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Hydrophobic Molecular Treatments of Cellulose-based or Other Polysaccharide Barrier Layers for Sustainable Food Packaging: A Review

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Paper, nanocellulose, and other polysaccharide-based materials can be excellent candidates for food packaging barrier layers, except that they tend to be vulnerable to moisture. This article reviews published research describing various chemical treatments having the potential to render hydrophobic character to such layers. Emphasis is placed on systems in which hydrophobic monomers are used to treat either particles or sheets comprised largely of polysaccharides. A goal of this review is to identify combinations of materials and procedures having promise for scale-up to industrial production, while providing effective resistance to moisture. The idea is to protect the underlying polysaccharide-based barrier layers such that they can continue to impede the transfer of such permeants as oxygen, greases, flavor compounds, and water vapor. A further goal is to minimize any adverse environmental impacts associated with the treatments. Based on the research articles considered in this review, promising hydrophobic treatments can be achieved involving silanes, ester formation, other covalent interactions, plasma treatments, and to some extent by various treatments that do not require formation of covalent bonds. The article is designed such that readers can skip ahead to items of particular interest to them.

DOI: 10.15376/biores.17.2.Szlek

Keywords: Water resistance; Contact angles; Polysaccharides; Silanes; Paper; Films

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INTRODUCTION

Motivating Goals

Protect the barrier layer

The motivating goal of this review article is to identify propitious approaches to achieve effective and eco-friendly water-barrier capability for use in single-use food packaging systems. As has been described elsewhere, it is possible to form various polysaccharides, including nanocellulose and related composites, into dense layers having promising ability to block the transport of oxygen (Aulin *et al.* 2010; Hubbe *et al.* 2017). Because of the high density of hydrogen bonding that can be achieved within highly refined paper-like structures, especially when coated with materials such as nanocellulose or starch, it is possible to achieve high resistance to grease, even without usage of fluorochemicals (Hubbe and Pruszynski 2020). Such structures are highly regarded from an environmental standpoint because they are mainly composed of photosynthetically renewable materials that are inherently biodegradable. On the other hand, such structures composed of polysaccharides, including cellulose, are susceptible to effects of aqueous solutions, which can cause the films and structures to swell, weaken, and become non-resistant to oxygen, water vapor, and other permeants (Fotie *et al.* 2020).

A second goal of this review is to consider a parallel strategy in which the surfaces of cellulose nanomaterials are molecularly treated to render them hydrophobic. In such cases, a hydrophobic molecular treatment has the potential to render polysaccharide-based material compatible with various hydrophobic plastics (Dufresne 2011). In such a form, the nanocellulose (or other polysaccharide-based particles) could perform better in various water-resistant composite films in combination with suitable oleophilic matrix polymers.

As represented by the illustration in Fig. 1, the present review focuses on processing strategies that involve molecular treatments of surfaces – often at the monomolecular or sub-monomolecular coverage level.

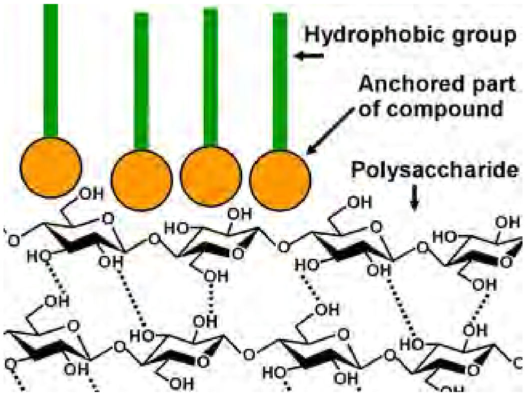


Fig. 1. Conceptual illustration of an ideal hydrophobic molecular treatment of a polysaccharide substrate. The orange circle represents a part of the hydrophobic compound that is anchored to the substrate. The green "stick" represents the hydrophobic part. Dotted lines suggest hydrogen bonding, which would be vulnerable to wetting by water.

In principle, it is possible to convert the hydrophilic surfaces of cellulose and various other biopolymers to a highly hydrophobic state by surface derivatization or adsorption (Cunha and Gandini 2010a,b; Samyn 2013; Hubbe *et al.* 2015b; Farhat *et al.* 2017). Such approaches are appealing from a general environmental perspective, since the effects often can be achieved with a minimum amount of material. For instance, a monomolecular layer or sublayer of a suitably anchored hydrophobic compound may be sufficient to achieve a high level of water repellency (Hubbe 2007; Oh *et al.* 2011; Kumar *et al.* 2016; Krishnamurthy *et al.* 2020). Questions to be considered in this review article include (a) whether such treatments are sufficient to meet the needs for various packaging applications and (b) whether such treatments can meet expectations for eco-friendliness.

Minimal adverse environmental impact

In present production, a leading strategy to protect paper and other polysaccharide-based structures from wetting involves application of a polyethylene laminate film (Borch 1991; Vinayagamoorthy 2017). For instance, most milk cartons are assembled as a sandwich, with a paperboard layer between two polyethylene laminate layers (Kirwan 2013). To prevent failure of such cartons at cut edges (*e.g.* at the bottom interior), and at pinholes in the laminate film, the paperboard will have been hydrophobically treated – usually with alkylketene dimer sizing agent (Dumas 1981; Ehrhardt and Leckey 2020). The format is illustrated in Fig. 2.

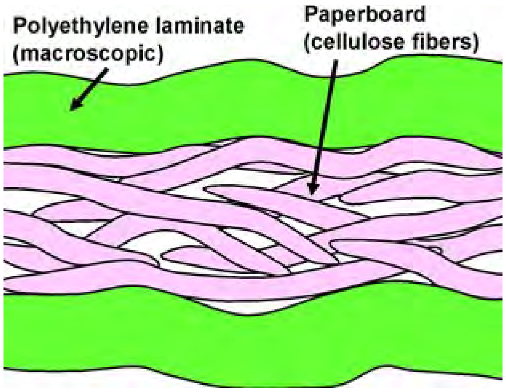


Fig. 2. Basic layered cross-sectional format of a typical milk carton. The green coloration indicates a hydrophobic nature, whereas the pink coloration indicates a weak negative ionic charge when in contact with an aqueous solution.

It is technically possible to recycle milk cartons, separating and recovering both the papermaking fibers and the plastic (Srivatsa and Markham 1993). However, most cartons currently are not recycled. This may be due to such factors as the wet condition of many used food packages, concerns about contamination by food, and the complex nature of such waste materials. Rather, a high proportion of food-related waste becomes landfilled (Kakadellis and Harris 2020). Some other modern single-use food containers can be even more difficult to recycle, due to strongly-adhering layers of different materials, such as aluminum foil (Keles and Dundar 2007) or non-biodegradable plastics (Mulakkal *et al.* 2021), which are often firmly attached to a layer of paper. When such packaging material becomes tossed out as litter or follows storm drains into water bodies, it contributes to the load of non-degrading matter present in the environment (Eriksen *et al.* 2014; Jambeck *et al.* 2015; Avio *et al.* 2017). As such, it can interfere with marine life in profound ways (Gregory 2009). In addition, the fluorochemical treatments that have been relied upon to achieve greaseproof characteristics in products for fast foods have raised environmental concerns (Curtzwiler *et al.* 2021). The perfluorochemical treatments are bioaccumulative and resistant to breakdown in the environment (Houde *et al.* 2011; Kabadi *et al.* 2018; Trier *et al.* 2018). By contrast, certain polysaccharide-based films that have been molecularly surface-treated to render them hydrophobic have shown rapid biodegradation (Chen *et al.* 2021). There is a need for more research of such issues.

Bioplastic films, some of which can be melt-extruded, have received much attention as a promising option for replacing petroleum-based polyolefin films. Though such films can serve as effective barriers to aqueous media (Singha and Hedenqvist 2020; Attallah *et al.* 2021), concerns have been raised regarding their biodegradability (Emadian *et al.* 2017). For instance, it appears that the rate-determining step for degradation of poly(lactic acid) (PLA) in the environment is abiotic, and that a temperature over about 55 °C is needed to bring about meaningful degradation (Agarwal *et al.* 1998; Karamanlioglu *et al.* 2014; Hubbe *et al.* 2021). Even though PLA can be prepared from plant-based materials, it persists for a very long time without degrading in natural environments, such as soils and seawater.

In many studies, relatively thick layers of hydrophobic polymers have been prepared by casting from nonaqueous solution, followed by evaporation (Rhim and Ng 2007). Though such technologies can be effective for preparation of water-resistant plastic film layers, there can be extra expenses involved in recovery of the solvents (Kim *et al.* 2014) and there are concerns about environmental effects of the solvents (Chemat *et al.* 2019; Fadel and Tarabieh 2019). So-called green solvents can be employed as a means to decrease such concerns (Clarke *et al.* 2018; Sheldon 2019). However, the macroscopic nature (many times thicker than a monolayer) suggests a much greater time required for biodegradation.

Yet another approach involves mixing a polysaccharide-based aqueous solution with suitable water-soluble but relatively hydrophobic copolymers such that the resulting film is hydrophobic. This approach can involve addition of such copolymers as styrene maleic anhydride (SMA) or styrene acrylate (SA) to a solution of starch that is applied to paper’s surface at a size press of a paper machine (Iselau *et al.* 2015, 2018; Bildik Dal and Hubbe 2021). Upon drying, the amphiphilic copolymer becomes oriented at the surface in such a way as to resist wetting by water. Though such approaches have merit, bulk coatings such as these will be regarded as outside of the scope of the present article.

To address the need for truly biodegradable food packaging systems, while still providing effective protection against penetration of aqueous solutions, it will be assumed in the present review article that promising solutions are likely to involve *(a) systems that are mainly based on photosynthetically renewable materials, (b) hydrophobic treatments of surfaces such that water resistance is achieved with approximately a monolayer of coverage, and (c) application systems that mainly avoid the utilization of organic solvents*.

The idea that protection against water can be achieved with approximately a monolayer of well-chosen and anchored monomers is not new. The paper industry has relied for many years on such internal sizing treatments as alkylketene dimer (AKD) and alkenylsuccinic anhydride (ASA) to achieve a range of water resistance (Dumas 1981; Hubbe 2007). Commercial specimens of both ASA and AKD are understood to contain a mixture of alkyl chain lengths. These additives are conventionally added to the cellulose fiber slurry before the formation of the paper sheet, and they spread and become covalently bound to the surfaces of the cellulosic fibers during the drying process. For example, AKD is the most common internal sizing treatment for achieving a hydrophobic paper structure in milk cartons (Dumas 1981; Ehrhardt and Leckey 2020). Such cartons, as already mentioned, ordinarily are protected on both sides by laminated films of polyethylene. However, the AKD treatment is needed due to cut edges of the sandwich structure (inside of each carton) as well as pinholes in the plastic layers (Tufvesson and Lindström 2007). In addition to conventional internal sizing agents used by papermakers, a wide range of treatment options have been considered in the scientific literature. These treatments, which are tabulated in the appendix of this article, are a main focus of this review.

Not interfere with a barrier layer

A key requirement for any treatment intended to impart hydrophobic character to an eco-friendly packaging system may be that it should not interfere with or defeat other required functions of the same layer of material. Two such requirements can be critical. First, the treatment ought not to defeat the oxygen-blocking ability of a film layer that is intended to have that capability. Second, the treatment ought not to harm the strength of the layer, especially in cases where the layer is intended to provide strength to the package. Such interferences are represented schematically in Fig. 3, where it is suggested that the presence of various compounds might interfere with the hydrogen-bonded structures within polysaccharide-based films.

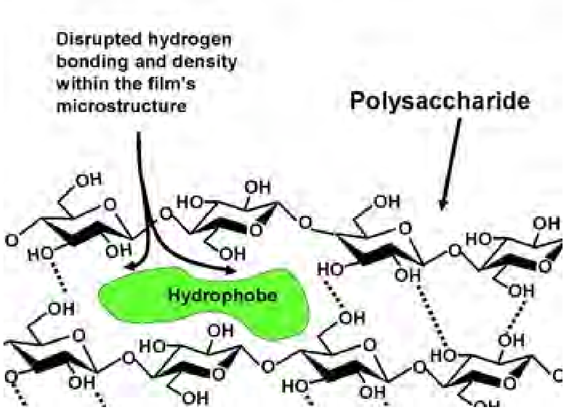


Fig. 3. Sketch illustrating the concept of interference of hydrogen bonding within a polysaccharide-based structure due to the presence of certain hydrophobic compounds

Studies have shown that incorporation of various hydrophobic components or plasticizers into nanocellulose films, during their preparation, have the potential to degrade the oxygen barrier performance of that film (Lagarón *et al.* 2004; Hansen *et al.* 2012). The hydrophobic groups can interrupt the patterns of hydrogen bonding, thus providing less resistant paths for diffusion of the nonpolar molecules. In addition, water itself tends to swell and plasticize such structures, greatly increasing their oxygen permeability (Aulin *et al.* 2010).

