethanol/water mixtures.	Abdelmouleh *et al.* 2002
Cellulose	Mercerization	-	+	0	0	+	+	+	+	0	+	+	0	18	Changes the crystallinity and roughens the surface.	Albinante *et al.* 2013
Various	Chem. Vapor deposition	-	+	0	+	0	+	-	-	0	+	+	0	14	Can be done at low temperature and modest vacuum, *e.g.* for paper.	Alf *et al.* 2010
Oxidized cellulose	Cat. surfact. after TEMPO	0	+	+	+	0	+	+	+	+	+	0	+	21	Admicelles and hemimicelles are formed.	Alila *et al.* 2007
Cellulose fibers	Cationic surfactant	0	+	+	+	0	+	+	+	+	+	-	+	20	Self-assembly shown.	Alila *et al.* 2005
Microfibril. cellulose	Silylation, CDMIPS	-	0	-	-	0	-	-	-	0	0	0	++	9	Superhydrophobicity was achieved at high treatment.	Andresen *et al.* 2006
Cellulose nanofibers	Acetylation	+	-	0	-	0	-	+	0	-	+	+	+	13	Acetic anhydride reagent with pyridine catalyst. Crystallinity decreased. Became hydrophobic.	Ashori *et al.* 2014
Wood	Oxidation	+	+	0	0	+	+	0	0	0	+	+	0	12	Oxidation promotes glue bonding, partly by removing wax and fatty acids.	Back 1991

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Cellulosic fibers	Silanes: functionalized	-	+	0	-	0	+	-	-	0	+	+	++	15	Superhydrophobic “roll-off” and “sticky” effects shown.	Balu *et al.* 2008
Bionano-composites	Pickering emulsions	0	+	0	+	0	-	-	0	+	+	-	+	14	Clay nanoparticles are applied with silane emulsified in water.	Bayer *et al.* 2009
Various reviewed	Corona discharge	-	0	-	-	0	+	-	0	-	+	+	0	10	Corona treatment generates radicals that can last for minutes and allow grafting.	Belgacem & Gandini 2005
Various reviewed	Covalent bonds	0	-	-	-	0	0	-	-	0	0	+	+	9	Notes that covalent bonds provide the best resistance to water.	Belgacem & Gandini 2005
Cellulose membrane	Lipid nanoparticles	+	+	+	+	+	0	+	0	+	0	-	+	19	Lecithin-trisearin nanoparticles from homogenization were imbedded in regenerated cellulose of membrane.	Benavente *et al.* 2010
Cellulose hydrogel	Long-chain amidation	0	+	0	0	0	0	0	0	0	-	+	+	14	TEMPO-oxidized cellulose reacted with long-chain amine with carbodiimide and hydroxy-succimide as catalyst	Benkaddour *et al.* 2014
Cellulose fibrils, NCC	Gas-phase esterification	+	0	-	-	0	-	+	0	0	-	+	+	12	Palmitoyl chloride reaction starts at outside of cellulose crystals	Berlioz *et al.* 2009
Cellulose	Cationic surfactants	0	+	+	+	+	+	0	0	+	+	-	+	19	Adsorption isotherms were obtained on pure cellulose.	Biswas & Chattoraj 1997
NCC	Esterification	-	-	-	-	0	-	-	0	0	-	+	+	7	Methyladipoyl chloride compared with acetic and sulfuric acid treatment for solvent dispersibility.	Blachechen *et al.* 2013

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Cellulose sheets	UV-induced grafting	-	-	-	0	0	-	-	0	0	-	+	+	8	UV-grafting of fluorinated acrylic chains did not hurt bulk properties.	Bongiovanni *et al.* 2011
Cellulose films, fibers	*In-situ* gen. of Au, Ag	-	-	-	-	0	-	-	0	0	-	+	0	6	Amination pretreatment provides seed coordination sites.	Boufi *et al.* 2011
Cellulosic surfaces	Admicellar polymerization	-	+	-	+	0	+	-	0	+	0	+	+	15	Three steps of adsorption, co-adsorption, & polymerization.	Boufi & Gandini 2001
Cellulose thin films	Porphyrin grafting	-	-	-	-	0	-	-	0	0	-	+	+	7	Carbonyldiimidazole used to activate surfaces for porphyrin grafting.	Boufi *et al.* 2008
Paper	Esterification	+	+	+	+	0	+	+	+	0	+	+	+	22	Single-step hydrolysis and esterification of amorphous cellulose with HCl and organic acid.	Bourbonnais & M-archessault 2010
CNC	Esterification & diminution	0	+	-	-	0	-	0	0	-	0	+	+	11	HCl with acetic or butyric acid to make esterified nanocrystals.	Braun & Dorgan 2009
Cotton or paper	Layer-by-layer	-	-	0	0	0	-	-	0	+	-	-	0	7	Azlactone polymer	Buck and Lynn 2010
Various reviewed	Ring-opening polymerization	-	-	0	0	0	0	-	0	0	-	+	+	10	Grafting of cellulose with caprolactone or L-lactide.	Carlmark *et al.* 2012
Cellulose fibers	Organosilanes	-	-	-	-	0	-	-	0	0	+	+	+	9	Conditions required for coupling evaluated.	Castellano *et al.* 2004
NCC	Poly-capro-lactone	-	0	-	-	0	-	-	0	0	-	+	+	8	Increased water resistance found.	Chen *et al.* 2009
Bleached SW kraft	Organo-clay adsorption	+	+	0	+	0	+	0	0	+	+	-	+	18	Nano-scale roughness gave high hydrophobicity.	Chen & Yan 2012
Bacterial cellulose	Amidoximated	-	+	-	-	0	-	-	0	0	0	+	0	9	Alkaline treatment with isocyanate to produce urethane linkage.	Chen *et al.* 2010

