Turning polysaccharides into hydrophobic materials: a critical review. Part 1. Cellulose

Ana Gisela Cunha · Alessandro Gandini

Abstract This survey constitutes the first part of a comprehensive review, whose purpose is to provide a reasoned perspective in the field related to the preparation of new polysaccharide-based hydrophobic materials by scrutinizing the actual state of its art. This part of the review is entirely dedicated to cellulose, by far the most probed natural substrate, where publications dealing with both chemical and physical treatments aimed at inducing a substantial increase in the hydrophobic character of the surface are critically examined. Furthermore, this initiative constitutes an attempt to emphasize the relevance of this topic within the broader context of the elaboration of novel materials based on renewable resources as a viable alternative to their fossil-based counterparts.

Keywords Polysaccharides · Cellulose · Hydrophobicity · Chemical modifications · Physical treatments

Introduction

The new millennium is witnessing a dramatic surge of interest in the search for novel macromolecular materials from renewable resources (Gandini and Belgacem 2008), involving wide ranging approaches, which are being tackled in both academic and industrial laboratories. This ongoing research has already produced a vast number of significant contributions, some of which are likely to be progressively converted into viable practical applications, either in partial substitution of counterparts derived from fossil resources, or as materials with original properties.

This state of affairs reflects the inevitable necessity of finding alternatives to the fossil-based products (covering energy and commodity requirements), awakened by the predictable scarcity of these sources, and is intimately associated with the pressing need to solve the global environmental problems. The steadily growing number of publications, patents, monographs and scientific meetings, coupled with the increasing investments by the public and private sectors to sustain these R&D initiatives are the best indicators of this reality.

Within the specific realm of polymer science and technology, the exploitation of renewable resources in the form of monomers, oligomers and natural polymers has now become a worldwide practice (Gandini and Belgacem 2008). Among these numerous alternative investigations, the renaissance of interest in the use of polysaccharides as starting materials for the production of novel derivatives is quite refreshing, considering that some of these natural polymers were the first source of "plastics" some 150 years ago, in the form of cellulose esters, well before the advent of

A. G. Cunha · A. Gandini (✉)
CICECO and Department of Chemistry,
University of Aveiro, Aveiro, Portugal
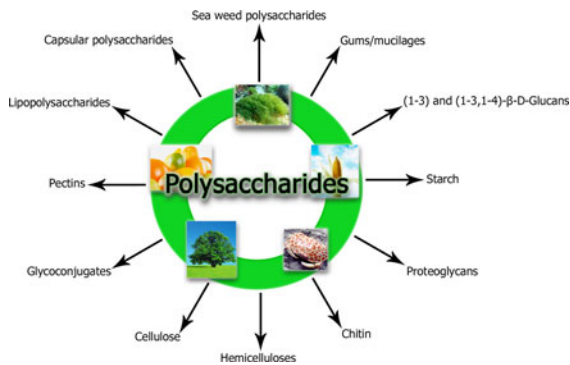e-mail: agandini@ua.pt

Fig. 1 Molecular diversity of polysaccharides [adapted from Ramesh and Tharanathan (2003)]

petrochemistry. Actually, these materials never lost their industrial and economical impact, as indicated by the present rise in cellulose acetate production.

The research activities related to the exploitation of polysaccharides are today spanning many new avenues, which concern the development of novel materials to be implemented in a number of domains, including the demand for healthier food and medicines (Ramesh and Tharanathan 2003).

Polysaccharides are carbohydrates formed by the condensation of monosaccharide residues through hemi-acetal or hemi-ketal linkages. They also exist as short oligosaccharide sequences or polymeric repeat units linked to other biopolymers, as in glycoproteins, glycolipids, etc. These important natural polymers are ubiquitous throughout the flora and fauna (Fig. 1), where they perform different functions and roles, such as structural performance, energy storage and gel formation, depending on their specific chemical structure, composition, molecular weight, and ionic character when applicable (Ramesh and Tharanathan 2003). Because of their functional diversities, polysaccharides are exploited both in food and non-food industries (Ramesh and Tharanathan 2003).

Two reviews are offered here, dealing with one specific realm among the numerous research topics related to the modification of natural polysaccharides, namely their hydrophobization. The first installment is entirely devoted to cellulose, the most important member of the polysaccharide family, in the specific context of the material science. The second review will cover the other relevant members.

The hydrophobization, and especially the super-hydrophobization, of materials which are not naturally hydrophobic has been a topic of chemical research for at least 60 years (Fogg 1944; Hyde 1948), but it has only been in the last decade that interest in this field has been growing spectacularly, as witnessed by the exponentially increasing number of studies (Feng et al. 2002; Gao and McCarthy 2009; Gao et al. 2009; Li et al. 2007; Sun et al. 2005; Xu et al. 2009).

The hydrophobicity of a material may be assessed by the contact angle of a water droplet deposited onto its surface. In general, hydrophobicity is achieved, on the one hand, by lowering the surface energy, and more specifically the polar contribution to it, and, on the other, by creating adequate surface micro- and/or nano-morphologies, which hinder water spreading. When the water contact angle is higher than 90°, the corresponding material is conventionally defined as *hydrophobic* (Feng et al. 2002).

Non-hydrophobic materials may be rendered hydrophobic by appropriate modifications involving either physical treatment or chemical reactions applied to the surface or the bulk of the concerned substrate. Both approaches are discussed here in two separate sections dealing with the search for hydrophobic materials derived from cellulose.

Cellulose

Cellulose is the most abundant naturally occurring biopolymer, whose macroscopic morphology is always in the shape of fibers (Gandini and Belgacem 2008; Marsh 1942), as in such dominant manifestations as cotton, wood and annual plants. It consists of long chains of anhydro-D-glucopyranose units (AGU), each bearing three hydroxyl groups (one primary and two secondary moieties), with the exception of the terminal ones (Fig. 2). Cellulose is insoluble in water and in most common solvents (Marsh 1942; Krässig 1993), its poor solubility being attributed primarily to the strong intra- and inter-molecular hydrogen bonds within and among the individual chains (Krässig 1993).

Its supramolecular structure displays both crystalline (high order) and amorphous (low order) domains. The degree of crystallinity of cellulose, usually in the range of 40–60%, depends on the origin and pretreatment of the sample. The morphology of cellulose has a profound effect on its reactivity, with the hydroxyl groups located in the amorphous regions being readily

Fig. 2 Chemical structure of cellulose

Non-reducing end   Cellobiose $\frac{DP}{2}$ - 2   Reducing end
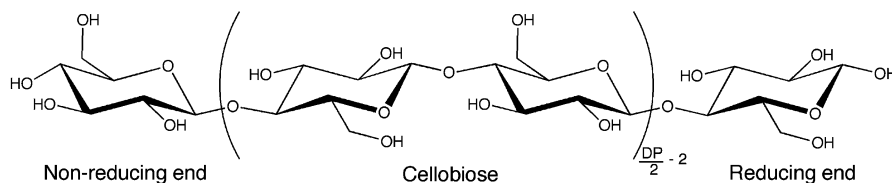
accessible and hence highly reactive, whilst those present in the more compact crystalline regions of high cohesive energy display much lower accessibility (Krässig 1993). The AGU units sitting at the surface of the cellulose fibers and pointing outwards are obviously topochemically very reactive, independent of the degree of crystallinity of filament inner core.

The poor solubility of cellulose has not hindered its most important historical utilizations in textiles, paper and cardboard, packaging, among others, and more recently as a reinforcing element in composite materials with macromolecular matrices. Concurrently, cellulose derivatives like esters and ethers have been exploited very successfully, as mentioned above, in a variety of domains, since their synthesis does not require cellulose to be initially dissolved (Belgacem and Gandini 2008). The only traditional technology involving cellulose dissolution is in rayon fiber chemical regeneration, a process which has found recent alternatives, namely with the use of N-methylmorpholine-N-oxide (NMMO) as a non-reactive solvent to produce high quality textile fibers.

The most innovative aspect related to cellulose chemistry reflects however the upsurge of the activities associated with renewable resources mentioned above, i.e., studies conducted within the last decade. They include two different domains, namely a whole variety of novel derivatives and the search for suitable applications (Heinze and Petzold 2008) and the modifications restricted to the surface or a modest thickness of the fibers aimed at providing them with specific properties and applications, which include, among others, their compatibilization with polymeric matrices in composite materials (Belgacem and Gandini 2005, 2008), improved dyeability, color steadfastness and the topic of the present review.