Limited studies have considered effects on strength when hydrophobic materials have been reacted on the surface of paper or other polysaccharide-based materials. It has been observed in industry that internal sizing of paper with such agents as ASA and AKD generally does not interfere with paper strength. This is despite the fact that the hydrophobic groups would be expected to get in the way of potential hydrogen bonds that otherwise could form across the zone between adjacent cellulosic fibers in molecular contact. It had been proposed that this is because the emulsified hydrophobic agents mainly remain in the form of droplets or waxy particles and do not spread to a significant extent over the fiber surfaces until near the end of the paper drying process (Hubbe 2014). By that point in the process, the bonded areas between the fibers are already well established. The increased temperature of the paper, after most of the water has been evaporated, can be expected to increase the vapor pressure of the ASA or AKD molecules, allowing them to migrate. Therefore, the mobilized AKD or ASA molecules, transported by surface diffusion (Shen *et al.* 2002; Shen and Parker 2003) or diffusing in the vapor phase (Akpabio and Roberts 1987; Yu and Garnier 2002; Zhang *et al.* 2007), are restricted to the remaining air-solid interfaces. This concept was recently confirmed by Korpela *et al.* (2021), who compared AKD and rosin soap sizing systems. The AKD sizing system had no adverse effect on paper strength. By contrast, rosin soap sizing, which is known to involve spreading of the sizing agent already in the wet state before formation of the paper sheet, thus decreased paper strength. In other relevant work, Bildik *et al.* (2016) showed that when AKD was dissolved in heptane, applied to an existing sheet of paper, followed by drying, the strength of the paper actually increased. In other words, rather than interfering with paper strength, the AKD material appeared to function as a kind of matrix phase within a paper-based fiber composite. These findings are consistent with the hypothesis that already-established bonded areas between cellulosic fibers tend not to be affected by the migrating sizing compounds.

The concerns just mentioned often can be overcome by use of a multi-layer structure. In fact, the use of multiple layers, each contributing different attributes, is a common strategy in creating packaging solutions (Ferrer *et al.* 2017; Helanto *et al.* 2019; Reichert *et al.* 2020). Thus, it will be tentatively assumed, in the presentation of this review, that a high-performing, low-cost, eco-friendly barrier to aqueous fluids will have high value even in cases where one or more additional layers may be required to provide strength or to block the transfer of oxygen, oils, fragrances, or water vapor, *etc.*

Factors Affecting Speed, Scalability

To be interesting to industrialists, each candidate unit operation needs to be suitable for scale-up to industrially relevant speeds and dimensions. Each unit operation, as well as the related equipment, must be considered relative to any limitations in maximum speeds. In addition, any required chemical reactions need to be compatible with continuous processing at high speed. Some types of unit operations of interest include vapor-phase application, plasma treatments, and the use of aqueous emulsions. These three approaches are illustrated schematically in Fig. 4. As will be discussed later, these three general approaches have been shown to offer favorable combinations of relatively quick hydrophobization, avoidance of organic solvents, and suitability for scale-up.

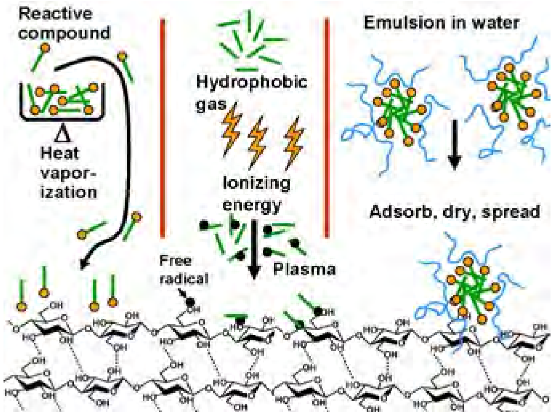


Fig. 4. Three solvent-free approaches (set off by the vertical bold lines) to hydrophobic molecular treatment of polysaccharide substrates. Note that the black circles represent odd-electron (free radical) groups. The light-blue wavy lines represent cationic polyelectrolytes.

Vapor-phase application

It is desirable if a hydrophobic compound to be conveyed in gaseous form to and reacted at the surface of a target material. Some of the silane-based treatment procedures to be considered in later sections of this article involve vapor-phase exposure and reaction (Fadeev and McCarthy 2000; Cunha *et al.* 2010b; An *et al.* 2011; Oh *et al.* 2011; Glavan *et al.* 2014; Lazzari *et al.* 2017; Yu *et al.* 2019; Jankauskaite *et al.* 2020; Zhao *et al.* 2020; Wulz *et al.* 2021). Acid chlorides, likewise, are sufficiently reactive that they can be transported as vapor to a surface that bears –OH groups and allowed to react, forming esters (Berlioz *et al.* 2009; Fumagalli *et al.* 2013; Wulz *et al.* 2021). Zhang *et al.* (2007) likewise achieved successful vapor-phase sizing with ASA, which is an anhydride of a dicarboxylic acid; parallel tests attempted with AKD failed, apparently due to the decomposition of AKD when it was heated. Yuan *et al.* (2005) likewise achieved successful vapor-phase reduction of the surface energy of a cellulose surface by treatment with an anhydride.

Plasma application

Plasma treatments of polysaccharide-based surfaces can be regarded as a distinct class of vapor-phase treatment (Siow 2018; Zhang *et al.* 2018). A key distinction is that the treatment is carried out in the presence of highly energized gas molecules, which induce reactivity to the hydrophobic species and to the surfaces. Belgacem and Gandini (2005), Kalia *et al.* (2009), and Belgacem *et al.* (2011) reviewed work involving such systems. In the case of silane-based treatments, plasma application can be used to activate hexamethyldisiloxane so that it reacts effectively and becomes bound to the substrate (Creatore *et al.* 2001, 2002; Mai and Militz 2004; Schneider *et al.* 2007, 2009; Deilmann *et al.* 2008a,b; Avramidis *et al.* 2009; Siliprandi *et al.* 2011; Chen *et al.* 2017; Mitschker *et al.* 2018; Yang *et al.* 2018; Kakiuchi *et al.* 2019; Cerny *et al.* 2021; Ma *et al.* 2021). Plasma also has been used to graft perfluorinated alkyl chains onto cellulose (Kong *et al.* 1992; Sahin *et al.* 2002, 2007; Navarro *et al.* 2003; Zhang *et al.* 2003; Balu *et al.* 2008; Toriz *et al.* 2008; Mirvakili *et al.* 2013; Siro *et al.* 2013). Starostin *et al.* (2015, 2016) used tetraethyl orthosilicate as an additive material for plasma treatment of polymers. Samanta *et al.* (2012) used a plasma system to react butadiene at cellulosic surfaces. In summary, plasma is able to achieve effective grafting of a wide range of compounds, not relying on the presence of reactive groups such as silanes, acid chlorides, or anhydrides.

Aqueous treatments involving emulsions

From an environmental standpoint, water-based formulations are generally regarded with favor. As a means to impart hydrophobicity, there are two main challenges. First, one has to figure out a way to convey a water-reactive hydrophobic compound in a water phase. The second challenge is that energy needs to be expended in a subsequent drying step. The first goal can be met by preparing the mixture as an emulsion, in which the droplets of hydrophobic compound are suspended in the water. In the case of AKD, such emulsions are formed above the melting point of the AKD and then immediately cooled, forming a dispersion of solid particles. Liang *et al.* (2013) used such an approach to treat cotton fabrics with a fluorinated trimethoxysilane. Related methods are widely used within the paper industry to treat the fiber furnish before the formation and drying of the sheet (Hubbe 2007; Ashish *et al.* 2019). In paper machine applications, the wet web needs to be dried in any case. Thus, the drying process can be used to induce ester formation between hydrophobic compound and a paper surface. In the case of ASA size, the reaction goes to completion, even before the end of the drying process. AKD is less reactive (Lindström and Larsson 2008). Thus, AKD may continue to react with the paper surface as the paper is in the form of a large reel or individual rolls, the interiors of which remain hot inside due to their size. Cationic polyelectrolytes such as cationic starch can be a good choice as an emulsifying agent. The starch can serve as a steric stabilizer, keeping the hydrophobic particles from colliding and coalescing. The cationic charge helps to retain the emulsion particle on fiber surfaces during paper's formation before it is dried. Though the general procedure is not as inherently fast as vapor-phased treatments, it can be appropriate when a material needs to be dried anyway during its manufacturing process.

Options for continuous treatment

The papermaking process, as just discussed, is an example of a continuous industrial process. There are other related continuous unit operations that can be used for rendering such material hydrophobic. For industrial applications, it is important that such operations can be carried out at a large scale and relatively high speed. For example, plasma treatment (Starostin *et al.* 2015) and chemical vapor deposition technology (Alf *et al.* 2010) have been considered for roll-to-roll application (Alf *et al.* 2010). Continuous application also has been studied for silane treatment (Yu *et al.* 2019). However, there is a continuing need for more research to be carried out at a pilot scale, thus providing a bridge between theoretical studies and commercial production.

Review Articles

This review builds upon earlier progress, much of which already has been reviewed in previous articles. Selected reviews are listed in Table 1, along with their areas of focus.

Table 1. Selected Review Articles Dealing with Hydrophobization of Cellulosic or other Polysaccharide-based Surfaces

Topic Area	Citation
Wood fiber chemical coupling and composites	Lu *et al.* 2000
Natural fiber surface modification and biocomposites	Mohanty *et al.* 2001
Wood modification with silicon compounds	Mai & Militz 2004
Cellulose surface modification for performance in composites	Belgacem & Gandini 2005
Cellulose heterogeneous modification for novel materials	Freire & Gandini 2006
Cellulose and other polysaccharides functionalization	Nishio 2006
Natural fiber pretreatments for composites	Kalia *et al.* 2009
Hydrophobization of polysaccharides	Cunha & Gandini 2010
Green composites	La Mantia & Morreale 2011
Wood conversion from hydrophilic to hydrophobic	Wang & Piao 2011
Natural fiber chemical treatments for composites	Kabir *et al.* 2012
Cellulose surface modification for hydrophobization	Samyn 2013
Nanocellulose chemical modification	Habibi 2014
Nanofibrillated cellulose surface modification	Kalia *et al.* 2014
Green modification of surfaces of cellulosic materials	Hubbe *et al.* 2015b
Nanocellulose modification to improve its properties	Bajpai 2017
Cellulose in-depth modification	Gandini & Belgacem 2016
Hemicellulose hydrophobization	Farhat *et al.* 2017
Nanocellulose for packaging applications	Hubbe *et al.* 2017
Ecofriendly composites	Moustafa *et al.* 2019
Nanofibrillated cellulose surface modification	Rol *et al.* 2019
Food packaging based on nanocellulose	Fotie *et al.* 2020
Polysaccharides used in coatings for food packaging	Nechita & Roman 2020

THEORETICAL BACKGROUND

To prepare for later discussion of specific types of hydrophobic modifications of polysaccharide surfaces, this section will review some principles that pertain in many situations. This will include a discussion of the most widely considered polysaccharides (cellulose, hemicellulose, starch, and chitosan), concepts related to hydrophobicity and wetting, procedures for relatively simple removal of various compounds from the surfaces (*i.e.* removal of contaminants), categories of treatment processes, some chemical principles, durability, biodegradability, and issues related to the use of multilayer structures in food packaging.

Polysaccharide Surface Chemistry and Barrier Properties

Cellulose

Sustainable single-use packaging can be based on polysaccharides as a main category of ingredients. The word polysaccharide refers to sugar polymers, *i.e.* photosynthetically renewable and biodegradable materials. The component monomeric sugars, *e.g.* glucose in the case of cellulose, are highly soluble in water. Cellulose can be described as a linear polymer of glucose in which the anhydroglucose units are connected by β-1,4 glycosidic linkages. The weight-average degree of polymerization of cellulose within cotton was reported as 3335 (Ling *et al.* 2019). For cellulose in wood, the corresponding values are about 9500 or 9600 and possibly as high as 15,000 (Goring and Timell 1962). The fact that cellulose is quite insoluble has been attributed to its structural regularity, linear form, and its tendency to form crystalline zones having high physical density and a highly regular pattern of hydrogen bonding both within (intra-) and between (inter-) the adjacent cellulose chains (Lindman *et al.* 2010). As explained in the cited article, the dense pattern of hydrogen bonding is supplemented by van der Waals forces, which play a dominant role in certain crystal planes of natural cellulose.