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Cellulose nanofibers	Saponin adsorption	+	+	+	+	+	0	+	+	+	-	-	0	18	Adsorption of natural saponins on cellulose nanofibers.	Cherian *et al.* 2012
Paper	Magnetic nanoparticles	-	+	+	-	0	0	+	-	-	0	+	0	12	Nanoparticles applied by CO_2 laser ablation	Chitnis & Ziaie 2012
Jute fibers	Oleoyl chloride	+	-	-	-	0	-	-	0	-	-	+	+	8	Applied in swelling & nonswelling solvents, yielding esterification	Corrales *et al.* 2007
Paper & bacterial cellulose	ZnO nano-structures	-	+	+	0	0	+	+	0	+	+	+	-	17	Precipitation from aqueous solution, then heat-dried (100 °C).	Costa *et al.* 2013
Cellulose fibers	Trifluoroacet-ylation	-	-	-	-	0	-	-	-	0	-	0	+	5	Esterification with trifluoroacetic anhydride with toluene & pyridine.	Cunha *et al.* 2006
Cellulose fibers	Silane, then acid hydrol.	-	-	-	-	0	-	-	0	-	-	+	+	6	Inorganic coating of linear Si-O-Si- applied.	Cunha *et al.* 2010a
Cellulose fibers	Gas-phase silanization	-	+	-	-	0	0	0	0	0	+	+	+	13	Gaseous trichloromethylsilane treatment.	Cunha *et al.* 2010b
Cellulose fibers	Trichloro-methylsilane	-	+	-	0	0	0	0	0	0	+	+	+	14	Gas-solid reaction use to prepare hydrophobic fibers.	Cunha *et al.* 2007a
Cellulose fibers	Trifluoroacet-ylation	-	+	-	0	-	0	0	-	0	+	0	+	11	Hydrolytic stability tested.	Cunha *et al.* 2007b
Cellulose fibers	Pentafluoro-benzoylation	-	-	-	-	-	-	-	-	0	-	+	+	5	Pentafluorobonzolization from solvent.	Cunha *et al.* 2007c
Natural fibers	Nanocellulose	+	0	+	0	+	-	-	0	+	-	-	+	13	Esterification proposed between nanocellulose and fiber surfaces.	Dai & Fan 2013
Cotton	Triglygerides transesterific.	+	+	+	0	0	+	+	0	0	+	+	+	20	Authors emphasize the green chemistry of their approach.	Dankovich and Hsieh 2007

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Cellulose fibers	Pulsed laser depos. PTFE	-	+	0	-	-	+	-	-	0	-	0	++	11	Teflon film was laser-deposited, as shown by preliminary work.	Daod *et al.* 2006
Cellulose	Phenoxyacetyl ester, etc.	-	0	0	-	0	-	0	0	-	-	+	+	9	Alkaline de-esterification with $FeCl_3$ used for analysis of substitution.	Dixon *et al.* 1979
MCC	Soybean oil	+	0	+	0	+	0	+	0	+	0	+	+	19	Ethanol solution, 100 ºC; destroys crystallinity; esterification proposed.	Dong *et al.* 2013
Nano-crystals	Long-chain grafting	0	-	0	-	0	-	-	0	0	0	+	+	10	This review article considers grafting strategies.	Dufresne 2010
Cotton	Fluorosilane	-	0	-	-	0	0	-	0	0	+	+	++	13	Superhydrophobic cotton was prepared by silane treatment.	Erasmus & Barkhuysen 2009
CNC	Azide, then ferrocene	-	-	-	-	0	-	-	0	0	-	+	+	7	Grafting with ethynylferrociene onto azide functionalized cotton-derived CNC.	Eyley *et al.* 2012
Cellulosic surfaces	Click: azide-mod. CMC	0	+	0	-	0	+	-	0	+	0	+	+	15	Cellulosic surfaces can be treated by adsorption of azide-modified CMC, which enables subsequent efficient graftin under ambient conditions.	Filpponen *et al.* 2012
Cellulose fibers	Fatty acid chlorides	+	-	+	-	0	+	0	0	-	0	+	+	14	Heterogeneous reaction with carried out with acid chloride in a toluene solution with pyridene	Freire *et al.* 2006
Cellulose nanofibrils	Poly-(ethylene glycol) graft	-	-	-	-	0	-	-	0	+	-	0	+	7	Ion-exchange attachment	Fujisawa *et al.* 2013

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CNC	Gas-phase esterification	+	0	+	+	0	+	0	0	0	0	+	+	18	Freeze-drying of CNCs from butanol, then exposed to palmoyl chloride vapor	Fumagalli *et al.* 2013
Paper handsheets	Cold plasma: myrcene or limonene	+	0	+	+	0	+	+	0	-	0	+	+	18	Cold plasma treatment was followed by exposure to unsaturated vegetable oils.	Gaiolas *et al.* 2009
Jute fiber	Graft polym., acrylonitrile	-	+	-	-	0	-	-	0	0	0	+	0	9	Acrylonitrile was graft-polymerized with Na periodate Cu sulfate.	Ghosh & Ganguly 1994
Bacterial cellulose nanopartic.	Ring-opening polymerizat.	0	0	0	-	0	-	-	0	0	-	+	+	10	Poly-(caprolacton) grafting of cellulosic –OH groups in absence of solvent.	Goodrich & Winter 2009
Eucalyptus bl. Kraft fib.	TiO_2 nanoparticles	-	-	-	-	0	-	-	0	00 0	-	+	+	7	TiO_2 nanoparticle LBL attachment to silane-treated cellulose	Gonçalves *et al.* 2009
Filter paper	Lbl treatment, then silane	-	+	0	-	0	-	-	0	0	-	0	++	11	The treatment increased surface roughness and decreased energy.	Gonçalves *et al.* 2008
Cotton	Plasma treatments	0	+	+	0	0	+	+	0	-	+	+	+	18	A variety of plasma treatments can get hydrophilicity or hydrophobicity.	Gorjanc & Gorensek 2010a,b
Cellulose microfibrils	Isopropyldimethyl-Cl-silane	-	-	-	-	0	-	-	0	0	-	+	+	7	Reaction from toluene solution with imidazole to trap the HCl.	Gousse *et al.* 2004
Regen. cellulose	Pullulan abietate LBL	+	+	+	0	+	0	+	0	+	0	0	+	19	Essentially adsorption of a specialized surfactant.	Gradwell *et al.* 2004
Lyocell fibers	Plasma amination	-	0	0	0	0	+	0	0	-	-	+	+	12	The treatment improved compatibility with PLA.	Graupner *et al.* 2013