Another innovative aspect related to cellulose has to do with the domain of its nanofibers, which has literally exploded in the last few years, as clearly illustrated by two very recent reviews (Habibi et al. 2010; Siró and Plackett 2010), which deal with their preparation, characterization, surface treatments and potential applications.

The preparation of highly hydrophobic cellulose-based materials has stimulated a large number of studies, and the topic is still hot, because of their potential applications in such important areas as papermaking, textile and packaging, further motivated by the exploitation of an environmental friendly renewable resource, as opposed to fossil-based counterparts (Gandini and Belgacem 2008).

Chemical modifications

The necessity to confer hydrophobic characteristics to such a hydrophilic biopolymer as cellulose has always been part of the history of papermaking, particularly with respect to the sizing operation. Sizing is generally conducted at the wet-end part of the papermaking process (Roberts 1996) in order to reduce the papers' tendency to absorb liquids, e.g. to ensure the drying of an ink without smudging or excessive in-depth penetration, or to retain the mechanical strength of cardboard in a dump atmosphere, as with egg containers. The most common sizing agents used in papermaking are alkenyl succinic acid anhydride (ASA), alkyl ketene dimer (AKD) and rosin, which are added to the fiber suspension in the form of emulsions (Gess and Rende 2005; Lindstrom and Larsson 2008; Roberts 1996).

The development of new sizing methods is witnessing renewed attention (Bourbonnais and Marchessault 2010; Werner et al. 2010; Zhang et al. 2007), not only within the traditional area of papermaking, but more broadly within the context of cellulose hydrophobization.

Zhang et al. (2007), for example, recently studied a new method of sizing, which consisted in the possibility of delivering the AKD and ASA molecules to cellulose from a vapor phase (Fig. 3). This original study was focused on the chemical composition of the vapors of both sizing agents at typical papermaking temperatures, using FTIR spectroscopy.
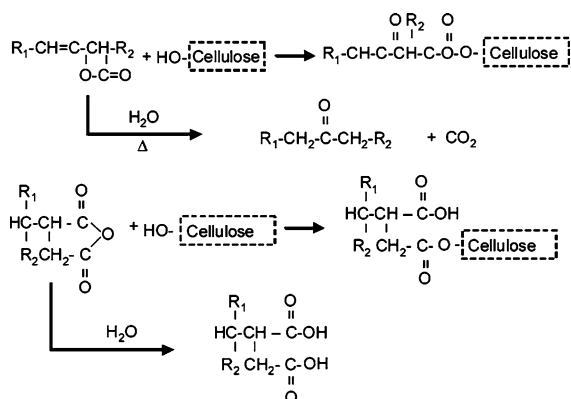
Fig. 3 Reaction mechanisms of AKD (above) and ASA (below) with cellulose, as proposed by Zhang et al. (2007)

The authors concluded that the ASA vapors were constituted by the same molecules as those of this compound in the liquid phase, whereas the AKD vapors were rich in fatty acids, indicating the occurrence of their thermal hydrolysis and concluded that only ASA could be used to hydrophobize cellulose using this technique.

AKD has also been employed to prepare superhydrophobic papers using three alternative introduction techniques, namely (1) airblasting with cryoground micro particles, (2) crystallizing from organic solvents and (3) spraying with Rapid Expansion of Supercritical Solutions (RESS) (Werner et al. 2010). The green character and simplicity of the cryogrinding-airblasting method was favoured over the use of an organic solvent, but the RESS method, produced a higher hydrophobicity. A lot of work was devoted to the measurements of wetting, but no comment was provided about the long-time stability of these coatings and about the nature of the interaction between the deposited AKD and the surface cellulose macromolecules. Whether AKD actually reacts with the surface OH groups of the paper cellulose fibers or is simply adsorbed on them through polar interactions, is still a source of debate among specialists (Roberts 1996) and this could explain the lack of specific interpretation in this study. Notwithstanding this issue, it is important to emphasize that this approach provides the additional advantage of the possibility of its continuous application, i.e., its potential industrial implementation.

Other studies on the hydrophobization of cellulose, not necessarily associated with paper properties,

started in the late 1970's with the elaboration of cellulose esters, of both alkyl and aryl carboxylic acids, for enzyme immobilization tests (Butler 1975; Dixon and Butler 1977; Dixon et al. 1979). The esterification of cellulose is the oldest polymer modification reaction known and its relevance has never lost its impact. In the last few decades, long chain cellulose esters have still been prepared by grafting fatty acids and their derivatives onto cellulose, either by surface or bulk reactions, employing various methods (Berlioz et al. 2009; Boufi and Belgacem 2006; Bras et al. 2007; Crepy et al. 2009; Freire et al. 2006; Pasquini et al. 2008; Peydecastaing et al. 2006). These cellulose derivatives, which were elaborated with different substrates and purposes, showed an enhanced hydrophobic character with water contact angles some times exceeding 90°. The recent contribution from Berlioz et al. (2009) purports to have achieved an efficient gas-phase esterification of the surface of the cellulose nanofibers, but does not provide any convincing evidence related to the proposed structure of the ensuing cellulose palmitate.

Transesterification reactions were also applied to cellulose in its purest form, viz. cotton, in order to generate water repellent textiles, by its modification with triglycerides from several vegetable oils, including soybean, rapeseed, olive and coconut oils (Fig. 4) (Dankovich and Hsieh 2007). The most hydrophobic cotton derivative was obtained by transesterification with soybean oil, yielding a water contact angle of about 80°.

Cellulose, in the form of a cotton fabric, was chemically modified through a two-stage process, in order to attain antibacterial properties (Jantas and Górna 2003). In the first stage, the cotton fabric was treated with chloroacetyl chloride in a THF/pyridine (solvent/catalyst) system, in order to incorporate chloroacetate groups. During the second stage, the chloroacetylated cotton was reacted with the potassium salt of a bioactive 1-naphthylacetic acid, giving a cellulose-1-naphthylacetic acid adduct. The FTIR-ATR results confirmed the occurrence of this second chemical reaction, and showed that the ensuing derivatives, besides having acquired a highly bactericidal activity against *Escherichia coli*, also displayed a high hydrophobicity, with water contact angles higher than 120°.

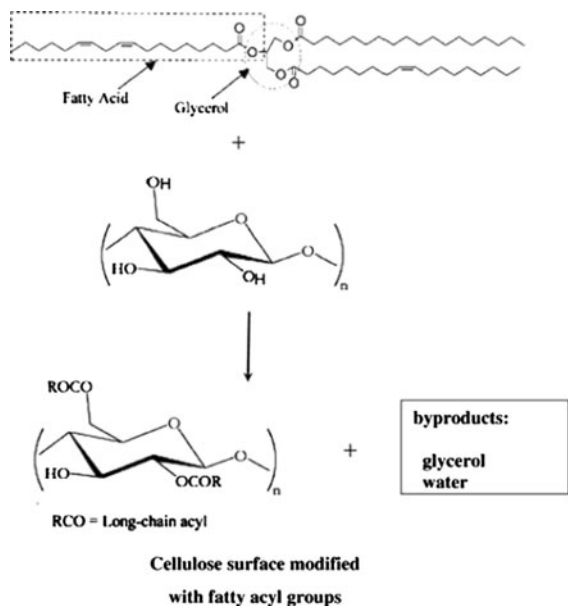A recent report on the esterification of cellulose nanofibers, conducted with the purpose of providing

Fig. 4 Transesterification reaction between cellulose and triglycerides (Dankovich and Hsieh 2007)

Table 1 Contact angles for water and diiodomethane on trifluoroacetylated cellulose fibers (Cunha et al. 2006)

Sample (time/temperature)	DS	Contact angle (°)	
		Water	Diiodomethane
1 h/50 °C	0.04	126 ± 2	104 ± 2
5 h/50 °C	0.14	126 ± 3	103 ± 3
5 h/80 °C	0.30	119 ± 2	94 ± 3

them with hydrophobic properties (Janoobi et al. 2010), called upon its conventional acetylation with acetic anhydride. The water contact angles attained exceeded 110°, which is a surprisingly high value for a degree of substitution of about one (i.e. with a very large number of OH groups still present on these macromolecules), considering that even a fully acetylated cellulose gives a water contact angle close to 50°.