An intermediate degree of hydrophilic character of purified cellulose surfaces can be attributed mainly to the presence of some –OH functional groups, which are polar and which are able to form hydrogen bonds with water molecules (Hatakeyama and Hatakeyama 1998). The effects of these –OH groups depend on their orientation. This phenomenon was demonstrated by Yamane *et al.* (2006), who regenerated solid cellulose from solutions by addition to contrasting fluid media. When the cellulose was regenerated in the presence of water, it developed a hydrophilic surface, *i.e.* a low contact angle with water. By contrast, if the cellulose was regenerated within a non-polar medium, it developed a relatively hydrophobic surface. Figure 5, which uses the atom locations shown by Yamane *et al.* (2006), shows how the hydrophilic –OH groups are located above and below the cellulose chain when it is presented in the “front” view in the cited article. The hydrogens that are bonded to oxygen are shown in a brighter blue to represent their partial positive charge that is induced by the electronegative oxygens. By contrast, hydrogens not associated with oxygen mainly are presented above and below the chain shown in the “edge” view. These findings are consistent with the relatively high levels of crystallinity in typical samples of cellulose, in combination with the fact that the –OH groups on a cellulose molecule are oriented in a planar manner. Thus, different crystal planes of cellulose have different wettability.

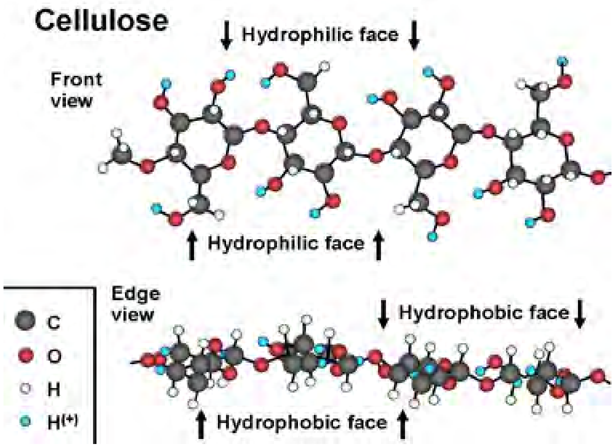


Fig. 5. Representations of cellulose chains in "front" and "edge" view (redrawn based on Yamane *et al.* 2006), showing that hydrophilic –OH groups are mainly on certain faces, and at least one face of the cellulose-I crystal generally lacks –OH groups

Plant-derived cellulose has relatively few carboxylic acid groups (-COOH) before industrial processing. Strong alkaline pulping, as in the case of the kraft process, can develop –COOH groups (metasaccharinic acid) at the reducing ends of cellulose macromolecular chains (Van Loon and Glaus 1997). The –COOH groups of polysaccharides typically have pK_a values in the range of about 3.3 to 5, meaning that at neutral pH most of them will be in dissociated form, giving them a negative ionic charge (Laine *et al.* 1996). The high polarity of charged groups, depending on their frequency at a surface, can provide a relatively large contribution to water-wettability (Hansen 2007; Notley and Norgren 2010).

The barrier properties of cellulose have been well demonstrated in the case of nanofibrillated cellulose (NFC), which is also referred to as cellulose nanofibril. A review article by Aulin *et al.* (2010) documents the development of high resistance to both oxygen and oils when aqueous suspensions of NFC are formed into a film. The impenetrability to these non-polar substances, when dry, has been attributed to a high film density and a high cohesive energy density, both of which can be attributed to a high density of hydrogen bonding (Lagarón *et al.* 2004). However, these barrier properties have been found to deteriorate when such films are exposed to liquid water or high levels of relative humidity.

Hemicelluloses

The hemicelluloses present within woody materials typically provide the strongest contribution to hydrophilic character. There are two main roles that can be envisioned for hemicellulose in packaging. First, hemicellulose serves as a bonding agent between the fibers in paper products. Second, hemicellulose can be considered as an option for preparing thin films that might be applied onto paper surfaces (Hansen *et al.* 2012; Borjesson *et al.* 2019; Shao *et al.* 2020). Trees commonly used for papermaking have about 25 to 35% of hemicelluloses (Pettersen 1984). Hemicelluloses can be briefly described as copolymers of two or more types of sugar unit. Degrees of polymerization of hemicellulose in wood are typically in the range of 100 to 200 (Pettersen 1984). In contrast to cellulose, hemicelluloses have irregular structures, including side groups or acetylation along the chain. The plural form of the word hemicelluloses is used within scientific literature due to the presence of two or more copolymer structures in a typical type of wood. The irregular structure of hemicelluloses implies a higher accessibility of water to –OH groups, leading to a higher tendency to wet and to swell in water, compared to cellulose. This concept is supported by the finding that the swelling of wood is decreased progressively during the thermal destruction of hemicellulose (Repellin and Guyonnet 2005). A contribution to negative charge, in the range of 2 to 50 μeq/g of pulp, can be attributed to the susceptibility of hemicelluloses to hydrolytic cleavage of acetyl groups during alkaline treatment, and the value can rise to 100 μeq/g with peroxide bleaching (Pranovich *et al.* 2003). Various researchers, as discussed in earlier review articles, have considered the incorporation of hemicellulose into films that can be potentially useful in packaging (Cunha and Gandini 2010a,b; Farhat *et al.* 2017). As described in the cited articles, hydrophobic treatments or hydrophobic extruded layers are required when using hemicellulose-based films in such applications. Figure 6 provides examples of hemicelluloses present in softwood (Eronen *et al.* 2011) and hardwood (Ebringerova and Heinze 2000) pulps.

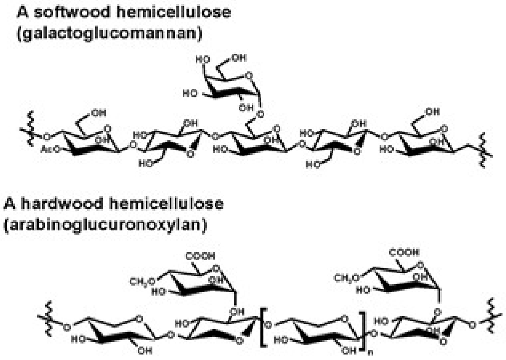


Fig. 6. Major components of softwood and hardwood hemicelluloses

Lignin

Relative to cellulose and hemicellulose, the lignin component of woody materials is more hydrophobic, especially in its natural state (Kang *et al.* 2019). Lignin can be generally described as the product of various reactions among monolignol compounds, such a coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol (Boerjan *et al.* 2003). These become joined during the biosynthesis of lignin by oxidative coupling. The lignin in softwoods (conifers) is mainly derived from coniferyl alcohol, yielding guaiacyl lignin groups. The lignin in hardwood species has a majority of lignin structures derived from sinapyl alcohol, yielding syringyl lignin groups. Figure 7 shows examples of two of the most common linkage structures present in native softwood lignin (Chang and Jiang 2019). The generally hydrophobic nature of lignin can be attributed to its high content of aromatic groups, thus giving a relatively high ratio of carbon to oxygen atoms (Maksimuk *et al.* 2020). The cited article says that carbohydrate-free lignin can have a composition of 70% carbon, 6.5% hydrogen, and 23.5% oxygen on a mass basis. By contrast, the chemical formula for cellulose (and various other polysaccharides) implies 40.00% carbon, 6.67% hydrogen, and 53.33% oxygen. Note that in the examples shown in Fig. 7, though some hydrophilic phenolic –OH groups will be present, a majority of such positions will be occupied by the more hydrophobic methoxyl (-OCH_3) groups. Also, though some aliphatic –OH groups will be present in lignin, the proportion of such groups is much lower than in polysaccharides. Within a tree, the lignin provides rigidity, protection against compression, and relatively strong resistance to natural biodegradation.

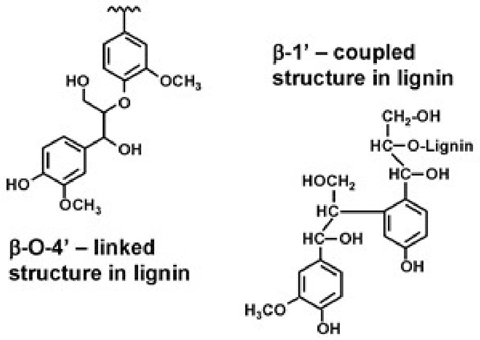


Fig. 7. Examples of the two most common linkage structures within native softwood lignin

Extractives

In addition to the three main ingredients of wood (cellulose, hemicellulose, and lignin), the trees commonly used in papermaking commonly contain about 1 to 2% of extractives. Higher levels, *e.g.* 2 to 29%, can be present in tropical woods (Choong and Achmadi 1991). As illustrated in Fig. 8, the extractives can include fatty acids, triglyceride fats comprising fatty acid groups, various unsaponifiable compounds, and, in the case of conifers, resin acids, including rosin and related compounds in the terpene family (Back and Allen 2000).

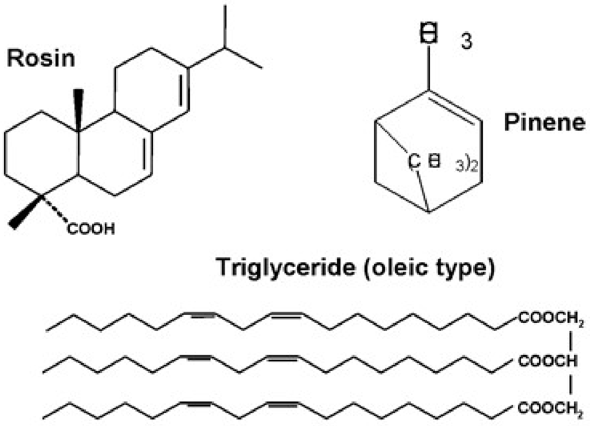


Fig. 8. Common forms of extractives present in softwood material

The hydrophobic nature of the extractives is evident from their name, since the solvents used for the extraction of wood are oleophilic. Although the relative content is generally low, the hydrophobic nature of extractives provides a driving force for them to migrate to the air-solid interfaces of wood-based materials during the passage of time (Swanson and Cordingly 1956). In addition, the drying of wood has a tendency to draw extractives to the point where evaporation is taking place, often near or at the surface (Mottonen and Karki 2010). Extractives also have a strong tendency to self-associate (Hubbe *et al.* 2020). The likely presence of extractives in cellulosic materials can pose a challenge when one attempts to determine the reasons for hydrophobicity of cellulosic specimens after various surface treatments; it is always possible that residual extractives are contributing to the observed effects, regardless of what other compounds have been added.

Chitosan

Due to its widespread availability as a byproduct of crustacean harvesting, chitin is widely regarded as a promising polysaccharide for eco-friendly product formulations (Elsabee *et al.* 2009; Aranaz *et al.* 2010; Deng *et al.* 2017; Bhardwaj *et al.* 2020). By treatment of crustacean shells with strong base, chitin can be converted to chitosan, which has a chemical structure almost identical to that of cellulose. The main difference is that amine groups are present in the C2 positions in place of the –OH groups that would be there in the case of cellulose (Dash *et al.* 2011). Due to the presence of the amine groups, chitosan can be solubilized in weakly acidic water, especially after addition of acetic acid, such that the pH is below the pKa of the functional amines. As illustrated in Fig. 9, the acidity results in protonation of the amine groups. The solubilized chitosan can subsequently be formed into films, which can be considered for medical (Rinaudo 2006; Elsabee *et al.* 2009; Dash *et al.* 2011) or food-contact purposes (van den Broek *et al.* 2015; Deng *et al.* 2017; Vikele *et al.* 2017). It has be observed that chitosan films, even when relatively pure, can resist wetting by water (Cunha *et al.* 2008; Vikele *et al.* 2017; Bhardwaj *et al.* 2020). Such hydrophobicity sometimes has been attributed to the presence of hydrophobic extractives (Cunha *et al.* 2008). Recently it was suggested, however, that such hydrophobicity comes about due to the self-orientation of the films during their drying; the idea is that the non-polar sides of the chitosan chains become exposed outwards toward the air phase, thus decreasing the free energy of the system (Hubbe 2019).