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Wood fibers	Vinyltrimeth-oxysilane	-	0	0	-	0	-	-	0	0	0	+	+	10	Sitka spruce fibers treated with vinyltrimethoxysilane from CH_3OH.	Gregorova *et al.* 2009
CNC	Sulfate esters	0	+	-	-	+	-	0	0	-	-	0	0	9	It was not possible to remove all of the sulfur after hydrolysis with sulfuric acid.	Gu *et al.* 2013
Cellulose	ARGET, ATRP grafts	-	-	-	-	0	-	-	0	0	-	+	+	7	Grafting of MMA, styrene, and glycidyl methacrylate.	Hansson *et al.* 2009
Oxidized cellulose	Grafting aminated acrylates	-	-	-	-	0	-	-	0	0	-	+	+	7	TEMPO oxidation, followed by amine treatment and amidation reaction.	Harrisson *et al.* 2011
CNC	Epoxypropyl-TMAmmon Cl	-	+	-	0	0	-	-	+	-	-	+	-	8	The nanocrystals were initially negative due to sulfate groups.	Hasani *et al.* 2008
TMP fibers	Xylans	+	+	+	-	+	0	+	+	+	0	0	0	18	Adsorption at high temperature and pH rendered the fibers more hydrophilic.	Henriksson & Gatenholm 2002
Regener'd cellulose	Adsorption of receptor	-	-	-	-	0	-	-	0	+	-	0	+	7	Surfaces were modified by Theophylline-(ethylene glycol).	Hierrezuelo *et al.* 2014
Coir or palm EFB	Esterification	0	+	0	-	0	-	+	0	0	-	+	+	13	Pure acetic anhydride treatment of the fiber mat.	Hill & Abdul Khalil 2000
Coir or palm EFB	Silane	-	0	-	-	0	-	-	0	0	-	+	+	8	Fiber mat treated with methacryl-oxypropyltrimethoxy silane	Hill & Abdul Khalil 2000
Coir or palm EFB	Titanate	-	-	-	-	0	-	-	0	0	-	+	0	5	Neopentyl(diallyl)oxytri(dioctyl) pyrophosphate titanate in toluene	Hill & Abdul Khalil 2000

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Nanofibril cellulose	Chlorocholine chloride	-	-	-	-	0	-	-	0	0	0	+	0	7	Trimethylammonium-modified CNF was obtained in two steps.	Ho *et al.* 2011
Bacterial cellulose	I_2 and acetic anhydride	+	+	0	-	0	-	+	0	0	-	+	+	14	Solvent-free acetylation using iodine as the catalyst.	Hu *et al.* 2011
Paper	$CaCO_3$ and fatty acid	+	+	+	0	+	0	+	+	+	+	-	++	22	Low-cost eco-friendly materials precipitated onto fibers for paper.	Hu *et al.* 2009
Cellulose fiber	Atomic layer deposition of $TiNO_x$	-	0	-	-	0	-	-	0	0	+	+	0	9	$TiNO_x$ coatings were applied at low temperature to improve implant compatibility.	Hyde *et al.* 2009
Cotton fabrics	Various finishes	-	+	0	+	0	+	0	0	0	+	+	0	16	Sizing agent for the cotton fabrics based on urea-formaldehyde resin.	Ibrahim *et al.* 2013
Bacterial cellulose CNC	Acetylation	+	-	0	0	0	-	+	0	0	+	+	+	15	Nanofibril properties were profoundly affected.	Ifuku *et al.* 2007
Wood fibers	Polyelect. multilayers	-	+	0	-	0	-	-	0	+	-	-	+	9	Polyvinylamine, with or without hydrophobic substitution, was layered with polyacrylate.	Illegard *et al.* 2012
CNC	TEMPO-oxidized	-	+	0	0	+	0	0	+	0	0	+	0	15	Cellulose crystals with highly anionic surfaces were prepared.	Isogai *et al.* 2011
Filter paper	Amphiphobic rough TiO_2	-	0	-	-	0	-	-	0	-	-	+	++	9	Etching of paper in alkaline solution was followed by sol-gel deposition of TiO_2.	Jin *et al.* 2012

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Nano-cellulose	TEMPO-oxid., then octa-decylamine	0	+	-	-	0	0	0	0	0	-	+	+	12	Complex resists dissociation at low pH.	Johnson *et al.* 2011
Cellulose nanofibers	Previous acetylation	+	+	0	-	0	-	+	0	0	-	+	+	14	Acetylation of kenaf, followed by mechanical isolation of nanofibers.	Jonoobi *et al.* 2010
Nanofibrillar cellulose	Azide-mod. CMC adsorp.	0	+	0	-	0	-	-	0	+	0	+	+	13	Click-functionalization of CMC, which is adsorbed on fibers	Junka *et al.* 2014
Sisal fibers	Bact. cellulose & MMA	-	+	-	-	0	-	-	0	0	-	+	+	9	Fenton's reagent was used to initiate the MMA solution reaction.	Kalia & Vashistha 2012
Cotton	Supercritical CO_2	0	+	0	-	0	-	+	+	0	-	+	0	13	Created large pleat-like wrinkles suitable for nanoparticles	Katayama *et al.* 2012
Cotton	Ag nanopart., alklyl silane	-	+	0	0	0	0	0	0	0	0	+	++	16	Treatment with KOH and $AgNO_3$ was followed by ascorbic acid reduction and octyltriethoxysilane.	Khalil-Abad & Y. 2010
CNC	Alkenylsucc-inic anhydride	-	0	0	-	0	-	-	0	0	-	+	+	9	NCC was immersed in neat ASA and heated to 145 ^oC.	Khoshkava & Kamal 2013
Bacterial cellulose	Acetic anhydride	+	0	0	-	0	-	+	0	0	-	+	+	13	The cellulose was immersed in concentrated acetic anhydride.	Kim *et al.* 2002
Sisal fibers	Mercerization, soy protein	0	+	0	0	+	-	+	+	0	0	0	0	15	Mercerization with 2M NaOH helps later adsorption of soy protein.	Kim & Netravali 2010
Cotton fibers	AgCl in SiO_2 matrix	-	+	-	0	0	-	+	-	+	0	+	0	12	Sol-gel precursor followed by in-situ AgCl precipitation	Klemencic *et al.* 2012
Paper	Aminosilane	-	0	-	-	0	0	-	0	0	+	+	+	11	Silane coupling treatment with amine functionalization.	Koga *et al.* 2011