Fluorinated organic compounds are known to display remarkable hydrophobic-lipophobic properties, which depend on the nature of the fluorine-containing moiety and its fluorine content (Pagliaro and Ciriminna 2005). To take advantage of these properties, recent investigations called upon trifluoroacetic anhydride as the esterification reagent for the surface of cellulose fibers. The reaction was carried out both in the gas (Ostenson et al. 2006; Yuan et al. 2005) and the liquid phase (Cunha et al. 2006, 2007a). The presence of the CF$_3$ groups at the cellulose surface gave rise to strongly hydrophobic and lipophobic properties, as can be verified, for the case of the liquid phase system, by the high contact angles with both polar (water) and non-polar (diiodomethane) liquids, presented in Table 1 (Cunha et al. 2006).

Given the high sensitivity to hydrolysis of the trifluoroacetate moiety, this modification was shown to be readily reversed by liquid water and even by a moist atmosphere. This peculiar feature has an obvious bearing in the context of applications in which the biphobic character of the fibers' surface only constitutes a temporary requirement, after which the fibers can be readily recycled following rapid hydrolysis.

Similarly, Nyström et al. (2006) reported the surface modification of cellulose fibers with a long perfluoroalkyl chain, which was grafted either directly or through an intermediate layer of OH-bearing polymers. Once again, a highly hydrophobic character was attained, but the authors failed to recognize the hydrolytic sensitivity of the grafted perfluoroester moieties.

More stable perfluorinated cellulose derivatives were prepared in our group by the surface esterification of cellulose fibers with two other perfluorinated reagents, viz., pentafluorobenzoyl chloride, PFBz (Cunha et al. 2007b), and 3,3,3-trifluoropropanoyl chloride, TFP (Cunha et al. 2007c), under controlled heterogeneous conditions. We characterized the ensuing materials by elemental analysis, FTIR spectroscopy, X-ray diffraction (XRD), thermogravimetry, and surface analyses (XPS, ToF–SIMS, and contact angle measurements). The occurrence of the grafting was demonstrated by direct techniques, such as FTIR, XPS and ToF–SIMS, whereas both the hydrophobic and lipophobic character of the fluorine-containing modified surfaces were found to have increased significantly compared with those of the pristine fibers, even for very modest degrees of substitution (Table 2).

Contrary to the trifluoroacetate cellulose counterparts, pentafluorobenzoylated and trifluoropropanoylated cellulose derivatives showed to be more stable towards hydrolysis, only undergoing it in a highly alkaline aqueous medium, like any carboxylic ester (Fig. 5).

Numerous studies report the modification of cellulose fibers with several silane coupling agents, such as vinyldimethylethoxyethylsilane (**A**), vinyltrimethoxysilane

Table 2 Contact angles on cellulose fiber substrates before (PC) and after esterification with PFBz and TFP (Cunha et al. 2007b, 2007c)

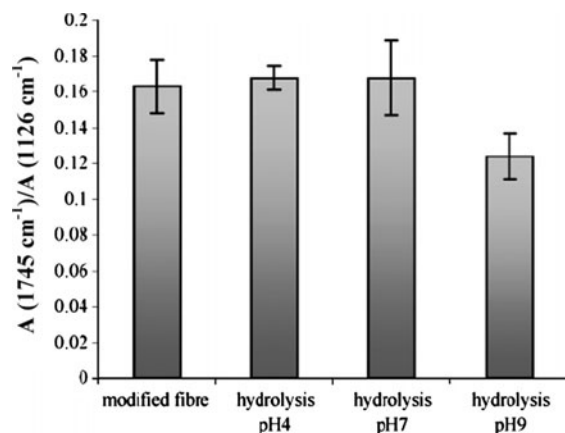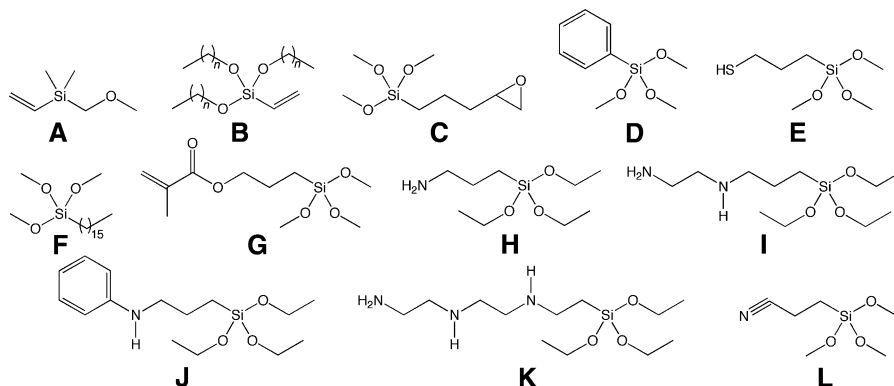| Sample (time/temperature)	Reagent	DS	Contact angle (°)	
			Water	Diiodomethane
PC	–	–	56 ± 1	37 ± 2
5 h/50 °C	PFBz	0.014	120 ± 1	71 ± 6
5 h/65 °C		0.23	124 ± 2	73 ± 1
5 h/80 °C		0.39	128 ± 1	82 ± 2
2 h/RT	TFP	<0.006	113 ± 2	84 ± 2
2 h/65 °C		0.03	117 ± 1	86 ± 2
2 h/100 °C		0.30	122 ± 2	91 ± 4

Fig. 5 Hydrolysis of the pentafluorobenzoyl groups grafted onto the cellulose fibers as a function of pH, as determined by FTIR-ATR (Cunha et al. 2007b)

($n = 0$) (**B1**) and vinyltriethoxysilane ($n = 1$) (**B2**), γ-glycidylpropyltrimethoxysilane (**C**), phenyltrimethoxysilane (**D**), γ-mercaptopropyltriethoxysilane (**E**), hexadecyltrimethoxysilane (**F**), γ-methacrylopropyl-trimethoxysilane (**G**), γ-aminopropyltriethoxysilane (**H**), (2-aminoethylamino)-propyltriethoxysilane (**I**), 3-(phenylamino)-propyl-triethoxy silane (**J**), 3-(2-(2-aminoethylamino)-ethylamino)-propyl-triethoxysilane (**K**) and cyanoethyltrimethoxysilane (**L**) (Fig. 6) (Abdelmouleh et al. 2002, 2004; Belgacem and Gandini 2005, 2009; Castellano et al. 2004; Gonzalez et al. 1999a, 1999b; Matuana et al. 1999; Park et al. 2004; Pickering et al. 2003; Pothan et al. 2002; Redondo et al. 2002; Sreekala and Thomas 2003).

Evidence for the actual occurrence of the coupling reaction and a thorough study of the mechanism involved are only found in a few of those investigations (Castellano et al. 2004; Gonzalez et al. 1999a, 1999b). These authors proved convincingly that the condensation reaction between the siloxane alkoxy moieties and the cellulose hydroxyl groups only takes place if traces of water are present, provoking the

formation of Si–OH groups, which are the functions really responsible for the coupling, and this only above about 90 °C.

In the case of the modification with **F**, the water contact angles increased from 40° for the pristine cellulose surface, to more than 100° for the modified surface, which confirmed the efficiency of the coupling (Abdelmouleh et al. 2004; Castellano et al. 2004). In this context, a double-grafting was applied as well, which consisted in the use of siloxanes bearing a polymerizable function (Abdelmouleh et al. 2004; Castellano et al. 2004), followed by the co-polymerization of **G**-modified cellulose fibers with styrene (St) or methyl methacrylate (MMA). The surface energy of the ensuing materials decreased and its polar component became negligible, which proved the attainment of a highly hydrophobic character. Similarly, **C**- and **H**-modified substrates were subsequently treated with an aliphatic amine and an
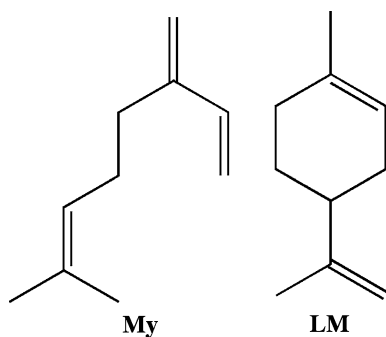
Fig. 6 Structure of the silane coupling molecules used to graft cellulose fibers

Fig. 7 Chemical structure of myrcene (My) and limonene (LM)

Fig. 8 Chemical structure of the fluorosiloxanes used for the modification of cellulose fibers: 3,3,3-trifluoropropyl trimethoxysilane (TFPS) and *1H,1H,2H,2H*-perfluorooctyl trimethoxysilane (PFOS) (Ly et al. 2009)

aliphatic oxirane, respectively, giving rise to an epoxy coating covalently linked to the fibers, which again displayed a strong increase in hydrophobicity (Abdelmouleh et al. 2004).