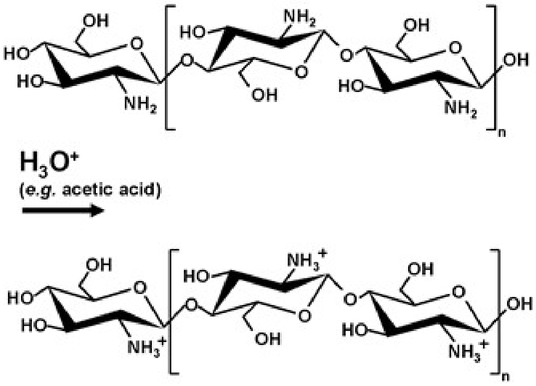


Fig. 9. Chemical structure of chitosan, also showing its transformation to a cationic species when exposed to acidic conditions

Starches

When plants have a need to store energy in a recoverable form, starch biosynthesis is a prime evolutionary option. When the energy is needed by the plant, the starch can easily be converted to glucose by the action of amylase enzymes (van der Maarel *et al.* 2002). Starch availability has subsequently become greatly amplified by the cultivation practices of humans, and it has become widely used in various formulations, including films for food packaging (Jimenez *et al.* 2012; Prabhu and Prashantha 2018). Due to its water-solubility, some differences in the way it crystallizes, and its abundance hydroxyl groups, starch is widely regarded as a hydrophilic material (Herman *et al.* 1989). Cunha and Gandini (2010a,b) reviewed modifications to convert starch to a hydrophobic material. In addition, the wettability of starch surfaces has been shown to be affected by the orientations of the macromolecular segments (Sundari and Balasubramanian 1997; Immel and Lichtenthaler 2000; Shrimali *et al.* 2018; Bildik Dal and Hubbe 2021). The challenge remains, however, that starch-based films are generally prone to swelling in water, and their barrier properties suffer due to the effects of high humidity, especially if a plasticizer is present (Mali *et al.* 2005).

Hydrophobicity and Wetting

To provide background for later discussions in this article, some aspects regarding surface hydrophobicity will be summarized here, including literature references to fuller descriptions. The principles to be discussed in this section are well established, and they can be helpful in understanding the role of the chemical treatments to be considered later in this review. Key areas of focus will be contact angles of water, morphological aspects affecting contact angle, and issues related to the compatibility of different phases that come into contact. These topics were reviewed in a more general manner by Sengupta and Han (2014), who focused on the best-established theories.

Contact angles

The ability of a material to resist penetration by liquid water or an aqueous solution can be estimated based on a knowledge of its contact angles, in combination with estimates of the size of its pores (Hubbe *et al.* 2015a). When tests are conducted on relatively flat surfaces, the contact angle, as well as the differentiation between wettable and nonwettable surfaces, can be defined as shown in Fig. 10.

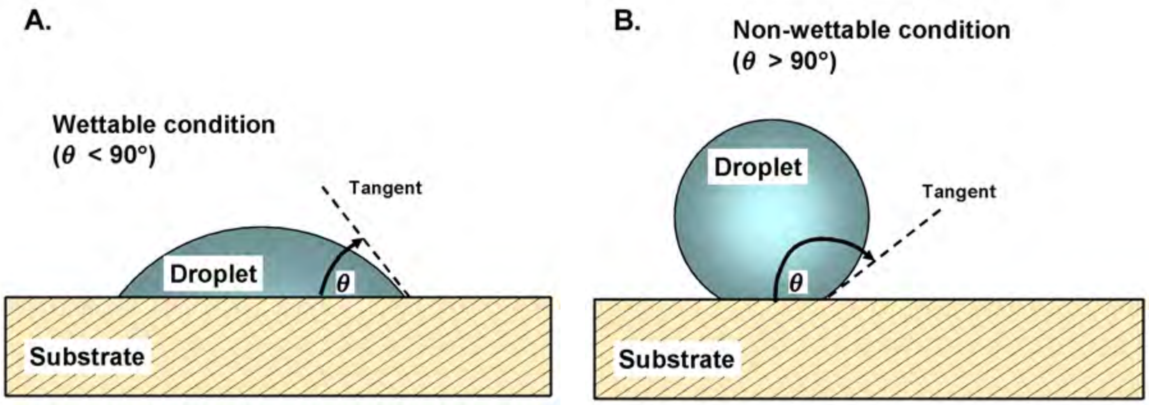


Fig. 10. Schematic illustration defining the contact angle of a liquid on a flat substrate, where surfaces having contact angle values below 90° are defined as wettable (A), and those with contact angles above 90° are non-wettable (B)

Theoretical descriptions to account for contact angles generally start by assuming a perfectly smooth, flat, nonporous substrate having no chemical variabilities. On such an ideal surface, one can expect that the angle of contact would be a function of the interfacial tensions acting in three directions, as illustrated in Fig. 12. Young (1805) proposed such a concept and introduced Eq. 1,

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \tag{1}$$

where γ_{SV} is the interfacial tension at the solid-vapor boundary, γ_{SL} is the interfacial tension at the solid-liquid boundary, and γ_{LV} is the well-known surface tension of the liquid, in the presence of its own vapor in the gas phase.

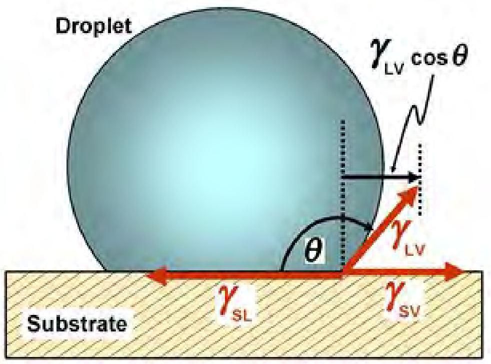


Fig. 11. Representation of the interfacial force balance proposed by Young

Whereas the interfacial tension in at the air-liquid interface (γ_{LV}) can be measured directly (Hartland 2004), there is no direct way to measure either of the other two interfacial tension terms in Eq. 1, *i.e.* the solid-liquid interfacial tension and the solid-air (or solid to vapor) interfacial tension. Because the solid will have a very limited ability to stretch reversibly, it can be questioned whether the two unknown terms can be regarded as thermodynamic quantities (Hubbe *et al.* 2015a). As discussed in the cited work, there have been protracted efforts to resolve the theoretical issues and to obtain practical results, but no comprehensive theoretical approach has received full acceptance. It follows that there is a need for fresh, creative thinking and a focus on general principles.

In general, it is known that wettability of a liquid on a certain smooth solid will be favored by a high degree of molecular interactions between the liquid and the solid. On the other hand, relatively poor wettability will be expected in cases where the molecules within the fluid interact more strongly with each other than with the molecules at the solid surface. This situation can be illustrated by the example of a droplet of pure water on a flat slab of pure paraffin wax. Within the water phase, the molecules interact strongly by means of hydrogen bonding, polar interactions (which may be treated as part of the hydrogen bonding interaction), and van der Waals – London dispersion forces (Liang *et al.* 2007). Among those forces, the interaction between the two phases involves only the dispersion forces.

Paraffin wax can be regarded as a prototypical non-wettable surface. It is composed just of alkyl chains. These are completely nonpolar and have only a moderate Hamaker constant, which governs the magnitude of the dispersion force interactions (Visser 1972, 1995). Surfaces that are coated by a monolayer for perfluorinated alkyl groups, *e.g.* polytetrafluoroethylene, have even lower values of the dispersion content due to the low polarizability of the electrons in the outermost molecular orbitals (Visser 1972). By contrast, if a surface contains exposed polar hydroxyl groups, as in the case of typical cellulosic materials, the surface free energy is expected to be much higher. The cellulosic surface would be expected to interact with a water droplet through hydrogen bonding and polar interactions in addition to the van der Waals – London dispersion forces. Based on these considerations, if the goal is to impede the spreading and permeation of water, then it makes sense to treat the cellulosic or other polysaccharide surface either by derivatizing the –OH groups or by covering them up. Such approaches will be discussed in this article.

Rates of permeation

If the pores are modeled as simple cylinders, perpendicular to the plane of a porous film, then the rate of penetration and the distance penetrated at time equal to *t* are given by (Lucas 1918; Washburn 1921),

$$\mathrm{d}l/\mathrm{d}t = \gamma_{\mathrm{LV}}\, R \cos\theta / (4\eta\, l) \qquad (2)$$

$$l = [(R\, \gamma_{\mathrm{LV}} \cos\theta]\, t/(2\eta)]^{1/2} \qquad (3)$$

where *r* is the equivalent radius of the pores (based on the cylindrical pore model), η is the dynamic viscosity, *v* is the average velocity of fluid flow into the capillary, *L* is the distance of permeation at time *t*, and *t* is the elapsed time after the initial wetting. These equations, though highly idealized, have been found to be useful as a starting point in understanding the rates of permeation of liquids through paper and related substrates (Aspler *et al.* 1984; Aspler and Lyne 1984). The model is illustrated in Fig. 12.

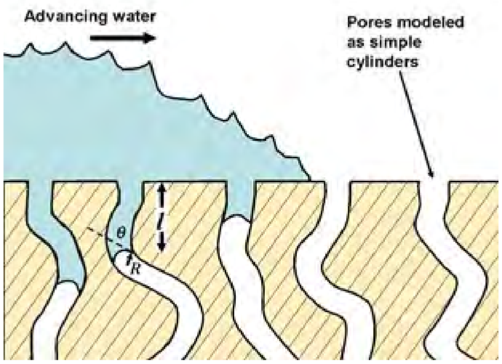


Fig. 12. Sketch illustrating the Lucas-Washburn model of the wetting of a porous solid

Morphological aspects

The measuring of contact angles of water onto cellulosic surfaces is prone to relatively high levels of scatter of the data. Much of that scatter usually can be attributed to various scales of roughness, or of porosity, on typical surfaces. Roughness can be expected to affect wetting contact angles in two general ways – equilibrium effects and hysteresis effect. The equilibrium effects were first described and estimated by Wenzel (1936). Wenzel essentially made a correction to Young's equation. The purpose was to account for the greater amount of surface area, per unit of planar area, when the material is rough. Thus, Wenzel's equation can be expressed as:

$$r_w\, [\gamma_{SV} - \gamma_{SL}] = \gamma_{LV} \cos\theta \qquad (4)$$

In Eq. 4, r_w is the roughness coefficient (ratio of real surface area to planar surface area), and the other parameters have the same definitions as before. The practical effect of the roughness coefficient in Eq. 4 is that it predicts contact angles to be further away from 90 degrees, compared to a smooth surface. Thus, systems that would be classed as "wetting" (with contact angles below 90°) would be predicted to be even more wetting when a realistic level of roughness is assumed, rather than using the model of a perfectly smooth surface. Likewise, systems that would be classed as “nonwetting” (angles > 90° on an ideal smooth surface) would be even more non-wetting when roughness is taken into consideration.

When the surfaces have large roughness or pores, relative to the scale of random wave action at the liquid surfaces (de Gennes 1985; Piao *et al.* 2010), then it is reasonable to anticipate hysteresis effects. Strong evidence of the importance of hysteresis effects is provided by observed differences in advancing and receding contact angles on real surfaces, including cellulosic surfaces (Gardner *et al.* 1991). Two idealized situations can impede the movement of a three-phase contact line on a wetted surface – relatively large, oriented features and deep pores. As described in more detail elsewhere (Piao *et al.* 2010; Hubbe *et al.* 2015a), when there is a ridge of roughness that exceeds the scale of wavelike thermal motion at the liquid surface, the local value of contact angle will not be the same as the contact angle relative to the overall plane of the surface. It makes intuitive sense that certain patterns of roughness can contribute to hysteresis. However, one usually does not know enough detail of the surface features to make accurate estimates of advancing or receding contact angles on rough surfaces.

To estimate the effects of pores or deep valleys on a surface, relative to contact angles and wettability, most researchers have based their calculations on the work of Cassie and Baxter (1944). The governing equation can be expressed as,

$$\cos\theta = f_1 \cos\theta_1 + f_2 \cos\theta_2 \tag{5}$$

where θ is the observed contact angle, θ_1 is what the value of contact angle would have been if all of the surface had been of type “1”, θ_2 is what the value of contact angle would have been if all of the surface had been of type “2”, and f_1 and f_2 are proportional amounts of interface corresponding to the two compositions, each in comparison to a hypothetical planar surface area. When using the approach of Cassie and Baxter, it is important to be aware that there are some incorrect mathematical expressions that are in common usage (Milne and Amirfazli 2012). By setting one of the theta terms in Eq. 5 to 180°, it is possible to account for the complete non-wettability of an empty pore. The equation then can be used to account for super-hydrophobic systems, which arise when small pillars of hydrophobic solid are surrounded by suitably deep valleys. The same equations also can account for instances where superhydrophobic systems fail, meaning that the valleys within such structures become filled with the wetting liquid (Hubbe *et al.* 2015a). Once that occurs, such systems are readily wetted by water.