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Membrane	Plasma poly-octafluoro-cyclobutane	-	+	-	0	-	0	-	-	-	0	+	+	9	Plasma-induced polymerization of added monomer.	Kong *et al.* 1992
Viscose fabric	Dielectric barrier disch.	0	+	-	+	0	+	+	+	-	+	+	0	17	Silver and copper modified after DBD treatment.	Kramer *et al.* 2013
Various	3D polymer grafting	-	-	-	-	-	-	-	-	0	-	+	+	5	The material has a regenerative character due to its depth.	Kuroki *et al.* 2013
CNC	Ring-opening polymerization	0	-	0	-	0	-	-	0	0	-	+	+	9	Removal of impurities by solvent extraction improved grafting.	Labet & Thielemans 2011
Paper	Alkenylsuccinic anhydride	+	+	+	+	0	+	+	+	+	+	+	+	23	Mono-unsaturated vegetable oil yielded excellent ASA sizing agent.	Lackinger *et al.* 2012
Methyl-cellulose film	Gamma-irrad. Grafting, CNC	0	+	-	0	0	0	-	0	0	0	+	+	13	Acrylic acid or silane was grafted. CNC improved barrier properties.	Lacroix *et al.* 2014
Bacterial cellulose	Hexanoic acid	-	-	-	-	0	-	-	0	0	-	+	+	7	Freeze drying allowed a higher level of ester formation.	Lee & Bismark 2012
Bacterial cellulose	Hexanoic, dodecanoic, acetic acids	-	-	-	-	0	-	-	0	0	-	+	+	7	Hydrophobicity increased with chain length.	Lee *et al.* 2011
Bamboo fiber	Lysine-based diisocyanate	0	0	-	0	0	0	0	0	0	-	+	0	11	Carbamoylation to form urethane from the dry materials with heating.	Lee & Wang 2006
Cellulose fibers	Layer-by-layer lignosulfonate and CPAM	0	+	+	0	0	-	0	0	+	-	0	0	13	Hydrophobicity increased with increasing numbers of layers.	Li *et al.* 2012

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Cellulose fibers	Layer-by-layer lignosulfonate and Cu^{2+}	0	+	+	0	0	-	0	0	+	-	0	0	13	Lignosulfonate-Cu^{2+} complexes were formed.	Li *et al.* 2011
Cellulose	Trichloro-methylsilane	-	0	-	0	0	0	0	-	0	0	+	++	13	Superhydrophobic.	Li *et al.* 2007
Cellulose	K methyl siliconate	-	+	0	0	0	-	-	-	0	-	+	++	12	Superhydrophobic surfaces were achieved by immersion.	Li *et al.* 2008
Cellulose	TiO_2 precoat & silanation	-	0	-	-	0	0	-	-	0	-	+	++	10	Superhydrophobic surfaces were achieved by nanocoating.	Li *et al.* 2010a
Bacterial cellulose	PLA-co-PGMA	-	-	-	-	0	-	-	0	0	-	+	+	7	Adsorption of PLA-co-PGMA improved matrix compatibility.	Li *et al.* 2010b
Cotton fabrics	Fluorinated SiO_2 sols	-	0	-	-	0	-	-	-	0	0	+	++	10	SiO_2 hydrosols were hydrophobized with tetraethoxysilane, applied to cotton by dipping, then fluorosilane and heating of cotton fabrics.	Liang *et al.* 2013
Aspen wood fibers	Titanate coupling agent	-	-	-	-	0	-	-	0	0	-	+	0	6	Titanate reacted from hexane with heating.	Liao *et al.* 1997
CNC	Graft poly-caprolactone	-	0	-	-	0	-	-	0	0	-	+	+	8	Beneficial to PLA composite formation and properties.	Lin *et al.* 2009
Wood fibers	Layer-by-layer poly-DADMAC & bentonite	0	+	+	-	0	-	0	0	+	-	0	0	12	Wood fibers were modified by alternating layers of montmorillonite and poly-DADAMC.	Lin and Renneckar 2011a

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Wood fibers	Layer-by-layer poly-DADMAC & bentonite	0	+	+	-	0	-	0	0	+	-	0	0	12	Adsorption of poly-DADMAC correlated to fiber charge.	Lin and Renneckar 2011b
Cellulosic fibers	Nanoclay	0	+	+	+	0	+	+	+	+	+	0	0	20	Fluff pulp fibers were treated with poly-DADMAC, then montmorillonite clay to reduce inter-fiber bonding.	Lindstrom *et al.* 2008
Paper	Alkylketene dimer	+	+	+	+	0	+	+	+	+	+	+	+	23	Review of alkylketene dimer sizing of paper	Lindstrom and Larsson 2008
Cellulose fibers	Polymer multilayers	0	+	+	-	0	-	0	+	+	-	0	+	14	Polyelectrolyte multilayers led to changes in wettability.	Lingström *et al.* 2007
Nanofibril cellulose	Acrylics from aqueous	-	+	-	-	0	0	-	0	0	0	+	+	11	Grafting with cerium radical initiator from aqueous system.	Littunen *et al.* 2011
Cellulose fibers	Polyphenol	+	0	+	-	0	-	0	0	0	-	+	+	13	Guaiacol oligomers prepared by Fe(III)-mediated coupling, forming nanoparticles at the fiber surface	Liu *et al.* 2010
Cellulose fibers	Caprolactone & PLA	-	-	-	-	0	-	-	0	0	-	+	+	7	Ring-opening polymerization was enhanced by copolymer treatment.	Lönnberg *et al.* 2006
MFC blch. sulfite SW	Caprolactone	-	-	-	-	0	-	-	0	0	-	+	+	7	Grafting from toluene suspension with benzyl alcohol initiator.	Lönnberg *et al.* 2011
Microfibr. cellulose	Silane coupling agents	-	-	-	-	0	-	-	0	0	-	+	+	7	Silane coupling agents were used for the modifications.	Lu *et al.* 2008
Broken fibers	Layer-by-layer polyelectrol.	-	+	+	-	0	-	-	0	+	-	0	+	11	Polyallylamine hydrochloride and polystyrene sulfonate, *etc.*	Lvov *et al.* 2006