Surface modified cellulose samples were also obtained by their treatment with a cold plasma in the presence of **A** and **F** (Gaiolas et al. 2008). The ensuing materials were extensively soxhlet extracted in order to remove the physically adsorbed unbound molecular moieties, before being characterized by water contact angle measurements, which gave an increase from 40 to 100°, and XPS.

The same authors also succeeded in grafting reactive natural products, namely myrcene (My) and limonene (LM) (Fig. 7), on the surface of cellulose fibers, using the same cold plasma treatment (Gaiolas et al. 2009). Here, the water contact angle increased from 30° for the unmodified substrate to more than 100° for treated samples.

Ly et al. (2009) recently reported the grafting of the surface of two model cellulose fibers, Avicel (AV), and Whatman paper (WP), with two fluorine-bearing alkoxysilanes, previously used by Gonçalves et al. (2008) (see "Physical treatments" section), viz. 3,3,3-trifluoropropyl trimethoxysilane (TFPS) and *1H,1H,2H, 2H*-perfluorooctyl trimethosysilane (PFOS) (Fig. 8).

The ensuing modified fibers were soxhlet extracted before being characterized by elemental analysis, contact angle measurements, X-ray photoelectron spectroscopy and Scanning Electron Microscopy (SEM), which showed that the grafting had indeed occurred. The fluorinated moieties appended onto the surface of the cellulose macromolecules produced a strong hydrophobic effect, as revealed by the increase in water contact angles on both substrates, which
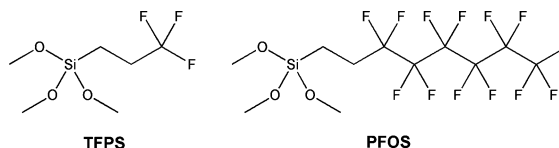
went from about 50° before modification, to 115 and 125° for TFPS- and PFOS-modified samples, respectively (Table 3). Moreover, the determination of the polar contribution to the surface energy $\left(\gamma_s^p\right)$ using Owens–Wendt's approach, gave a dramatic decrease from about 20 mJ/m^2 for the pristine celluloses to practically 0 after modification (see Table 3).

A similar approach was implemented by Erasmus and Barkhuysen (2009) with the aim of preparing a superhydrophobic and self-cleaning cotton fabric, except that they only applied the treatment with *1H,1H, 2H,2H*-perfluorooctyl triethoxysilane (FOS). The water contact angle measurements revealed the formation of a highly hydrophobic surface after the modification with different concentrations of FOS. A superhydrophobic character, with a water contact angle exceeding 150°, was only attained when the FOS concentration was 20% with respect to the cotton weight. The self-cleaning ability of the FOS-modified cotton fabric was also investigated with encouraging results.

A water-borne fluoroalkylsiloxane, nanosized silver particles and an unspecified reactive organic–inorganic binder were used to prepare water and oil repellent and antimicrobial cotton fibers using different procedures (Tomšič et al. 2008). Contact angle measurements using different liquid probes (water, diiodomethane and n-hexadecane) were used to demonstrate the hydrophobic and oleophobic properties of the treated substrate, which were maintained even after 10 washings. FTIR and XPS spectroscopic measurements revealed the presence of fluorine atoms and C–F vibrational bands. The antibacterial activity of these modified textiles was also demonstrated by the reduction in the *Escherichia coli* and *Staphylococcus aureus*. This study would have gained in thoroughness had the authors provided more information about the chemistry of their system.

Yet another investigation on omniphobic cellulose fiber organic–inorganic hybrids was recently conducted

Table 3 Surface energy and water contact angles on the surface of AV and WP, before and after modification with TFPS and PFOS (Ly et al. 2009)

Sample	Water contact angle (°)	Surface energy (mJ.m^{-2})		
		γ_s^d	γ_s^p	γ_s
AV	47	31.8	23.9	55.7
TFPS-treated Av	115	27.8	1.1	28.9
PFOS-treated AV	125	20.3	0.5	20.8
WP	50	32.1	20.2	52.3
TFPS-treated WP	116	26.1	0.6	26.7
PFOS-treated WP	129	19.8	0.1	19.9

in our group using (3-isocyanatopropyl)triethoxysilane as the source of cellulose OH coupling (through the NCO moiety) and of sol–gel processing (Cunha et al. 2010a). Fig. 9 illustrates the various pathways adopted in this study.

The micro/nano surface asperities thus generated on the fibers' surface were complemented by incorporating perfluoromoieties as a source of an additional chemical phobic character. These materials displayed strong biphobic surfaces with contact angles as high as 140° for water and 134° for the non-polar diiodomethane.

We developed a remarkably simple and straightforward method to attain a high hydrophobicity through the gas-phase coupling of trichloromethylsilane (TCMS) onto the surface of cellulose fibers, in the presence of small amounts of moisture (Cunha et al. 2010b). TCMS reacts with both the surface OH groups of cellulose and with the water present and generates a surface coverage whose chemical features, shown schematically in Fig. 10 for the different possible constructs, depends on the actual experimental conditions. These structures were accompanied by a surface morphology that displayed micro- and nano-asperities as shown in Fig. 11.

After extraction of the cellulose-unbound species, water contact angles higher than 130° were measured together with correspondingly high contact angles with non-polar liquids, showing that highly bi-phobic cellulose surfaces had been generated by the concomitant action of nano-roughness and chemical inertness. This novel approach, which bears both clear green chemistry and viable economic connotations, further enhanced by the fact that air can be used as the carrier gas instead of nitrogen, is being extended successfully to other OH-bearing natural and synthetic polymers (Cunha et al. 2010c).

Interestingly, despite the important number of studies on cellulose silylation, no published report is available on complementary investigations associated with the hydrolysis of these silyl ethers moieties.

A different approach for appending long aliphatic chains, perfluoro homologues, or PDMS onto the surface of cellulose fibers was recently proposed (Nyström et al. 2009), based on the use of the ATRP

Fig. 9 Scheme of the chemical modification of cellulose fibers with ICPTEOS and of the acid hydrolysis of the modified fibers (Cunha et al. 2010a)
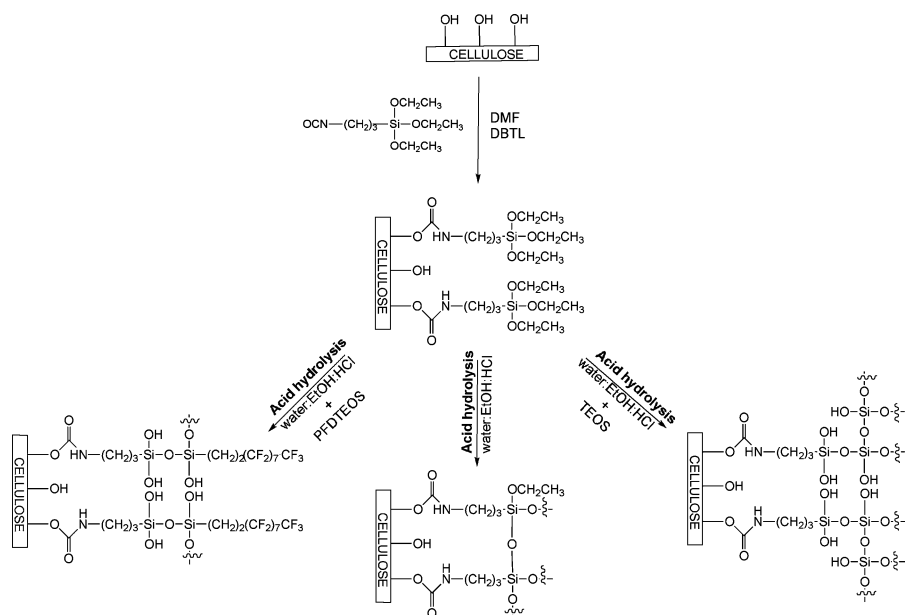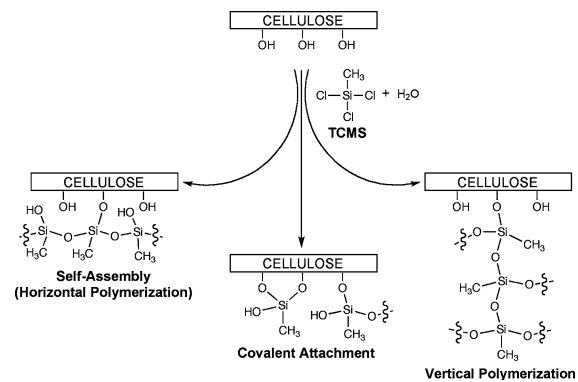
Fig. 10 Schematic representation of the possible products of the reaction of TCMS with a cellulose substrate in the presence of controlled humidity (adapted from (Fadeev and McCarthy 2000))
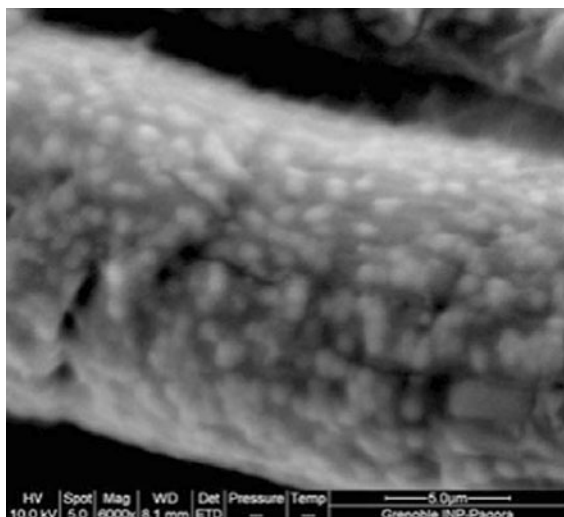