Compatibility

In addition to affecting wettability and permeation by fluids, the hydrophobic treatment of a cellulosic surface also has potential to affect the compatibility of the material when it is being considered as a reinforcement within a composite. Some examples are listed in a recent review article that considered the use of cellulose-based reinforcements of different size within a series of different plastic phases (Hubbe and Grigsby 2020). Whereas the data reported in the literature failed to show any strong relationship between composite properties and the size of the reinforcing particles, the hydrophobic treatment of those particles has been repeatedly shown in the literature to provide a strength advantage. Another situation in which bonding at interfaces can be critically important in packaging applications is when a cellulosic film needs to adhere to an adjacent film layer, which might be oleophilic (Mittal 2010; Lee *et al.* 2019).

Two conditions need to be fulfilled in order to achieve strong adhesion at a phase boundary within a polymer matrix or between a cellulosic film and an oleophilic film. The first of these is that during the formation of that boundary, often at a temperature above the melting point of the matrix, one of the materials needs to fully wet the other surfaces (Good 1992). Due to the relatively low surface tensions of common polymers such as melted polyethylene, polypropylene, polyesters, *etc.*, in combination with the relatively high surface free energy of dry cellulosic surfaces, it is reasonable to expect full wetting to occur. Studies have shown that such polymer melts have a low contact angle with clean, dry cellulosic surfaces, which is consistent with the concepts pioneered by Young (1805) and those who further developed theories related to wettability. The second condition, which is harder to achieve, is that the two phases either need to be connected by covalent bonds or there has to be a least a moderate amount of three-dimensional molecular overlap at the boundary, *i.e.* mixing among molecular segments from each adjacent phase (Aradian *et al.* 2000). This concept is illustrated in Fig. 13. Such overlap is likely to be absent at an interface formed between a hydrophobic polymer phase (for instance when it is cooling form a melted condition) and a polysaccharide phase. The reason is that the strongly hydrogen bonded material resists association with the molecular chains of the nonpolar phase (Blokzijl and Englberts 1993). Thus, the mutual solubility of the two phases will be low. A higher number of hydrogen bonds are able to form if the polysaccharide material bonds mainly with itself rather than having its segments mix to a significant extent with those of a polyolefin in an interfacial region. Such effects contribute to an inherent reluctance for different types of polymer chains to intermix with each other (Flory 1942).

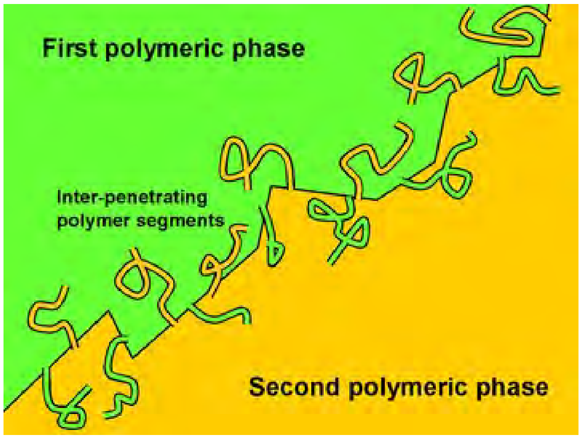


Fig. 13. Concept of inter-mixing of polymeric segments at the boundary between two well-adhering phases

As will be seen later in this article, when discussing strategies for surface modification of cellulosic surfaces, various covalent reactions at surfaces of polysaccharide films and particle surfaces have the potential to attach a variety of alkyl or other functionalities. As will be reported, not only can such treatments render the surfaces hydrophobic, but they also can provide the polysaccharide surfaces with a means to locally intertwine with the adjacent matrix material, thus forming bonds strong enough to resist delamination at those interfaces (Hubbe and Grigsby 2020). Such findings are consistent with the intermixing of polymers at the interface, especially in the melt condition (Zhang *et al.* 2011).

Removal of Loosely Bound Substances

Before reviewing some fundamentals related to surface derivatization and grafting of polysaccharide materials, it is first important to consider issues related to the likely presence of loosely bound hydrophobic substances already present at those surfaces. Natural materials can contain a variety of waxes, oils, and fatty substances. As mentioned earlier, these may have already migrated to air-solid interfaces (Swanson and Cordingly 1956; Bildik Dal and Hubbe 2021). Though such unbound, generally monomeric substances can be expected to be compatible with various oleophilic polymer melt materials, they provide a point of weakness at the interface. Adhesion scientists often refer to weak boundary layers when they are explaining instances of low adhesion strength (Gardner *et al.* 2008).

As noted in a review article by Bajpai (2017), adhesion at cellulosic surfaces often can be improved by removal of loosely bound materials. This can be done with alkaline solutions, which have the ability to saponify esters, as well as to convert fatty acids to their soap forms (Mercantili *et al.* 2014) so that they are readily washed from the surfaces. It is likely that some of the benefit of mercerization, involving treatment of cellulosic materials with relatively strong alkali (Albinante *et al.* 2013), is due to removal of saponifiable monomeric compounds. Such effects also can be achieved by extraction with organic solvents (Belgacem and Gandini 2005).

Treatment Classes

In the next main section of this article, which deals with different chemical modifications, a variety of process options will be mentioned. Since each such option could be considered for a range of different chemistries, it makes sense to compare and describe the process options in advance. To begin, Fig. 14 provides a pictorial summary of the options, which include vapor-phase transfer, plasma, aqueous solvent, aqueous emulsion, non-aqueous solvents, and enzymatic treatments.

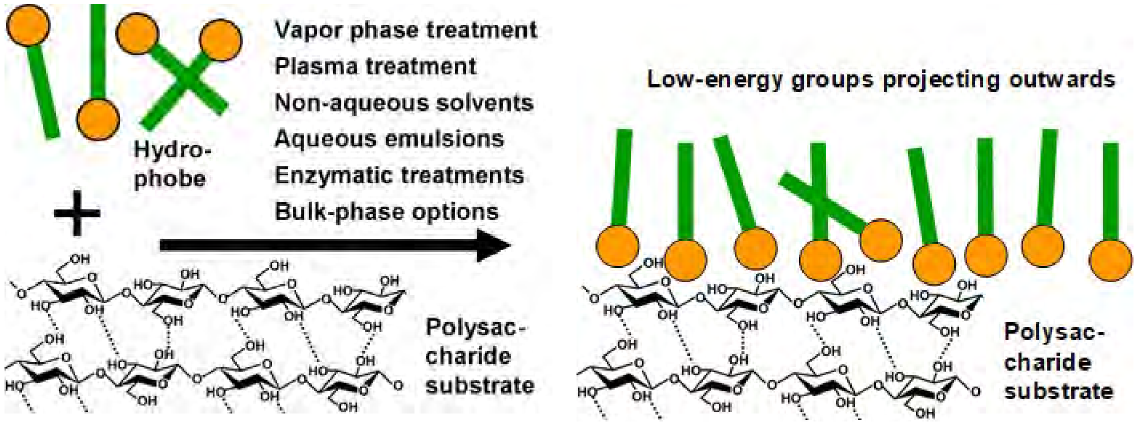


Fig. 14. Depiction of process options for hydrophobization of polysaccharide-based surfaces

Vapor-phase

Vapor-phase treatment can be an attractive option for industrial processing because it offers a potential way to avoid the handling of solvents, including the possible evaporation or collection of those solvents after the treatment. A key requirement is that the substance to be distributed must have high chemical stability above its boiling point.

In addition, it has to be sufficiently reactive in order to achieve a suitable level of covalent bonding with the treated solids, presumably during a continuous processing operation.

Hydrophobization of polysaccharide-type surfaces by vapor-phase treatment has been widely reported (Fadeev and McCarthy 2000; Yuan *et al.* 2005; Oh *et al.* 2011; Fumagalli *et al.* 2013; Glavan *et al.* 2014; Jin *et al.* 2015; Lazzari *et al.* 2017; David *et al.* 2019; Yu *et al.* 2019; Jankauskaite *et al.* 2020; Leal *et al.* 2020; Zhao *et al.* 2020; Shang *et al.* 2021; Wulz *et al.* 2021). Fumagalli *et al.* (2013) noted that surface esterification, brought about by treatment with palmitoyl chloride, was restricted to surface reactions. The resulting cellulose nanocrystal aerogels were readily dispersible into organic media. Lindström and Larsson (2008) reviewed relevant literature and reported effective vapor-phase treatment of paper with alkenylsuccinic anhydride (ASA), leading to a high degree of hydrophobicity. A similar approach was found not to work for the alkylketene dimer (AKD) sizing agent, an effect that was attributed to decomposition of the AKD when it was heated (Zhang *et al.* 2007; Lindström and Larsson 2008).

Chemical vapor deposition is a gas-phase treatment in which the selected monomers are able to react with each other to form a polymeric layer on the treated surface (Alf *et al.* 2010). Such treatment, often carried out under vacuum, can be tailored to provide programmed patterns, *i.e.* a type of printing on the surface. Chemical vapor deposition has been used as a means to develop hydrophobicity on polysaccharide-based surfaces (Balu *et al.* 2008; Cunha and Gandini 2010a,b).

Plasma

Though plasma treatments can be regarded as vapor-phase treatments, they take place in the presence of energetic gas species. Free radical compounds present within a plasma can activate compounds present both within the plasma and on the treated surfaces (Andreozzi *et al.* 2005; Saleem *et al.* 2021). Hence, various components of the mixture can be caused to react covalently with a treated substrate (Belgacem and Gandini 2005). Plasma treatments are a favored way to treat surfaces with certain types of silane compounds, such as hexamethyldisiloxane (Avramidis *et al.* 2009; Starostin *et al.* 2016; Kakiuchi *et al.* 2019). Likewise, Balu *et al.* (2008) reported the effective preparation of superhydrophobic cellulose fibers by plasma treatment in the presence of pentafluoroethane, which is an otherwise non-reactive compound.

Aqueous emulsions

As a means of minimizing environmental impacts, there is an incentive to employ liquid water as a medium for conveying hydrophobic compounds to the surfaces of polysaccharide materials. A challenge is presented by the fact that the materials to be placed onto the surfaces generally are insoluble in water. One way to overcome this dilemma is to prepare an emulsion, using a suitable stabilizer (Mai and Militz 2004; Peydecastaing *et al.* 2006; Yuan *et al.* 2006; Dankovich and Hsieh 2007; Liang *et al.* 2013; Ganicz *et al.* 2020). Thus, the material to be distributed is in the form of tiny droplets (*e.g.* 1 µm). This is a very common approach used in modern papermaking when adding hydrophobic agents to the fiber suspension (Dumas 1981; Hubbe 2007; Lindström and Larsson 2008; Bildik Dal *et al.* 2020). In those applications, it can be advantageous to employ cationic starch or a cationic acrylamide copolymer as a stabilizer, since the positive charge will help to retain the sizing agent at fiber surfaces during the formation of the sheet. As another alternative, emulsions can be stabilized with nanoparticles; such formulations are known as Pickering emulsions (Bayer *et al.* 2009; Li *et al.* 2021b).

Non-aqueous solvent

Hydrophobic agents suitable for treatment of polysaccharide-based surfaces are often soluble in non-polar solvents. Some ideal attributes when selecting such a solvent might include high solubility of the compound of interest, relatively low boiling point (*e.g.* in the range 35 to 100 °C), adequate chemical stability, and sufficiently low viscosity. Such properties make it likely that the solvent can be used for casting of the solution on a specimen of interest, followed by evaporation (Kalia *et al.* 2014). The following studies employed casting from a nonpolar solvent as a way to place hydrophobic compounds at cellulosic surfaces (Siqueira *et al.* 2010; Bayer *et al.* 2011; Wang *et al.* 2015; Rukmanikrishnan *et al.* 2020a,b). An advantage of many organic solvents is that they do not react with such functional groups as chlorosilanes, acid chlorides, and anhydrides. By contrast, the possibility of premature reaction with water is a drawback of the emulsion systems just discussed. The use of solvents in the application system may incur additional costs for the solvent itself, the energy needed for its evaporation, and the capital and operating costs for solvent recovery (Seyler *et al.* 2006).