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Cellulose	Fluorosilane coupling	-	0	-	-	-	-	-	-	0	-	+	+	6	Reaction from an alcohol-water solution.	Ly *et al.* 2009
HW & SW sawdust	Styrene xanthate	-	+	-	-	0	-	-	0	0	-	+	+	9	Graft polymerization using peroxide ferrous ion initiation system.	Maldas *et al.* 1988
HW & SW sawdust	Isocyanates	-	+	-	0	0	0	-	0	0	0	+	+	12	Poly[methylene(polyphenyliso-cyanate) and two others	Maldas *et al.* 1988
HW & SW sawdust	Alkoxysilanes	-	-	-	-	0	-	-	0	0	-	+	+	7	Vinyltri(2-methoxyethoxy)silane and two others	Maldas *et al.* 1988
Cellulose fibers	ATRP	-	-	-	0	0	-	-	0	0	-	+	+	8	Atom transfer radical polymerization (ATRP) reviewed.	Malmstrom & Carlmark 2012
Cellulose fibers	RAFT	-	-	-	0	0	-	-	0	0	-	+	+	8	Reversible addition fragmentation chain-transfer (RAFT) reviewed.	Malmstrom & Carlmark 2012
Cellulose fibers	Alkyne functionaliz.	-	0	-	-	0	0	-	0	0	0	+	+	10	Esterification by alkaline aqueous or H_2o/isopropanol treatment of fibers.	Mangiante *et al.* 2013
Palm fibers	Zr oxychloride → ZrO_2 NPs	-	+	-	0	0	0	+	0	+	0	0	0	13	In-situ formation of nanoparticles at the fiber surface.	Martins *et al.* 2013
Nanofibril cellulose	Ag nanoparticles	0	+	0	-	0	-	-	-	+	-	0	0	9	Electrostatic assembly of Ag NPs on NFC using layer-by-layer.	Martins *et al.* 2012
Paper handsheets	Dual plasma treatment	-	+	-	0	-	+	-	-	-	0	+	++	12	Oxygen plasma (for roughness) followed by fluorocarbon plasma.	Mirvakili 2013
Nanofibrill. cellulose	Anhydrides in ionic liquid	0	-	-	-	0	-	-	0	0	-	+	+	8	Surface grafting was achieved with organic anhydrides in ionic liquid.	Missoum *et al.* 2012a
Nanofibrill. cellulose	Long aliphatic isocyanates	-	-	-	-	0	-	-	0	0	-	+	+	7	Organization of chains was in a crystalline waxy form.	Missoum *et al.* 2012b

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Nanofibrill. cellulose	Nanoemulsion of AKD	0	-	-	-	0	-	-	0	0	-	0	+	7	Treatment with alkylketene dimer stabilized by cationic surfactant. System not heat-cured.	Missoum *et al.* 2013b
CNC	Polystyrene graft, ATRP	-	0	-	-	0	-	-	0	0	0	+	+	9	2-bromoisobutyryl bromide mod. For ATRP with CuBr/PMDETA triamene system brush.	Morandi *et al.* 2009
Paper	PTFE-penetrated	-	-	0	-	-	-	-	-	+	-	0	+	6	Carried out in supercritical fluoroform.	Mori *et al.* 2008
Rice husk	ATRP graft of PMMA, PAN	-	-	-	-	0	-	-	0	0	0	+	+	8	Roughness and hardnesses of the surfaces were evaluated.	Morsi *et al.* 2011
MCC	Surface acetylation	0	-	-	-	0	-	-	0	0	-	+	+	8	Acetyl chloride was reacted with MCC to improve dispersion in PLA.	Mukherjee *et al.* 2013
Cellulose acetate	F^- ion implantation	-	+	0	-	0	-	+	0	-	-	+	-	9	Nanofiltration with salt rejection was achieved using accelerator.	Mukherjee *et al.* 2005
Natural fibers	Steam explosion	+	+	+	-	+	0	+	+	-	0	0	-	15	Review	Mukhopadhyay & Fangueiro 2009
Natural fibers	Plasma	0	+	0	0	0	+	0	0	-	0	+	0	14	Review: Plasma can be applied only to one side of the substrate.	Mukhopadhyay & Fangueiro 2009
Bagasse fibers	Zr oxychloride → ZrO_2 NPs	-	+	-	0	0	0	+	0	+	-	0	0	12	30-80 nm particles were deposited heterogeneously.	Mulinari *et al.* 2010
CTMP fibers	Fluorosilane plasma	-	-	-	0	-	0	-	-	0	0	+	+	8	The fluorosilane plasma resulted in a bound, cross-linked film.	Navaro *et al.* 2003