Fig. 11 Scanning electron micrograph of TCMS-treated cellulose fibers at × 6000 magnification

mechanism, but the processes involved to reach highly hydrophobic surfaces appear to be rather laborious and cumbersome, compared with the more straightforward systems discussed in this review.

Very recently, investigations aimed at the synthesis of the so called "continuous fiber-reinforced composites" led to the elaboration of new cellulose-based hydrophobic materials. The approach consists in attaching a polymeric matrix to the surface of cellulose fibers *via* chemical coupling, in such a way that the long chains appended to the fiber surface form macromolecular entanglements with those of

the polymer matrix (Ly et al. 2010; Paquet et al. 2010). One of the investigations reported in this context, describes the grafting of cellulose fibers by polycaprolactone (PCL) following a reaction pathway in which phenyl isocyanate was used as an OH-blocking agent, and 2,4-toluene diisocyanate (TDI) as the PCL-cellulose coupling mediator (Fig. 12) (Paquet et al. 2010). The occurrence of the grafting was proved by the presence of nitrogen in the elemental analysis and XPS spectra of the modified and soxhlet-extracted fibers. After the modification, the water contact angle was higher than 90° and stable with time, while the polar component of the surface energy decreased from about 30 mJ/m^2, for the pristine substrate, to practically zero after appending the PCL grafts. These modified cellulose materials maintained their biodegradable character, albeit with slower kinetics.

The second contribution to this strategy described the coupling of cellulose with different oligoether chains, namely poly(ethylene) (POE), poly(propylene) (PPG) and poly(tetrahydrofuran) (PTHF) glycols of different lengths, following the same reaction pathways discussed above for the PCL-cellulose preparation (Li et al. 2010a) . The ensuing grafted fibers were characterized by contact angle measurements, elemental analysis, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), which gave clear evidence for the successful occurrence of grafting. The water contact angles of the PPG-grafted cellulose substrates were found to increase with increasing PPG length, as summarized in Table 4. Furthermore, the biodegradability of these oligoether-grafted fibers was shown to be maintained.

Physical treatments

Physical treatments are often applied to cellulose in order to impart a hydrophobic character to its surface. Several approaches, such as the surface treatment with cold-plasma (Balu et al. 2008; Barni et al. 2007; Kong et al. 1992; Mukhopadhyay et al. 2002; Navarro et al. 2003; Sahin 2007; Sahin et al. 2002) or laser (Daoud et al. 2006), or the mere coating of the surface of cellulose with different polymers, without covalent attachments (Bayer et al. 2009; Daoud et al. 2004; Gonçalves et al. 2008, 2009; Li et al. 2008, 2010a, b; Sarkar et al. 2010; Tang et al. 2010; Vilčnik et al. 2009; Vince et al. 2006; Xu et al.
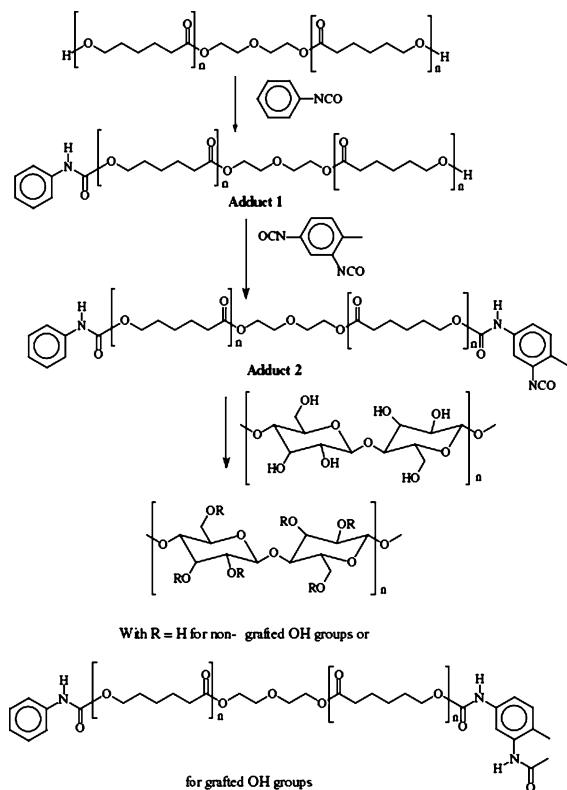
Fig. 12 Three-step procedure for grafting cellulose with PCL, as carried out by Paquet et al. (2010)

Table 4 Surface energy and water contact angles on Whatman paper (WP) before and after grafting with PPG (Ly et al. 2010)

Sample	DP	Water contact angle (°)	Surface energy (mJ.m^{-2})		
			Dispersive	Polar	Total
WP	0	22	25.9	34.9	60.8
	34	95	31.9	3.9	35.8
	42	99	30.1	0.8	30.9
PPG_WP	51	105	26.1	0.2	26.3
	69	113	32.4	0.3	32.7

2010; Xue et al. 2008; Yang and Deng 2008; Zhang et al. 2003), are examples of this type of approach.

Boufi and Gandini (2001) studied the formation of polymeric films on cellulose fibers by admicellar polymerization using a cationic surfactant, namely hexadecylpyridinium chloride (CTP). The addition of 2-ethylhexylacrylate (EHA) and styrene (St) to the admicellar channels and their subsequent polymerization resulted in the formation of a hydrophobic

polymer sleeve around the fibers, as can be verified in Table 5, which gives both the measured contact angles and the surface energies related to the cellulose fibers before and after these polymerizations. A considerable increase in the water contact angle (hydrophobic character) gave rise to the corresponding decrease in the polar component of the surface energy, γ_s^p. The microscopic observation of the modified fibers clearly confirmed the presence of the polymer sleeves and suggested that their relative fragility could be a negative feature at the time of incorporating them into a polymer matrix. It follows that the positive green character associated with a system involving water as a medium needs further investigation in order to minimize the latter negative connotation.

Low power plasmas can induce the polymerization of a precursor gas on a substrate surface, as well as introduce functional groups under specific conditions. The modification of the cellulose fibers' surface using cold-plasma in the presence of fluorinated gases or monomers usually gives rise to highly hydrophobic, generally even superhydrophobic, surfaces (Balu et al. 2008; Barni et al. 2007; Kong et al. 1992; Mukhopadhyay et al. 2002; Navarro et al. 2003; Sahin 2007; Sahin et al. 2002). An investigation carried out by Sahin et al. (2002) at the beginning of the twenty-first century clearly illustrates this approach, in which paper substrates were plasma irradiated in the presence of CF$_4$ and the surface modification evaluated by XPS and FTIR-ATR as a function of the exposure time, power parameters and the CF$_4$ pressure. With this kind of treatment, the authors succeeded in preparing cellulose substrates with high hydrophobicity, characterized by water contact angles as high as 147° for papers incorporating about 40% of fluorine.