Enzymatic

An enzyme can be defined as a protein structure having the ability to catalyze a chemical reaction (Engel 2020). Because enzymes are biological products, they function in aqueous systems and generally are effective at convenient temperatures. Kudanga *et al.* (2010) used laccase enzyme to catalyze the reaction of fluorophenols to lignocellulosic surfaces. Dong *et al.* (2014) employed laccase enzyme as a means to attach dodecyl gallate to the surfaces of jute fibers. Likewise, Cusola *et al.* (2015) used an enzymatic approach to induce hydrophobicity of paper-based materials. All three sets of authors proposed a phenolic ether structure as a means of holding long-chain alkyl groups at the cellulosic surfaces. More recently, lipase was used to connect laurate alkyl chains to cellulose nanocrystals with the formation of ester linkages under aqueous conditions (Yin *et al.* 2020). Stepan *et al.* (2013) earlier had demonstrated the attachment of stearate groups to hemicellulose in the presence of lipase. An aqueous enzymatic derivatization of ethylcellulose with poly-hydroxybutyrate chains had been reported by Iqbal *et al.* (2014). Thus, it appears likely that enzymatic approaches will become more widely utilized for such surface treatments.

Chemical Principles

As an organizing concept, it will be assumed in this research that the most favorable hydrophobic surface treatments of polysaccharide surfaces, depending on the details of what is needed, will have a lot to do with energies. First to be considered will be the activation energies needed to form covalent bonds. Next will be the energies of adsorption, which may be important in cases where no covalent bonding is anticipated. Third, there may be a role of energy in hydrophobic associations that contribute to stabilization of a hydrophobic surface on a polysaccharide surface. The adsorption of polyelectrolytes has energy implications that differ from those of smaller molecules.

Activation energies

The importance of activation energies was already apparent in the earlier discussion of enzymes. As was noted, enzymes can promote the formation of specific covalent bonds. The rates of each of the covalent reactions to be considered in this review article will depend at least partly on its activation energy. Such issues will determine the degree to which some important reactions of interest take place and what can be done to promote the desired reactions. The rate-limiting step of many reactions, including those involved in derivatizations at polysaccharide surfaces, is often constrained by a need to reach a transition state. That energy of activation (E_a) generally corresponds to an energy saddle that lies between the reagent system and the bonded state (Gandour and Schowen 1978; Engel 2020). The situation is shown graphically in Fig. 15. It has been argued that the role of an enzyme is to help stabilize a transition state, which may effectively lower the energy of that state (Schramm 1998).

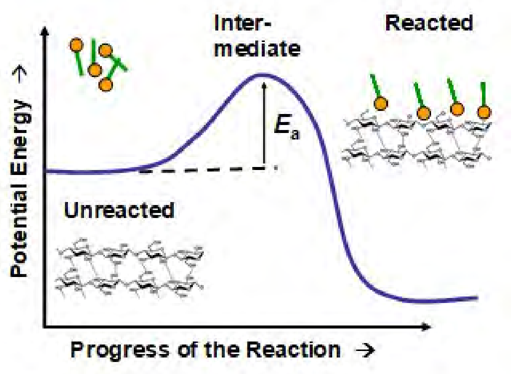


Fig. 15. Typical diagram of how the potential energy of interaction is likely to change as a function of the progress of a reaction, *i.e.* the reaction of a hydrophobic compound with the surface of a polysaccharide substrate

The concept of activation energy also can provide a framework for thinking about the types of covalent bonds that are likely to meet the requirements for effective and efficient modification of polysaccharide surfaces. The required input of energy to achieve reaction needs to be in the right range to be achieved at convenient temperatures and short time intervals. It has been argued that the tension within the five-membered ring of the anhydride group in the ASA sizing agent raises the energy of that species; thus, less energy is needed in order to reach the transition state for ester formation with the –OH groups of a polysaccharide surface (Hill *et al.* 1998; Shi *et al.* 2016). Thus, the rate of reaction of ASA with polysaccharide surfaces, such as cellulose, is relatively high. However, high reactivity of a certain anhydride compound with –OH groups on polysaccharides is often correlated with relatively high reactivity with water as well, leading to wasteful hydrolysis. Thus, acid chlorides, which have very high reactivity with the surface –OH groups, are usually restricted to water-free treatment systems, such as solvent application or vapor-phase application (see Table C in the Appendix).

Adsorption and desorption energies

Energy likewise may play a key role in systems aiming to modify surfaces by adsorption phenomena. Unlike the situations just discussed, there is usually little or no activation energy to overcome when the added compounds are becoming adsorbed from solution onto a target substrate. In typical cases, there is a favorable free energy of adsorption when the adsorbing species, initially present in the water phase, contains a hydrophobic group (Al-Ghouti and Al-Abisi 2020; Bildik Dal and Hubbe 2021), as is being considered here. In some cases the adsorption may be further favored by the presence of cationic groups, which are attracted to the negative ionic charges on typical polysaccharide-based substrates (Biswas and Chattoraj 1997; Al-Ghouti and Al-Abisi 2020). Only in cases where both the adsorbate and the solid substrate have the same (usually negative) sign of net charge is there likely to be an energy barrier opposing spontaneous adsorption of aqueous dissolved species that contain substantial hydrophobic groups (Wernert and Denoyel 2016). In the absence of such an energy barrier, rates of adsorption onto cellulose-based surfaces are typically governed by diffusion mechanisms (Douven *et al.* 2015; Hubbe *et al.* 2019).

Once a hydrophobic compound has adsorbed from aqueous solution onto a polysaccharide-based substrate, then the energy of adsorption can be instrumental in keeping it there. In general, the likelihood that a monomeric species escapes from the surface will be determined by a summation of adhesion energy contributions, including van der Waals, electrostatic, and entropic terms related to changes in the randomness of the system (Werth and Reinhard 1997; Ghosh *et al.* 2001; Enell *et al.* 2005). Because the attachment of a polymer involves the summation of contributions from many connected segments in the chain, spontaneous desorption is much more difficult. A sufficient energy of adsorption also is expected to be critical to the structural integrity of hydrophobic layers applied by adsorption to polysaccharide type surfaces intended for packaging applications.

Self-assembly

In addition to the substrate-adsorbate energies of interaction, the stability of a hydrophobic monomolecular layer at a surface exposed to water can also be strongly affected by tendencies for self-assembly among the adsorbing molecules. Self-assembly can be defined here as the tendency of certain hydrophobic groups to organize themselves into continuous condensed monolayers at various interfaces (Hubbe *et al.* 2020). As described in an earlier review article, such contributions to formation of hydrophobic layers are especially prominent in the case of compounds having long-chain alkyl groups (Hubbe *et al.* 2020). The contribution of hydrophobic groups to self-assembly of hydrophobic layers has been proposed in several studies (Renneckar *et al.* 2006; Aranaz *et al.* 2010; Li *et al.* 2011; Aarne *et al.* 2013; Hu *et al.* 2017; Wan *et al.* 2017; Malakhova *et al.* 2018; Cai *et al.* 2021). Within such layers it is common for the hydrophobic molecules to be pressed tightly together, *i.e.* condensed, as a compact monolayer. In principle, the presence of a condensed monolayer of nonpolar groups at a surface tends to resist not only water, but also it tends to be unfavorable for adhesion of other materials to that surface (Garoff and Zauscher 2002; Faucheux *et al.* 2004).

Macromolecular redundant interactions

A polymer chain can have multiple points of attachment. In addition, a polymer in solution, due to its connected nature, has only a relatively small change in randomness when comparing the polymer in solution to its adsorbed state. As a consequence, the adsorption of polymers onto surfaces tends to be more favored thermodynamically than it would be based merely on the enthalpy of interaction (Fleer *et al.* 1993). Strong binding to cellulosic surfaces can be expected especially when contributions from entropy are bolstered by the presence of hydrophobic groups. For example, styrenemaleic anhydride (SMA) is well known as a water-dispersible copolymer that is used in combination with size-press starch to make paper hydrophobic (Bildik Dal and Hubbe 2021). As discussed in the cited review article, SMA and similar size-press additives appear to migrate to the polysaccharide surfaces during the process of drying from a water solution.

Durability

The energy-related issues addressed in the previous subsection can be viewed as aspects related to the desired durability of hydrophobic effects to be incorporated into packing systems. A typical single-use container may need to resist continual or intermittent moisture both inside and out. The external moisture might consist, for instance, of condensate during its storage within a refrigerator. There is a need for eco-friendly, low-weight systems that are able to match the durability of such materials as glass, polycarbonate, or aluminum foil, *etc.* Not only must the hydrophobic effects be achieved initially, but they also need to persist in spite of abrasive action (Milionis *et al.* 2016).

Lability

At the same time that one needs a food packaging system to be able to endure long-term exposure to water, along with the stresses and abrasion of scuffing and handling, it also needs to break down. Two goals need to be met simultaneously – resisting aqueous solutions during the period of usage, and being susceptible to relatively fast biodegradation if and when the package is discarded to the environment. One important tactic for designing a material that breaks down is to incorporate molecular weak links into it, *i.e.* labile bonds. The silicon-carbon bond is a prime candidate for such effects. The chemical approaches to forming such bonds are well known (Bei *et al.* 2012), but they do not occur in nature. Apparently, there may not be a sufficient evolutionary advantage of creating an inherently weak bond as part of a biological process. On the other hand, it could be proposed that natural breakdown of such a bond could constitute a planned decomposition if the item were to end up in a natural environment.

Three-dimensionality

The development of a three-dimensional structure can be used as part of a strategy to achieve sufficiently durable structure, relative to the planned usage of a packaging system, while at the same time being able to incorporate weak or labile bonds, favoring the package's natural breakdown. This scenario appears to describe certain layered structures formed by reaction of alkoxysilanes (Jankauskaite *et al.* 2020). This topic will be considered more deeply when discussing that type of surface treatment.

Chemical crosslinking in the course of curing of surface layers can be achieved during chemical vapor deposition, which contributes to durability (Alf *et al.* 2010). Crosslinking also occurs during the curing of unsaturated oils (Dankovich and Hsieh 2007).

Biodegradability

Most currently used food packaging systems meet or exceed their required barrier properties and durability requirements, but they lack biodegradability. Further discussion of reported findings related to biodegradability appear later in this review article, but some general points can be made at the outset. First, one needs to keep in mind that there is only a weak correlation between "bio-based" and "biodegradable" (Robertson 2014). The molecular modification of any material has the potential to block its susceptibility to biological degradation. Attributes such as hydrophobicity generally tend to make materials less biodegradable, regardless of their origin (Luckachan and Pillai 2006; Yamano *et al.* 2014). A likely explanation is that enzymes are relatively large molecules, such that they cannot penetrate below the outer surface. Hydrophobic character makes it less likely that a packaging material will swell in water. In the absence of such swelling, the enzymes lack access to the bulk phase. However, some initial breakdown, leading to fracturing or swelling of the surface layers, can provide the needed access to enable them to cleave various bonds. Another key point is that abiotic changes are sometimes required before significant enzymatic biodegradation can begin, as was mentioned in the case of PLA in the Introduction of this article.

Layer Options

Before considering the effects of various specific hydrophobic treatments of surfaces, there are some general points related to layered structures that have general applicability. First, multilayered films already can be regarded as a well-established strategy in food packaging (Stasiek 2005; Lim *et al.* 2008; Lamnawar and Maazouz 2009; Garofalo *et al.* 2018; Mizielinska *et al.* 2020). Second, sometimes the addition of material to a barrier film is able to plug defects, such as holes (Martinpolo *et al.* 1992). The overall barrier properties often can exceed those of the individual components acting alone (Garofalo *et al.* 2018). However, the melt flow compatibility and interfacial integrity can be challenging (Lamnawar and Maazouz 2009). The references cited in this paragraph generally relate to the use of non-biodegradable, synthetic polymers. The challenge to be considered in this work is to achieve comparable effects by application of essentially molecular layer treatments in combination with photosynthetically renewable polysaccharides in the form of films or paper-like structures.

REPORTED EXPERIMENTAL FINDINGS AND INTERPRETATION

General Considerations

Having outlined, in the previous section, some key factors related to the creation of barrier layers having the ability to resist water penetration, the next step will be to consider literature dealing with different chemical treatments. As noted earlier, attention in this article is focused on strategies that rely on as little as one molecular layer of a hydrophobic substance to achieve such resistance. The goal of this section is to describe progress that has been achieved in development of surface treatments that can serve as the main barrier to water transport into and through a package or wrapper that is intended to protect food.