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Cellulose fiber (or mica model surface)	Adsorption of block F co-polymers	-	+	0	+	-	+	-	-	+	+	0	+	14	Co-polymers of 2-(dimethylamine) ethyl methacrylate and tri-fluoroethyl methacrylate were adsorbed.	Nurmi *et al.* 2010
Paper	Nano-$CaCO_3$, pectin, ASA	0	+	+	+	0	+	+	+	+	+	0	+	21	Pectin and ASA were applied with nanoPCC to make hydrophobic paper.	Nypelo *et al.* 2011
Nanofibrill. cellulose	CMC & nano-PCC	+	+	+	+	+	+	+	+	+	+	0	0	22	The slightly cationic nano-PCC was bound with the CMC	Nypelo *et al.* 2012
Bio-fiber surfaces	ATRP glycidyl methacryate, then chains	-	-	-	0	0	-	-	0	0	0	+	++	11	Post-functionalization achieve results similar to perfluorination.	Nystrom *et al.* 2009
Paper	Polyhydroxy-butyrate	+	+	+	0	+	0	+	0	+	0	0	++	21	Precipitation by phase separation giving micro-roughness and hydrophobicity.	Obeso *et al.* 2013
Ragwort leaf	Layer-by-layer fluoroalkanes, & TiO_2, PAA	-	+	-	-	0	-	-	-	+	-	0	++	10	Layer-by-layer assembly of fluoroakylsilane with TiO_2 and poly(acrylide acid) for roughness.	Ogawa *et al.* 2007
Nanofibrill. cellulose film	TEMPO oxid., EDS/NHS, protein attach.	0	+	0	-	+	0	-	0	0	0	+	0	13	Proteins were attached to the surface by steps of TEMPO oxidation, activation, and functionalization	Orelma *et al.* 2012a,b
Bacterial cellulose	Phosphoryl-ation	-	+	0	-	+	0	+	0	-	-	0	0	11	Phosphoric acid treatment in DMF with urea.	Oshima *et al.* 2008

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Nanofibrill. cellulose	Click chemistry	-	+	0	0	0	0	-	0	0	0	+	+	13	Reactive azide groups attached by esterification; then reactivated with propargyl amine (Cu catalyst)	Pahimanolis *et al.* 2011
Cellulose fibers	Cationic latex	-	+	0	0	0	+	-	+	+	+	+	+	17	Cationic polymer latex added during papermaking rendered the paper hydrophobic & impervious.	Pan *et al.* 2013
MCC & bleached kraft fiber	Graft poly-caprolactone	0	-	-	-	0	-	-	0	0	-	+	+	8	The poly-caprolactone was blocked, then reacted to form NCO, to react with cellulose.	Paquet *et al.* 2010
Rice husk	Maleated poly propylene	-	-	0	0	0	0	-	0	0	0	+	+	11	MAPP treatment was from xylene.	Park *et al.* 2004
Rice husk	Silane	-	0	-	0	0	0	-	0	0	+	+	+	12	Silane treatment was from an ethanol/water mixture.	Park *et al.* 2004
Cellulose fibers	Surface esterification	+	0	0	-	0	-	-	0	0	-	+	+	11	Long-chain acid chlorides for preparation of LDPE composites.	Pasquini *et al.* 2008
Cotton fiber	Plasma & cationization	-	0	0	0	0	0	-	0	-	0	+	0	10	Plasma treatment followed by cationization	Patiño *et al.* 2011
Cellulose wet fibers	PVAm with graft TEMPO	-	+	0	+	0	+	-	0	0	0	+	0	14	Poly-vinylamine grafted to TEMPO reacted only with fiber surfaces.	Pelton *et al.* 2011
Cellulose	Surfactant	0	0	+	+	0	0	-	0	+	0	-	0	13	Surfactant adsorption on cellulose is a highly cooperative process.	Penford *et al.* 2007
Cellulose	Long-chain esters	+	0	+	-	0	0	+	0	0	0	+	+	16	Low degree of substitution gave high hydrophobicity.	Peydecastaing *et al.* 2006
Radiata pine fibers	Silane coupling	-	-	0	-	0	-	-	0	0	0	+	+	9	NaOH treatment aided silanization.	Pickering *et al.* 2003

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Cellulose nanofibrils	Silane treatment	-	0	-	-	0	-	-	0	0	-	+	+	8	3-Methacryloxypropyltrimethoxy-silane modification for PLA composites.	Qu *et al.* 2012
Microfibril. cellulose	Pure acetic anhydride	+	0	0	-	0	-	+	0	8	-	+	+	13	Bamboo cellulose was highly fibrilated, then acetylated.	Rampinelli *et al.* 2010
Wood	Layers of PEI, poly-DADMAC and PAA	-	+	+	-	0	-	-	0	+	-	0	0	10	The layers obscured the nano features but not larger features.	Renneckar & Zhou 2009
Microfibrill. cellulose	Acetic anhydride	0	-	-	-	0	-	-	0	0	-	+	+	8	The morphology of the fibers was not changed. Toluene medium.	Rodionova *et al.* 2011
Bacterial cellulose	Silane graft of peptices	0	-	-	-	0	-	-	0	0	-	+	+	8	Bacteriocidal agents were attached by silane grafting.	Rouabhia *et al.* 2014
Cellulose	RAFT	-	-	-	-	0	-	-	0	0	-	+	+	7	Review of reversible addition - fragmentation chain transfer graft polymerization.	Roy 2006
Nanofibrill. cellulose	Dodecyl gallate	+	+	+	-	+	0	+	0	+	-	+	+	18	Laccase-aided modification of unbleached NFC using dodecyl gallate.	Saastamoinen *et al.* 2012
CNC from cotton	HBr & sonic, TEMPO, alkylation, azidation	-	-	-	0	0	0	-	0	0	-	+	+	9	After the oxidative pretreatment and derivatization, click chemistry was used to create structures.	Sadeghifar *et al.* 2011
Paper	CF4-RF plasma	-	+	-	0	-	+	-	-	-	0	+	0	9	The two-sidedness after plasma treatment was evaluated.	Sahin 2007