The application of a double plasma treatment (Balu et al. 2008) consisting of (1) a nano-etched morphology produced by the ablation of the amorphous regions of the fibers' surface and (2) a thin fluorocarbon film generated by plasma-enhanced chemical vapor deposition using pentafluoroethane, resulted in water contact angles as high as 167°.

Another interesting experiment in this context was carried out by Barni et al. (2007), consisting in the characterization of a low pressure SF$_6$ discharge by means of plasma diagnostics, including radiofrequency electrical probes, Langmuir probes and optical emission spectroscopy, in which three different

Table 5 Contact angles of different liquids on the surface of cellulose fibers before and after in situ polymerization with St and EHA, and surface energies calculated from them (Boufi and Gandini 2001)

Sample	Contact angle (°)				Surface energy (mJ m^{-2})		
	Water	Ethylene glycol	Formamide	Diiodomethane	γ_s^p	γ_s^d	γ_s
Cellulose	32 ± 3	42 ± 3	25 ± 3	27 ± 3	20	30	50
Cellulose-St	92 ± 5	45 ± 3	40 ± 4	30 ± 3	4	32	36
Cellulose-EHA	90 ± 4	60 ± 4	58 ± 4	40 ± 4	1.2	37.8	39

polymeric substrates were modified, viz. poly(ethyleneterephthalate) (PET) fabrics and films, and cellulose (paper). The XPS analysis confirmed the occurrence of the grafting by the detection of bound fluorine atoms and the plasma treatment at low pressure was also found to produce some surface etching. Consequently, the original hydrophilic character of all these surfaces disappeared after the treatment and, in the case of the cellulose substrate, the water contact angle increased from 30° to more than 120°, for the most fluorinated surfaces.

The non-covalent attachment of different polymers onto the surface of cellulose fibers can be carried out using several techniques, such as by pickering emulsions (Bayer et al. 2009), layer-by-layer or multi-layer deposition (LbL) (Gonçalves et al. 2008, 2009; Ogawa et al. 2007; Yang and Deng 2008), dip-coating or immersion in the polymer solution (Daoud et al. 2004; Li et al. 2008, 2010b; Tang et al. 2010; Vilčnik et al. 2009; Xu et al. 2010; Xue et al. 2008), impregnation (Vince et al. 2006), physical deposition (Li et al. 2010a; Zhang et al. 2003), electro-spraying (Sarkar et al. 2010) or simply heating (Vilčnik et al. 2009).

An innovative multi-step nanoengineering process was recently developed by Gonçalves et al. (2008) in order to prepare superhydrophobic cellulose nanocomposites by combining three techniques, as sketched in Fig. 13, namely, (1) an LbL polyelectrolyte deposition, (2) a sol–gel silica precipitation and (3) a chemical grafting consisting in appending perfluorinated structures using 3,3,3-trifluoropropyl trimethoxysilane (TFPS) and FOS as coupling agents, which readily reacted with the surface Si–OH of the silica nanoparticles. The polyelectrolyte used was poly(diallyldimethylammonium chloride) and the silica deposition precursor was tetraethoxysilane (TEOS). Such an approach had the merit of providing a highly efficient hydrophobic character (water

contact angles approaching 150°) by combining an increased surface roughness, induced by the amorphous silica nanoparticles, with a reduction in its surface energy, provided by the perfluoro moieties. Each modification step was followed by SEM and AFM.

The same authors modified the surface of cellulose fibers using the hydrolysis of TEOS, octyltrimethoxysilane (OTMS) or phenyltrimethoxysilane (PTMS), followed by the LbL deposition of previously synthesized TiO$_2$ nanoparticles (Gonçalves et al. 2009). The ensuing hybrid nanocomposites were characterized by Raman, FTIR and ^{29}Si solid-state NMR spectroscopy, SEM and water contact angle measurements. The spectroscopic and microscopic analyses confirmed that the grafting had indeed occurred. After grafting with alkoxysilanes, the water contact angle increased from about 50° to more than 90°. The presence of TiO$_2$ nanoparticles provided the additional property of solar photoactivity.

Another study of hybrid cellulose materials displaying superhydrophobic properties obtained by physical treatments, called upon coating the fibers with titania and thereafter introducing an alkyl-chain silica layer produced by sol–gel chemistry (Li et al. 2010a), which resulted in water contact angles in the range 150–160°, although no proof of the suggested surface chemical structures resulting from these treatments was provided.

All the above cellulose hybrid materials can be potentially used as self-cleaning surfaces (although much experimental evidence is required to corroborate the attainment of this property) and as reinforcing agents in polymer matrices, among other potential applications.

Very recently, highly hydrophobic and/or oleophobic cellulose surfaces (cotton woven fabrics) were prepared by solution-immersion coating using two classes of hyperbranched polymers containing short
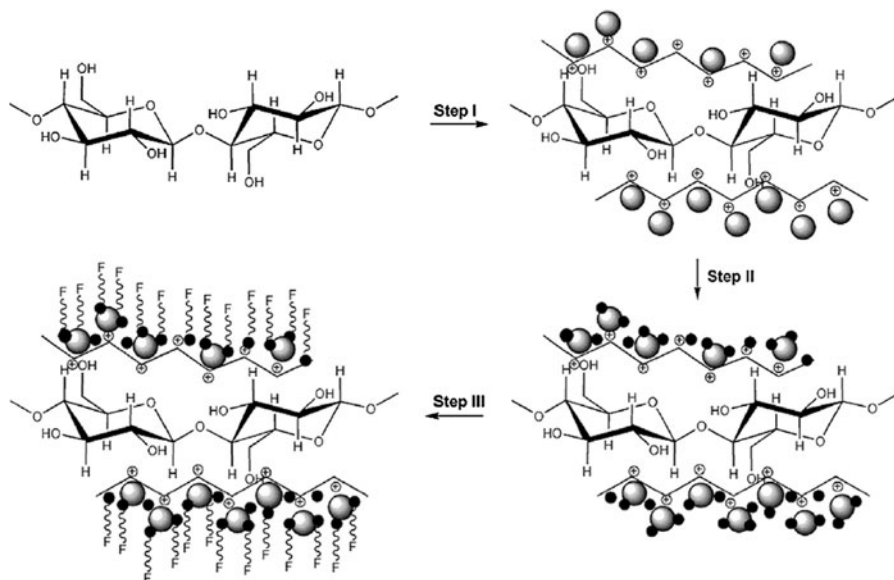
fluorocarbon chains (Tang et al. 2010) and characterized by SEM, AFM, XPS and contact angle measurements with water, hexadecane and decane. The majority of the treated samples presented simultaneously excellent water and oil repellency, suggested by the high static contact angles with water (139–146°) and apolar liquids (94–122°).

Conclusions

As this review clearly reveals, the search for original and effective methods of rendering cellulose hydrophobic has attracted very considerable attention, with particular emphasis in the last decade, where a flurry of interesting ideas was applied to that task with promising results. It is also true, however, that the topic should be considered as being still in its infancy and hence the need of further research involving both novel strategies and the optimization of those described here. The obvious next effort should concentrate on systems bearing a green character and an economically viable application potential.

References

Abdelmouleh M, Boufi S, Ab Salah, Belgacem MN, Gandini A (2002) Interaction of silane coupling agents with cellulose. Langmuir 18(8):3203–3208

Abdelmouleh M, Boufi S, Belgacem MN, Duarte AP, Salah AB, Gandini A (2004) Modification of cellulosic fibres with functionalised silanes: development of surface properties. Int J Adhes Adhes 24(1):43–54

Balu B, Breedveld V, Hess DW (2008) Fabrication of "roll-off" and "sticky" superhydrophobic cellulose surfaces via plasma processing. Langmuir 24(9):4785–4790

Barni R, Zanini S, Beretta D, Riccardi C (2007) Experimental study of hydrophobic/hydrophilic transition in SF6 plasma interaction with polymer surfaces. Eur Phys J Appl Phys 38(3):263–268

Bayer IS, Steele A, Martorana PJ, Loth E, Miller L (2009) Superhydrophobic cellulose-based bionanocomposite films from Pickering emulsions. Appl Phys Lett 94(16):163902

Belgacem MN, Gandini A (2005) The surface modification of cellulose fibres for use as reinforcing elements in composite materials. Compos Interface 12(1–2):41–75

Belgacem MN, Gandini A (2008) Surface modification of cellulose fibres. In: Belgacem MN, Gandini A (eds) Monomers, polymers and composites from renewable resources, 1st edn. Elsevier, Amsterdam, pp 385–400