Though it is possible to contemplate a single, uniform layer of material meeting all of the barrier needs of a package (for instance in the case of a glass bottle), the focus of this article is on the achievement of satisfactory barrier performance using systems that are all or mostly composed of renewable materials. Existing review reports already have addressed important related topics such as the blockage of oxygen permeation (Paunonen 2013; Hubbe *et al.* 2017; Wang *et al.* 2018). While a heavy, monolithic structure such as glass can be effective for denying transport of a wide range of permeants (*e.g.* water, water vapor, oils, aroma compounds, and flavors), the focus here is what can be done while relying mainly on renewable, organic compounds. In principle, the goal of meeting the water-barrier goals with near-monolayer molecular coverage represents an opportunity to make food packages that are much lighter than glass.

As indicated in earlier review articles, cellulose-based packaging plies that are effective for resisting permeation by oxygen and grease are often harmed by the presence of high relative humidity or liquid water (Ferrer *et al.* 2017; Hubbe *et al.* 2017; Hubbe 2021). For this reason, it will be assumed here that an excellent barrier layer against liquid water and that water vapor will be a very important factor in the development of paper-based multi-layer packaging for foods. It is proposed here that the packaging layer that is charged with the responsibility of blocking the transport of water molecules has the potential to preserve some or all of the ability of under-lying layers in a packaging structure to block transport of other important permeants, including flavors, oils, oxygen, and contaminants.

Tabulation of Reported Findings

Factors considered

Due to their length, tables summarizing information obtained from various reviewed articles are placed in the Appendix of this article. Separate tables are provided for different classes of hydrophobic treatments. In each case, the categories considered include the chemical agent used in the treatment (silane, ester, amine, ion pair, adsorbed monomer, adsorbed polymer plasma click chemistry, and other), the medium (*e.g.* aqueous, ethanol, gas phase), the type of substrate (*e.g.* cellulose, starch, natural fibers, nanofibrillated cellulose), the water contact angle (WCA), various details (*e.g.* temperature, time, concentration), and the author-year information.

Order of topics

The order of the subsections that follow is meant to reflect levels of recent research interest, as well as the degree of progress that has been achieved in preparing effective hydrophobicity under industry-friendly processing conditions. Thus, silicone-based treatments are considered first, followed by other covalent reactions with the –OH and amine groups of various polysaccharide-based barrier layers. Such reactions include esterification, amine formation, and click chemistry. Next to be considered are non-reactive strategies, such as the usage of ionic associations as a means to anchor hydrophobic groups. Last to be considered will be the usage of various hydrophobic substances, especially naturally derived materials such as waxes, which can contribute hydrophobicity to the surfaces despite their lack of specific anchoring mechanisms.

Silane-type Treatments

General issues

Silane, the precursor for many of the other compounds to be discussed here, consists of a central silicon atom with four bonds of hydrogen in a tetrahedral configuration similar to methane. Silane compounds can complex with transition metals and may spontaneously combust in the air. Siloxanes, on the other hand, have a central oxygen bonded with two silicon atoms to form a Si-O-Si linkage and may be either straight chained or branched molecules that form the backbone of silicone-based compounds and polymers. The major route to form siloxanes is through the condensation reaction of two silanols. This will be described in greater detail below.

Based on the number of relatively recent scientific articles, it seems that researchers regard silane-type surface treatments as a highly promising field (Witucki 1993; Owen and Williams 1991; Xie *et al.* 2010). The present literature search identified over 70 articles dealing with hydrophobization of polysaccharide-based surfaces by means of silane-related compounds. A likely reason for the popularity of this research topic may be the variety of chemical species that can be used, as will be discussed in this section. Though various silane treatments can be applied from the gas phase or from organic solvents, there is increasing interest in aqueous-based treatment strategies, which have the potential to minimize environmental impacts. The layers formed by these treatments are rich in Si-O bonds, and there can be a wide range of pendant groups, including hydrophobic alkyl groups.

Siloxanes are useful for surface coatings that induce water repellency through silanization, which occurs when organofunctional alkoxysilane molecules cover the surface of a substrate (Tilley and Fry 2015). It has been widely reported that reactions involving formation of Si-O-cellulose bonds can impart water repellency to the surface of paper, typically by reducing the surface energy of paper and increasing the water surface contact angles between controlled and treated samples. Cappelletto *et al.* (2012) reported findings from their research on the effect of increasing methyl substitution of silane/siloxane paper coatings and its effect on hydrophobicity using a simple and direct sol-gel application process of single and double layered coatings of different methyl-functionalized alkoxysilanes. Their data suggests that increasing methyl substitution increases the hydrophobicity of paper primarily due to its ability to be evenly coated across the surface of cellulose (Cappelletto *et al.* 2012).

Some literature sources have referred to siloxanes as glassy, glass-like, or glass-hybrid materials. This is likely due to the idea that strong Si-O-Si linkages correspond to the structure of silica glass and glass-like films formed through the polycondensation of alkoxysilanes that is followed by curing (Iwamiya *et al*. 2020). While some Si-O-Si linkages have been observed in siloxane modified cellulose paper substrates, usually by FTIR, this will typically only occur when there is three-dimensional condensation of the compounds on the cellulose surface, which is beyond the scope of this review. In the case of siloxane monolayers on cellulose, the conventional sol-gel process mentioned above is too harsh and would degrade untreated cellulose paper before the film can form (Iwamiya *et al.* 2020). Therefore, alternative methods used to apply a siloxane coating onto paper are often employed, which yield similar, but not identical, results. Often, in the case of cellulose substrates, the siloxane coating being referred to as glassy is based on quantitative thermal analysis and mechanical strength testing; this suggests the formed siloxane matrix significantly increases the paper's thermo-oxidative stability and brittleness (Cappelletto 2012; Iwamiya *et al.* 2012).

While siloxanes have been used in commercial products for over a half a century, members of this family of compounds have been characterized in recent literature as emerging contaminants (Fijalkowski *et al.* 2017; Coralli *et al.* 2021). This is likely due to their documented persistence in the natural environment, which may lead to accumulation. Siloxanes that bear organic groups beyond methyl could reasonably be expected to display characteristic organic behavior, but there is not such data to support this. Despite the abundance of each element on Earth and carbon's essential role in supporting living organisms, the bond of Si-C is not known to occur naturally. There is no known biological process or enzyme that naturally catalyzes the bonding or cleavage of Si with C, nor any methyl or organic group (Rucker *et al*. 2015). The biodegradation of Si-C bonded organosiloxanes occurs too slowly to be observed under standard test conditions, while alkoxysilanes, silyl esters, and D3 and D4 may be hydrolyzed during test time parameters (Rucker *et al.* 2015). The cited authors report that the water hydrolysis that drives Si-O cleavage, by comparison, may be observed in di-, oligo-, and polysiloxanes, alkoxysilanes, and silyl esters according to chemical reaction Schemes [1] through [3]. It is important to keep in mind that the rate of such a mechanism depends on chemical structure and related physical physicochemical properties and environmental conditions in which the reaction is set.

$$R_3SiOSiR'_3 + H_2O \rightarrow R_3SiOH + HOSiR'_3 \qquad [1]$$

$$R_3SiOR' + H_2O \rightarrow R_3SiOH + HOR' \qquad [2]$$

$$RC(=O)OSiR'_3 + H_2O \rightarrow RC(=O)OH + HOSiR'_3 \qquad [3]$$

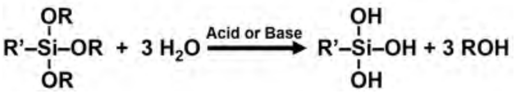
Schemes 1, 2, and 3. Initial hydrolysis steps of some silane-related compounds

Polydimethylsiloxanes, such as those often used in industry, are not known to hurt the composting process, but they are not considered compostable either, since they do not fully biodegrade within a reasonable period. It has been suggested that the biodegradation of such molecules is highly dependent on environmental moisture content. While polydimethylsiloxanes do not naturally biodegrade quickly in moist compost conditions, they have been shown to degrade by over half their original mass in 4 months after being placed into soil that is allowed to dry periodically (Lehmann *et al.* 2001; Rucker *et al.* 2015). With increasing drying of the soil, these compounds were characterized by increased rates of biodegradation, with some samples reaching an end mass 20 to 30% that of the original, though some degradation products were still present in the soil (Lehmann *et al.* 2001). More research should be conducted on improving the biodegradability of these compounds used in commercial products.

Tri-alkoxysilanes

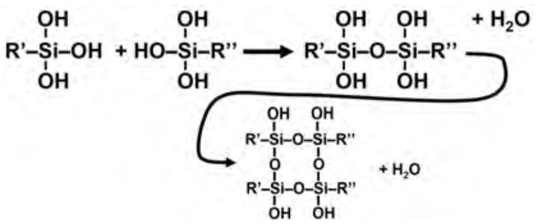
Siloxane copolymers may be classified depending on their structure and microstructure of various units of siloxane. The alkoxysilane class of compounds has attracted the most research attention for such purposes as hydrophobically modifying polysaccharide-type surfaces. The conditions that have been studied to achieve such effects are summarized in Table A in the Appendix.

The most commonly used forms of alkoxysilanes have three ethoxy or three methoxy groups, as illustrated in Scheme 4. These groups are susceptible to hydrolysis upon exposure to water. As a rule, two steps are incorporated into processes aimed at using alkoxysilanes to impart hydrophobic effects on plant-based materials. In the first step, as illustrated in Scheme 4, the alkoxide groups are hydrolyzed to an intermediate silanol form. In the second step, sometimes involving an adjustment of pH, the polysaccharide-based material is introduced, allowing the interfacial reaction to proceed.



$$R'\text{–}Si(OR)_3 + 3\,H_2O \xrightarrow{\text{Acid or Base}} R'\text{–}Si(OH)_3 + 3\,ROH$$

Scheme 4. Trialkoxysilanes and their initial hydrolysis



Scheme 5. Self-condensation of hydrolyzed trialkoxysilanes

Figure 16 illustrates a two-step process by which hydroxysilane species may become bound to a polysaccharide substrate (Xie *et al.* 2010). As shown, the first step is likely to involve hydrogen bonding. Next, depending on such factors as temperature, time, and loss of water through evaporation, covalent bonding and further condensation of the silanol functions can be expected. Note in the figure that such reactions, which might be called “curing”, involve the loss of water.

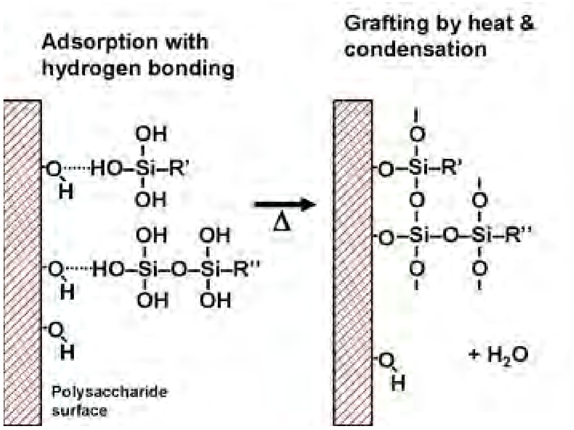


Fig. 16. Reaction of hydrolyzed silane compounds with hydroxylated surfaces, with the loss of water

For the first step, by adjusting the pH to an acidic range, the hydrolysis of alkoxide groups can take place while the subsequent condensation among these entities can be suppressed (Bel-Hassen *et al.* 2008). Table 2 lists some reported pH values that have been selected in reported studies when the goal has been to hydrolyze triethoxysilanes but to discourage their mutual condensation before they have had a chance to react with the polysaccharide surface. Thus, pH values in the range of about 3 to 5 are often chosen to allow formation of relatively stable intermediate silanol compounds, which then have a chance to individually react with the –OH groups on the surfaces of the polysaccharide substrate.