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Paper	CF4-RF plasma	-	+	-	0	-	+	-	-	-	0	+	++	12	Surface fluorination.	Sahin *et al.* 2002
Native, regenerated cellulose	TEMPO-med. oxidation	-	+	0	0	+	0	0	+	0	0	+	0	15	Regenerated cellulose is partly solubilized by TEMPO-mediated oxidation.	Saito *et al.* 2005
CNC	HCl hydrol of TEMPO-oxid. nanofibrillated cellulose	-	+	0	-	+	-	0	+	0	-	+	0	12	The softwood pulp was first TEMPO-oxidized and then HCl hydrolyzed to form nano-crystals.	Salajkova *et al.* 2012
Viscose Rayon	He/butadiene plasma	-	+	0	0	0	0	-	0	-	0	+	+	12	The plasma treatment rendered the cellulose hydrophobic.	Samanta *et al.* 2012
Paper	Vegetable oil & NPs	0	+	+	0	0	+	0	0	+	0	0	+	17	Vegetable oils and styrene maleimide nanoparticle coatings.	Samyn *et al.* 2013
CNC & NFC	Oligonucleotides binding domain to PAM attached.	0	+	+	+	+	0	-	0	+	0	0	0	16	DNA-type structures adsorbed preferentially on native cellulose 1; The DNA then helps in adsorption of polyacrylamide at high salt.	Sato *et al.* 2012
Cellulose nanopaper	Alkyl anhydrides	0	0	-	-	0	0	-	0	0	-	+	+	10	Vacuum filtration, solvent exchange with acetone, reaction with alkyl anhydrides, and hot-pressing.	Sehaqui *et al.* 2014
Cellulose film	PEG-coated polystyrene	-	+	+	+	0	0	-	-	0	+	+	+	17	Cellulose film was coated by polyethylene glycol-coated polystyrene nanospheres.	Seto *et al.* 1999

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CNC	Castor oil isocyanate	0	-	-	-	0	-	-	0	0	-	+	+	8	Grafting with isocyanate-terminated castor oil.	Shang *et al.* 2013
Cellulose acetate NFs	Fluorochem., SiO_2 NPs	-	-	-	-	-	-	-	-	0	-	+	++	7	Electrospun cellulose acetate NFs with fluorinated polybenzoxazine layer with silica nanoparticles.	Shang *et al.* 2012
Cellulose UF membranes	ATRP, poly-PEG-MA	-	0	0	-	0	-	-	0	0	-	+	+	9	ATRP was used to create a surface layer of copolymer.	Singh *et al.* 2008
Cannabis i. fibers	Acrylonitrile in air	-	+	-	0	0	0	-	0	0	-	+	0	10	The reaction in air was catalyzed by a redox initiator.	Singha & Rana 2012
CNC & MFC from sisal	Octadecyl isocyanate	-	-	-	-	0	-	-	0	0	-	+	+	7	In-situ solvent exchange.	Siqueira *et al.* 2010
NFC films	Dielectric barrier disch.	-	+	0	0	-	0	-	-	-	+	+	0	10	CF_4/O_2 mixture was used for the plasma treatment.	Siro *et al.* 2013
Cellulose fibers	Mill-induced periodate ox.	+	+	0	0	+	0	+	+	0	0	+	0	18	Dialdehyde cellulose microfibers produced by simultaneous wet milling and periodate oxidation.	Sirvio *et al.* 2011
Cotton fabric	Octadecylammonium Cl, C nanotubes	-	+	0	-	-	-	0	-	-	-	+	+	8	Cationic cotton made by reaction of epoxypropyltrimethylammonium Cl with NaOH and carbon nanotubes	Soboyejo & Old 2013
Paper	Plasma of acrylates	-	+	-	0	0	0	-	0	-	+	+	+	12	Butyl and ethylhexyl acrylates grafts with cold air plasma.	Song *et al.* 2013

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Microfibril. cellulose	CeIV oxidat., then glycidyl methacrylate	-	+	-	0	0	-	-	0	0	0	+	+	11	Epoxy functionality attached by Ce(IV) oxidation followed by glycidyl methacryate	Stenstad *et al.* 2008
Microfibril. cellulose	Hexamethylen diisocyanate	-	0	-	-	0	-	-	0	0	-	+	+	8	Reaction with hexamethylene diisocyanate in THF solvent.	Stenstad *et al.* 2008
Microfibril. cellulose	Succinic or maleic anhyd.	0	0	0	-	0	-	-	0	0	-	+	0	9	Anhydride reactions in THF for 20 h at room temperature.	Stenstad *et al.* 2008
CNF film	TEMPO oxid., cat. surfactant	0	+	0	0	0	0	0	0	0	+	0	+	15	After TEMPO-mediated oxidation, adsorption of CTAB	Syverud *et al.* 2011
CNC from cotton	Silane treatment	-	0	-	-	0	-	-	0	0	-	+	+	8	Isocyanatepropyltriethoxysilane reactions with –OH groups.	Taipina *et al.* 2013
CNC from cotton	Tosyl chloride, ring opening graft PEI	-	-	-	-	0	-	-	0	0	-	+	0	6	The derivatization resulted in amorphous cellulose.	Tehrani & Neysi 2013
Cellulose	Graft methyl acrylate	-	-	-	-	0	-	-	0	0	-	+	0	6	Reaction parameters were optimized for density of reaction.	Thakur *et al.* 2013a
Cellulosic fibers	Butyl acrylate grafting	-	-	-	-	0	-	-	0	0	-	+	+	7	Butyl acrylate grafting of *Saccharam ciliare* fibers using a redox initiator.	Thakur *et al.* 2013b
Cellulose fibers	Sol-gel coating	-	0	0	0	0	0	-	0	0	0	+	0	11	A sol-gel coating was applied to impart anti-microbial character.	Tomšič *et al.* 2008
Various celluloses	Long-chain fatty acid with tosyl chloride	+	-	-	-	0	-	-	0	0	-	+	+	9	Esterification DS decreased with increasing chain length and unsaturation.	Uschanov *et al.* 2011