Belgacem MN, Gandini A (2009) Natural fibre-surface modification and characterisation. In: Sabu T, Pothan L (eds) Natural fibre reinforced polymer composites: from macro to nanoscale. Old City Publishing, Philadelphia, pp 14–46

Berlioz S, SM- Boisseau, Nishiyama Y, Heux L (2009) Gas-phase surface esterification of cellulose microfibrils and whiskers. Biomacromolecules 10:2144–2151

Boufi S, Belgacem MN (2006) Modified cellulose fibres for adsorption of dissolved organic solutes. Cellulose 13(1):81–94

Boufi S, Gandini A (2001) Formation of polymeric films on cellulosic surfaces by admicellar polymerization. Cellulose 8(4):303–312

Bourbonnais R, Marchessault RH (2010) Application of polyhydroxyalkanoate granules for sizing of paper. Biomacromolecules 11(4):989–993

Bras J, Vaca-Garcia C, Borredon ME, Glasser W (2007) Oxygen and water vapor permeability of fully substituted long chain cellulose esters (LCCE). Cellulose 14(4):367–374

Butler LG (1975) Enzyme immobilization by adsorption on hydrophobic derivatives of cellulose and other hydrophilic materials. Arch Biochem Biophys 171(2):645–650

Castellano M, Gandini A, Fabbri P, Belgacem MN (2004) Modification of cellulose fibres with organosilanes: under what conditions does coupling occur? J Colloid Interface Sci 273(2):505–511

Crepy L, Chaveriat L, Banoub J, Martin P, Joly N (2009) Synthesis of cellulose fatty esters as plastics-influence of the degree of substitution and the fatty chain length on mechanical properties. ChemSusChem 2(2):165–170

Cunha AG, Freire CSR, Silvestre AJD, Neto CP, Gandini A (2006) Reversible hydrophobization and lipophobization of cellulose fibers via trifluoroacetylation. J Colloid Interface Sci 301(1):333–336

Cunha AG, Freire CSR, Silvestre AJD, Neto CP, Gandini A, Orblin E, Fardim P (2007a) Characterization and evaluation of the hydrolytic stability of trifluoroacetylated cellulose fibers. J Colloid Interface Sci 316(2):360–366

Cunha AG, Freire CSR, Silvestre AJD, Neto CP, Gandini A, Orblin E, Fardim P (2007b) Highly hydrophobic biopolymers prepared by the surface pentafluorobenzoylation of cellulose substrates. Biomacromolecules 8(4):1347–1352

Cunha AG, Freire CSR, Silvestre AJD, Neto CP, Gandini A, Orblin E, Fardim P (2007c) Bi-phobic cellulose fibers derivatives via surface trifluoropropanoylation. Langmuir 23(21):10801–10806

Cunha AG, Freire CSR, Silvestre AJD, Neto CP, Gandini A (2010a) Preparation and characterization of novel highly omniphobic cellulose fibers organic–inorganic hybrid materials. Carbohydr Polym 80(4):1048–1056

Cunha AG, Freire C, Silvestre A, Neto CP, Gandini A, Belgacem MN, Chaussy D, Beneventi D (2010b) Preparation of highly hydrophobic and lipophobic cellulose fibers by a straightforward gas–solid reaction. J Colloid Interface Sci 344(2):588–595

Cunha AG, Freire C, Silvestre A, Neto CP, Gandini A (2010c) unpublished results

Dankovich TA, Hsieh Y-L (2007) Surface modification of cellulose with plant triglycerides for hydrophobicity. Cellulose 14(5):469–480

Daoud WA, Xin JH, Tao X (2004) Superhydrophobic silica nanocomposite coating by a low-temperature process. J Am Ceram Soc 87(9):1782–1784

Daoud WA, Xin JH, Zhang YH, Mak CL (2006) Pulsed laser deposition of superhydrophobic thin teflon films on cellulosic fibers. Thin Solid Films 515:835–837

Dixon J, Butler LG (1977) Utilization of hydrophobic esters of cellulose for enzyme immobilization. Fed Proc 36(3):864

Dixon J, Andrews P, Butler LG (1979) Hydrophobic esters of cellulose-properties and applications in biochemical technology. Biotechnol Bioeng 21(11):2113–2123

Erasmus E, Barkhuysen FA (2009) Superhydrophobic cotton by fluorosilane modification. Indian J Fibre Text Res 34:377–379

Fadeev AY, McCarthy TJ (2000) Self-assembly is not the only reaction possible between alkyltrichlorosilanes and surfaces: monomolecular and oligomeric covalently attached layers of dichloro-and trichloroalkylsilanes on silicon. Langmuir 16(18):7268–7274

Feng L, Li S, Li Y, Li H, Zhang L, Zhai J, Song Y, Liu B, Jiang L, Zhu D (2002) Super-hydrophobic surfaces: from natural to artificial. Adv Mater 14(24):1857–1860

Fogg G (1944) Diurnal fluctuation in a physical property of leaf cuticle. Nature 154:515

Freire CSR, Silvestre AJD, Neto CP, Belgacem MN, Gandini A (2006) Controlled heterogeneous modification of cellulose fibers with fatty acids: effect of reaction conditions on the extent of esterification and fiber properties. J Appl Polym Sci 100(2):1093–1102

Gaiolas C, Costa AP, Nunes M, Silva MJS, Belgacem MN (2008) Grafting of paper by silane coupling agents using cold-plasma discharge. Plasma Process Polym 5:444–452

Gaiolas C, Belgacem MN, Silva L, Thielemans W, Costa AP, Nunes M, Silva MJS (2009) Green chemicals and process to graft cellulose fibers. J Colloid Interface Sci 330(2):298–302

Gandini A, Belgacem MN (2008) The state of the art. In: Belgacem MN, Gandini A (eds) Monomers, polymers and composites from renewable resources, 1st edn. Elsevier, Amsterdam, pp 1–16

Gao L, McCarthy TJ (2009) Wetting 101°. Langmuir 25(24):14105–14115

Gao L, McCarthy TJ, Zhang X (2009) Wetting and superhydrophobicity. Langmuir 25(24):14100–14104

Gess JM, Rende DS (2005) Alkenyl succinic anhydride (ASA). Tappi J 4(9):25–30

Gonçalves G, Marques PAAP, Pinto RJB, Trindade T, Neto CP (2009) Surface modification of cellulosic fibres for multipurpose TiO_2 based nanocomposites. Compos Sci Technol 69(7–8):1051–1056

Gonçalves G, Marques PAAP, Trindade T, Neto CP, Gandini A (2008) Superhydrophobic cellulose nanocomposites. J Colloid Interface Sci 324(1–2):42–46

Gonzalez AV, Uc JMC, Olayo R, Franco PJH (1999a) Effect of fiber surface treatment on the fiber-matrix bond strength of natural fiber reinforced composites. Compos B 30:309–320

Gonzalez AV, Uc JMC, Olayo R, Franco PJH (1999b) Chemical modification of henequén fibers with an organosilane coupling agent. Compos B 30:321–331

Habibi Y, Lucia LA, Rojas OJ (2010) Cellulose nanocrystals: chemistry, self-assembly, and applications. Chem Rev. doi: 10.1021/cr900339w

Heinze T, Petzold K (2008) Cellulose chemistry: novel products and synthesis paths. In: Belgacem MN, Gandini A (eds) Monomers, polymers and composites from renewable resources, 1st edn. Elsevier, Amsterdam, pp 343–368

Hyde JF (1948) Method of rendering glass water repellent. U.S. Patent 2439689:3

Janoobi M, Harun J, Mathew AP, Hussein MZB, Oksman K (2010) Preparation of cellulose nanofibers with hydrophobic surface characteristics. Cellulose 17(2):299–307

Jantas R, Górna K (2003) Antibacterial finishing of cotton fabrics. Fibres Text East Eur 14(1):88–91

Kong Y, Lin X, Wu YL, Chen J, Xu JP (1992) Plasma polymerization of octafluorocyclobutane and hydrophobic

microporous composite membranes for membrane distillation. J Appl Polym Sci 46(2):191–199

Krässig HA (1993) Cellulose: structure, accessibility and reactivity, 1st edn. Gordon and Breach Science Publishers, Amsterdam

Li S, Xie H, Zhang S, Wang X (2007) Facile transformation of hydrophilic cellulose into superhydrophobic cellulose. Chem Commun 4857–4859

Li S, Zhang S, Wang X (2008) Fabrication of superhydrophobic cellulose-based materials through a solution-immersion process. Langmuir 24:5585–5590

Li S, Wei Y, Huang J (2010a) Facile fabrication of superhydrophobic cellulose materials by a nanocoating approach. Chem Lett 39(1):20–21

Li G, Wang H, Zheng H, Bai R (2010b) A facile approach for the fabrication of highly stable superhydrophobic cotton fabric with multi-walled carbon nanotubes–azide polymer composites. Langmuir. doi:10.1021/la904337z

Lindstrom T, Larsson PT (2008) Alkyl ketene dimer (AKD) sizing—a review. Nord Pulp Pap Res J 23(2):202–209

Ly B, Belgacem MN, Bras J, Salon MCB (2009) Grafting of cellulose by fluorine-bearing silane coupling agents. Mater Sci Eng C 30(3):343–347

Ly EhB, Bras J, Sadocco P, Belgacem MN, Dufresne A, Thielemans W (2010) Surface functionalization of cellulose by grafting oligoether chains. Mater Chem Phys 120(2–3):438–445

Marsh JT (1942) An introduction to the chemistry of cellulose, 2nd edn. Chapman & Hall, London

Matuana LM, Balatinecz JJ, Park CB, Sodhi RNS (1999) X-ray photoelectron spectroscopy study of silane-treated newsprint-fibers. Wood Sci Technol 33(4):259–270

Mukhopadhyay SM, Joshi P, Datta S, Zhao JG, France P (2002) Plasma assisted hydrophobic coatings on porous materials: influence of plasma parameters. J Phys D Appl Phys 35:1927–1933

Navarro F, Dávalos F, Denes F, Cruz LE, Young RA, Ramos J (2003) Highly hydrophobic sisal chemithermomechanical pulp (CTMP) paper by fluorotrimethylsilane plasma treatment. Cellulose 10(4):411–424

Nyström D, Lindqvist J, Östmark E, Hult A, Malmström E (2006) Superhydrophobic bio-fibre surfaces via tailored grafting architecture. Chem Commun 34:3594–3596

Nyström D, Lindqvist J, Östmark E, Antoni P, Carlmark A, Hult A, Malmström E (2009) Superhydrophobic and self-cleaning bio-fiber surfaces via ATRP and subsequent postfunctionalization. ACS Appl Mater Inter 1(4):816–823

Ogawa T, Ding B, Sone Y, Shiratori S (2007) Super-hydrophobic surfaces of layer-by-layer structured film-coated electrospun nanofibrous membranes. Nanotechnology 18(16):165607

Ostenson M, Järund H, Toriz G, Gatenholm P (2006) Determination of surface functional groups in lignocellulosic materials by chemical derivatization and ESCA analysis. Cellulose 13(2):157–170

Pagliaro M, Ciriminna R (2005) New fluorinated functional materials. J Mater Chem 15(47):4981–4991

Paquet O, Krouit M, Bras J, Thielemans W, Belgacem MN (2010) Surface modification of cellulose by PCL grafts. Acta Mater 58(3):792–801

Park B-D, Wi SG, Lee KH, Singh AP, Yoon T-H, Kim YS (2004) X-ray photoelectron spectroscopy of rice husk surface modified with maleated polypropylene and silane. Biomass Bioenerg 27(4):353–363

Pasquini D, Teixeira EM, Curvelo AAS, Belgacem MN, Dufresne A (2008) Surface esterification of cellulose fibres: processing and characterisation of low-density polyethylene/cellulose fibres composites. Compos Sci Technol 68(1):193–201

Peydecastaing J, Girardeau S, Vaca-Garcia C, Borredon ME (2006) Long chain cellulose esters with very low DS obtained with non-acidic catalysts. Cellulose 13(1):95–103

Pickering K, Abdalla A, Ji C, McDonald AG, Franich RA (2003) The effect of silane coupling agents on radiata pine fibre for use in thermoplastic matrix composites. Compos A 34(10):915–926

Pothan L, Bellman C, Kailas L, Thomas S (2002) Influence of chemical treatments on the electrokinetic properties of cellulose fibres. J Adhes Sci Technol 16(2):157–178

Ramesh HP, Tharanathan RN (2003) Carbohydrates—the renewable raw materials of high biotechnological value. Crit Rev Biotechnol 23(2):149–173

Redondo SUA, Radovanovic E, Gonçalves MC, Yoshida IVP (2002) Eucalyptus kraft pulp fibers as an alternative reinforcement of silicone composites. I. Characterization and chemical modification of Eucalyptus fibers with organosilane coupling agent. J Appl Polym Sci 85(12):2573–2579

Roberts JC (1996) Paper chemistry, 2nd edn. Chapman & Hall, London

Sahin HT (2007) RF-CF4 plasma surface modification of paper: chemical evaluation of two sidedness with XPS/ATR-FTIR. Appl Surf Sci 253(9):4367–4373

Sahin HT, Manolache S, Young RA, Denes F (2002) Surface fluorination of paper in CF4-RF plasma environments. Cellulose 9(2):171–181

Sarkar MK, He F, Fan J (2010) Differential superhydrophobicity and hydrophilicity on a thin cellulose layer. Thin Solid Films 518:5033–5039

Siró I, Plackett D (2010) Microfibrillated cellulose and new nanocomposite materials: a review. Cellulose. doi:10.1007/s10570-010-9405-y

Sreekala M, Thomas S (2003) Effect of fibre surface modification on water-sorption characteristics of oil palm fibres. Compos Sci Technol 63(6):861–869

Sun T, Feng L, Gao X, Jiang L (2005) Bioinspired surfaces with special wettability. Acc Chem Res 38(8):644–652

Tang W, Huang Y, Meng W, Qing F-L (2010) Synthesis of fluorinated hyperbranched polymers capable as highly hydrophobic and oleophobic coating materials. Eur Polym J 46(3):506–518

Tomšič B, Simončič B, Orel B, Černe L, Tavčer PF, Zorko M, Jerman I, Vilčnik A, Kovač J (2008) Sol-gel coating of cellulose fibres with antimicrobial and repellent properties. J Sol Gel Sci Technol 47(1):44–57

Vilčnik A, Jerman I, Vuk AŠ, Koželj M, Orel B, Tomšič B, Simončič B, Kovač J (2009) Structural properties and antibacterial effects of hydrophobic and oleophobic sol-gel coatings for cotton fabrics. Langmuir 25(10):5869–5880

Vince J, Orel B, Vilčnik A, Fir M, Vuk AŠ, Jovanovski V, Simončič B (2006) Structural and water-repellent properties of a urea/poly(dimethylsiloxane) sol-gel hybrid and its bonding to cotton fabric. Langmuir 22(15):6489–6497

Werner O, Quan C, Turner C, Petterson B, Wågberg L (2010) Properties of superhydrophobic paper treated with rapid expansion of supercritical CO_2 containing a crystallizing wax. Cellulose 17(1):187–198

Xu QF, Wang JN, Smith IH, Sanderson KD (2009) Superhydrophobic and transparent coatings based on removable polymeric spheres. J Mater Chem 19(5):655–660

Xu B, Cai Z, Wang W, Ge F (2010) Preparation of superhydrophobic cotton fabrics based on SiO_2 nanoparticles and ZnO nanorod arrays with subsequent hydrophobic modification. Surf Coat Tech 204(9–10):1556–1561

Xue C-H, Jia S-T, Zhang J, Tian L-Q, Chen H-Z, Wang M (2008) Preparation of superhydrophobic surfaces on cotton textiles. Sci Technol Adv Mater 9:035008(7)

Yang H, Deng Y (2008) Preparation and physical properties of superhydrophobic papers. J Colloid Interf Sci 325(2):588–593

Yuan H, Nishiyama Y, Kuga S (2005) Surface esterification of cellulose by vapor-phase treatment with trifluoroacetic anhydride. Cellulose 12:543–549

Zhang J, France P, Radomyselskiy A, Datta S, Zhao J, Wv Ooij (2003) Hydrophobic cotton fabric coated by a thin nanoparticulate plasma film. J Appl Polym Sci 88:1473–1481

Zhang H, Kannangara D, Hilder M, Ettl R, Shen W (2007) The role of vapour deposition in the hydrophobization treatment of cellulose fibres using alkyl ketene dimers and alkenyl succinic acid anhydrides. Colloid Surf A 297(1–3):203–210