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Henequen fibers	Organosilane	-	-	0	-	0	-	-	0	0	-	+	+	8	Silane coupling agent covalent reaction was established.	Valadez-Gonzalez *et al.* 1999
Inkjet paper & textile	Oxygen plasma	0	+	+	0	+	+	+	+	0	+	+	0	20	Oxygen content of the surface was increased with 3 s exposure.	Vesel 2008
Regener'd cellulose membrane	Bock copol. monolayers	-	0	-	-	0	-	-	0	0	-	+	+	8	Poly(N-isopropylacrylamide)-block-(polyethyleneglycol)methacrylate grafted by ATRP.	Wandera *et al.* 2011, 2012
Kapok fiber	SiO_2 nano-particles, then alkyl silane	-	0	-	-	0	-	-	0	0	-	+	++	10	Silica nanoparticles deposited by sol-gel treatment, then silane used to impart hydrophobicity.	Wang *et al.* 2012
CNC	Acetylation, hydroxyethyl, hydroxypropyl	0	0	-	-	0	-	+	0	0	-	+	+	11	All three treatments rendered the crystals hydrophobic and dispersible in solvents.	Wang *et al.* 2006
Paper	Crystallizing wax	+	+	+	+	0	+	+	0	+	0	0	++	22	Rapid expansion of supercritical CO_2 containing wax.	Werner *et al.* 2010
Cellulose polymer	Isopentyl side chains	-	-	-	-	0	-	-	0	0	-	+	+	7	The hydrophobic material can react with acrylates.	Woo *et al.* 2006
Cellulose fabrics	Oligomeric si-lsesquioxane	-	+	0	0	0	0	-	0	0	0	+	0	12	The chemistry is related to crease recovery fabric.	Xie *et al.* 2010a
Cotton fabrics	SiO_2 NPs, ZnO nanorods silane treated	-	0	-	-	0	-	-	0	0	-	0	++	9	After the nanoparticles the surface was treated with dodecyltrimethoxysilane for superhydrophobicity.	Xu *et al.* 2010
Cellulose surfaces	Multivalent polysacchar.	+	-	-	-	+	-	0	0	0	-	+	+	11	Clickable cellulose surface.	Xu *et al.* 2012

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Cotton fabrics	Superhydrophobic	0	0	0	0	0	0	-	-	0	-	+	++	13	Silica nanoparticles deposited and reacted with stearic acid or silanes.	Xue *et al.* 2008
CNC	Acetic anhydride	+	+	0	-	0	-	+	0	0	-	+	+	14	Mild conditions with anhydrous phosphoric acid medium	Yan *et al.* 2013
Paper	Superhydrophobic	-	+	-	0	0	+	-	-	0	0	+	++	14	Silica nanoparticle deposition was followed by vapor silane treatment.	Yang and Deng 2008
Cellulose nanofibers	TEMPO oxid., then grafted with cysteine	+	+	0	0	+	-	0	0	0	-	+	0	14	Thiol-modified oxidized cellulose were embedded in electrospun PAN, for metal ion adsorption.	Yang *et al.* 2014
CNC	Sulfuric acid, & acetylation	+	+	0	-	0	-	+	0	0	-	+	+	14	The CNC whiskers were made with sulfuric acid, then acetylated.	Yang *et al.* 2013
Paper	TiO_2 NPs bioconjugation	0	+	+	+	+	0	-	0	+	0	+	0	17	Homogenous distribution was achieved by bioconjugation.	Ye *et al.* 2009
Cellulose substrate	Cat. SiO_2/TiO_2 sol	0	+	0	+	0	0	0	0	+	+	0	0	16	The layer is transferred to cellulosic surface to print disperse dyes.	Yin *et al.* 2013
Cellulose nanofibers	Acetic anhydride	+	+	0	0	0	-	+	0	0	-	+	+	15	The nanofibers had been created by water-jet impingement.	Yokota *et al.* 2012
Nematic ordered cellulose	Poly-methyl methacrylate	-	-	-	-	0	-	-	0	0	-	+	+	7	Living radical polymerization was used.	Yokota *et al.* 2012
Bamboo fiber	Methyl methacrylate	-	-	-	-	0	0	-	0	0	0	+	+	9	ATRP grafting	Yu *et al.* 2014a

Substrate	Modification system	Green origin of treatment	Avoids harmful solvents	Avoids toxic materials	Minimizes energy use	Biodegradable	Avoids material waste	Avoids petrochemicals	Product can be recycled	Does not hurt cellulose	Scale-up-friendly	Durable surface changes	Big effect on wettability	Overall score	Research highlights	Citation (year)
CNC	Poly-hydroxy-butyrate-co-hydr.valerate	-	0	-	-	0	0	-	0	0	0	+	+	10	Grafting by homogeneous acetylation with DMF and toluene diisocyanate coupling agent.	Yu & Qin 2014
Ethyl cellulose	Rosin-based polymers	+	-	0	-	0	-	-	0	0	0	+	+	11	ATRP "grafting from"	Yu *et al.* 2014b
Cellulose	Trifluoroacetic anhydride	-	+	-	+	-	0	-	0	0	+	+	+	13	Vapor-phase esterification	Yuan *et al.* 2005
CNC	Alkenylsuccinic anhydride	-	+	+	-	0	-	0	0	0	-	+	+	12	Freeze-drying, heating of aqueous emulsion to achieve acylation.	Yuan *et al.* 2006
Cellulose membranes	Sulfobetaine polymerization	-	-	-	-	0	0	-	0	0	0	+	0	8	RAFT polymerization of zwitterion to resist biofouling.	Yuan *et al.* 2013
CNC	Glycidyltrimethylammonium chloride	-	+	-	0	0	0	-	+	-	0	+	0	11	The CNC was first made with sulfuric acid, then cationized in NaOH with epoxy quaternary cpd.	Zaman *et al.* 2012
Cellul fibers	AKD and ASA	-	+	+	+	0	+	0	+	0	+	+	+	19	Vapor deposition	Zhang *et al.* 2007
CNC	Glycidoxypropyltrimethoxysilane	-	0	-	-	0	-	-	0	0	-	+	0	7	The treatment rendered the CNC compatible with polyurethane.	Zhang *et al.* 2012
Cotton fabric	NP plasma film	-	+	-	0	0	+	-	0	-	+	+	++	15	Plasma application of fluorinated nanoparticles onto cotton fabric.	Zhang *et al.* 2003
Cellulosic fibers	Layer-by-layer	-	+	0	-	0	-	-	+	+	-	0	0	10	Negatively and positively charged fibers were prepared.	Zheng *et al.* 2006
Cellulose	Xyloglucan	+	+	+	0	+	0	+	+	0	-	+	0	18	Review of enzymatic approaches	Zhou *et al.* 2007

++ = strongly positive effect; + = positive; 0 = neutral; - = negative (relative to environmental impacts)