Table 2. Selected pH Conditions for Prehydrolysis of Alkoxysilanes before their Exposure to Polysaccharide Surfaces

Reagent	Medium	Substrate	pH	Citation
Methyl tri-methoxysilane	Aqueous	Cellulose nanocrystals	Hydrolysis of MTMS at pH 3	Baatti *et al.* 2019
Vinyltriethoxy silane, etc.	Aqueous	Cellulose	0.05 M HCl for 30 min.	Beaumont *et al.* 2018
Glycidyloxy-propyl dimethylethoxy silane	Aqueous or ethanol	Nano-fibrillated cellulose	Acetic acid to pH=3	Cabrera *et al.* 2020
Methyl-methoxysilanes	Aqueous	Paper	0.05 M HCl	Cappelletto *et al.* 2012
Methacryloxy-propyltrimeth-oxysilane	Aqueous	Cellulose nanocrystals	Citric acid pH 5.4	Raquez *et al.* 2012
Aminopropyl trimethoxysilane	Water; ethanol	Nanofibrillated cellulose	5.5	Robles *et al.* 2018

Another way to suppress the premature self-condensation of hydrolyzed silane species is to carry out the reactions within a water-ethanol mixture, often having a ratio of 1:4 (Salon *et al.* 2005, 2007; Ly *et al.* 2009; Rachini *et al.* 2009, 2011; Hao *et al.* 2019) or 1:9 (Khalil-Abad and Yazdanshenas 2010; Wei *et al.* 2016; Indarti *et al.* 2019) water:ethanol.

Another remarkable feature of the alkoxysilane family is the great variety of substituent groups that can occupy the fourth position on the silicon atom. For instance, hydrophobic effects are routinely achieved when the substituent is an alkyl group. Commonly reported alkyl groups for such reagents range from methyl (Cappelletto *et al.* 2012; Baatti *et al.* 2019) to long-chain alkyl (Khalil-Abad and Yazdanshenas 2010; Wang *et al.* 2012; Le *et al.* 2016) groups. Thus, users of this technology need to pick and choose among many similar candidate compounds and select whichever one of them best meets their overall objectives, including minimization of costs. In principle, the long-chain alkyl varieties can be expected to impart a higher degree of hydrophobic character (Chen *et al.* 2020). However, the shorter-chain alkyl compounds might have advantages with respect to other attributes of the surface layer, such as the density of coverage (Nourry *et al.* 2016). Likewise, Erasmus and Barkhuysen (2009) achieved superhydrophobic behavior of cotton following treatment with a perfluorinated tri-alkoxysilane.

A wide range of conditions have been specified in research aimed at allowing the hydrolyzed silane entities to react with the –OH groups at the surface of the polysaccharide layer or particles. As shown in Table A, room temperature often has been selected for reacting the hydrolyzed alkoxide in solution with the polysaccharide surfaces, and the treatment times range from about 2 to 4 h. Sometimes a treatment time of 24 h has been selected (Lu *et al.* 2008). Such long treatment times might either be for convenience of lab schedules or to err on the side of completeness of the reaction. Notably, none of the cited studies seemed to be focusing on minimization of treatment times for continuous production. Abdelmouleh *et al.* (2002) studied adsorption isotherms to examine the nature of the interaction mechanisms between microcrystalline cellulose surfaces and silanes and found that prehydrolyzed trialkoxysilanes (2 hours, 80/20 ethanol/water solution) were only physically or weakly adsorbed onto the cellulose surface when applied at room temperature and could be completely desorbed at that stage via Soxhlet extraction with pure ethanol (Abdelmouleh *et al.* 2002).

After the selected period of reaction of the hydrolyzed silane with the substrate, a majority of the reported treatment procedures call for rinsing, followed by drying and heating. Presumably, the goal of the heating, often in the range 60 °C (Cunha *et al.* 2010a; Cappelletto *et al.* 2013) to 120 °C (Abdelmouleh *et al.* 2002; Cabrera *et al.* 2020), is to drive the following type of reaction to its completion,

$$R_3Si\text{-}OH + HO\text{-}R' \rightarrow R_3Si\text{-}O\text{-}R + H_2O$$

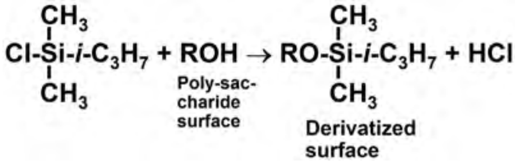
Scheme 6. Curing or annealing to complete the reaction with surface

where R may represent various entities and R' represents the polysaccharide substrate. Raquez *et al.* (2012) used the term "annealing" to denote such a process. Higher temperatures, such as 130 °C (Chun *et al*. 2012), can be used when treating relatively stable cellulose substrates when the goal is to decrease the time needed for full curing, which could be thought of as curing. Lower temperatures, such as vacuum drying without application of heat (Hao *et al.* 2019) are sometimes used when treating relatively delicate solids, such as starch nanoparticles. Times of curing are often in the range of 2 to 24 h, as can be seen from Table A in the Appendix. Note that most cited work, so far, has been focused on development of procedures that work well in the laboratory. Further development will be needed to determine conditions best suited for industrial-scale production.

Chlorosilanes

Vapor-phase treatments and non-aqueous solvents are commonly used as media for treatment of various surfaces with chlorosilanes. Summary information can be found in Table B of the Appendix. An inherent advantage of the vapor-phase approach is that there does not need to be any solvent recovery system. On the other hand, solvents can be a handy way to expose the selected substrate to a uniform concentration of the reactant. Another potential advantage of using a nonaqueous liquid medium, when using chlorosilanes, is that it then is possible to include an acid-scavenging component such as imidazole (Goussé *et al.* 2004). The latter is able to neutralize the HCl that is released when a chlorosilane entity reacts with a surface-bound –OH group or with water in the system.

Scheme 7 shows the main reaction of a chlorosilane with the –OH groups of a polysaccharide surface. Unlike the alkoxysilanes, which require at least some water to be present to complete the bonding with the substrate, the chlorosilane treatments typically are carried out in the complete absence of water.



$$Cl\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}i\text{-}C_3H_7 + ROH \rightarrow RO\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}i\text{-}C_3H_7 + HCl$$

Scheme 7. Reaction of a chlorosilane with a polysaccharide surface

As was true for the tri-alkoxysilanes just considered, the chlorosilanes category includes compounds with a very wide range of substituent groups, making it possible to achieve not only hydrophobic character, but many other properties as well. A range of alkyl groups have been used to achieve hydrophobicity in these systems. For instance, trichloromethylsilane has been used to achieve moderate levels of hydrophobicity of the treated surfaces (Cunha *et al.* 2010b; Li *et al.* 2007; Leal *et al.* 2020). There appears to be a lot of flexibility in the ratio of methylation to chlorine groups; thus, trimethylsilyl chloride also has been used (Duchoslav *et al.* 2021). Slightly greater hydrophobic character often can be achieved with increasing size of the pendant alkyl group (Fadeev and McCarthy 2000). However, the cited article shows that the dependency of water contact angle on the molecular mass of the alkyl chain is very weak. On the other hand, by use of perfluorinated alkyl substituted chlorosilanes, oil-resistant surfaces have been achieved (Xue *et al.* 2008; Aulin *et al.* 2009; Glavan *et al.* 2014).

Siloxanes

The third main approach that has been used to render surfaces hydrophobic by means of silane-type chemicals has employed the relatively non-reactive siloxane group of compounds, in combination with plasma treatments of the surfaces. See Table C of the Appendix for summary information from related studies. The most widely used compound for this type of system is hexamethyldisiloxane (HMDS) (Creatore *et al.* 2001, 2002;

Deilmann *et al.* 2008a,b; Avramidis *et al.* 2009; Cerny *et al.* 2021; Ma *et al.* 2021).

Plasma treatments are used by most researchers to induce bonding between the siloxanes and various substrates. The idea is that the high-energy gases can energize both the siloxane entity and the surface, creating free radicals and other such activated species. Thereby, one does not need to depend on any inherent reactivity in the applied compound. Atmospheric plasmas having relatively low energy are used most commonly in such research (Avramidis *et al.* 2009; Chen *et al.* 2017; Cerny *et al.* 2021; Ma *et al.* 2021). Oxygen plasmas also have been used (Creatore *et al.* 2001, 2002; Deilmann *et al.* 2008a,b). In theory, the radicals are relatively short-lived, and the goal is to achieve covalent attachment of adsorbed species.

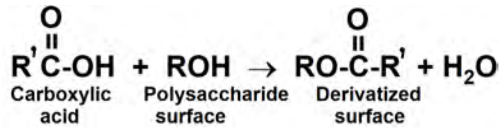
A very simple approach to the application of poly(dimethylsiloxane) was reported by Soz *et al.* (2021). Mixtures of the hydrophobic polymer and mineral particles were sprayed onto paper from tetrahydrofuran or isopropyl alcohol. The paper was allowed to dry in air, then heated to 120 °C for 36 h. Water contact angles up to 164° were obtained.

Esters

The esters of a wide range of carbohydrates, prepared either by means of surface treatments or pervasive reaction at the molecular level, represent a major category of industrial chemistry (Dixon *et al.* 1979; El Seoud and Heinze 2005; Cunha and Gandini 2010a,b; Wang *et al.* 2018). Reaction conditions need to be chosen with care in order to control not only the extent of surface reaction (Kim *et al.* 2002; Rodionova *et al.* 2011), but also whether or not the reactions are mainly restricted to the surfaces of a polysaccharide-based substrate (Berlioz *et al.* 2009). The fact that cellulose is insoluble in most common solvent systems can be counted as an advantage when the goal is to restrict the reaction to the surface; however, the cellulose itself may become increasingly soluble in nonpolar media as a result of the esterification itself. Related information can be found in some earlier review articles that dealt with surface-esterification of cellulose or other polysaccharides (Renneckar *et al.* 2006; Cunha and Gandini 2010a,b; Hubbe *et al.* 2015b; Wang *et al.* 2018). The goal here is to include more recent published findings and to emphasize treatment conditions that are relatively mild or likely to be eco-friendly.

Carboxylic acids

In principle, a carboxylic acid can be made to react to form an ester bond with a surface-bound –OH group as long as the temperature is high enough. As shown in Scheme 8, the reaction involves the release of one molecule of water, in the course of completing the ester linkage (Tsakos *et al.* 2015). Limitations of such an approach include possible degradation of the polysaccharide material (due to the elevated temperatures) and/or a low degree of reaction.



$$R'\overset{\overset{O}{\|}}{C}\text{-OH} + ROH \rightarrow RO\text{-}\overset{\overset{O}{\|}}{C}\text{-}R' + H_2O$$

Scheme 8. Esterification reaction of a carboxylic acid with an –OH group

Yoo and Youngblood (2016) reacted cellulose nanocrystals in combination with poly(lactic acid) (PLA) with long-chain alkyl fatty acids. The medium consisted of the

PLA melt. Reactions were carried out at 180 or 190 °C for about 30 min. When the same reaction was carried out in water, the required reaction time was doubled.

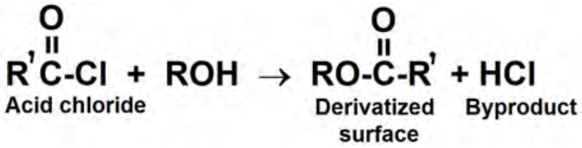
Lee *et al.* (2011) esterified bacterial cellulose with acetic, hexanoic, and dodecanoic acids in the presence of pyridine and toluene sulfonic acid at 50 °C for 2 h. In follow-up work using the same media, Lee and Bismarck (2012) reported the esterification of bacterial cellulose with hexanoic acid. In the latter study, freeze-drying of the bacterial cellulose before the reaction was found to promote a high degree of conversion to the ester. Peng *et al.* (2016) reacted carboxylic acid with CNC in DMSO medium at 60 °C overnight.

Peydecastaing *et al.* (2006) reported the long-chain esterification of cellulose powder by exposing it to a fatty acid emulsion. After the mixture was dried, it was heated to 195 °C for up to 6 h.

As can be learned from the foregoing examples, relatively high temperatures, along with long times and/or catalytic media generally are necessary when the reagent is an unmodified carboxylic acid. To address the lower reactivity of carboxylic acids, the focus of more recent studies has been on the use of coupling agents, such as 1’1-carbonyldiimidazole (CDI), carbodiimide, and 4-toluenesulfonyl chloride (TsCl). In the study by Peng *et al.* (2016), CDI-activated carboxylic acids were used to graft different side groups to cellulose nanocrystals (CNCs). The use of *in situ* activators expands the variety of carboxylic acids that can be used, while offering affordable pathways of esterification. However, the additional activation step extends the time length of the reaction, making it a longer, more complex process. Ultimately, the selection of this type of esterification would be driven by the specific needs of its final application and potentially the need for low-cost treatment (Peng *et al*. 2016).

Acid chlorides

Carboxylic acids can be converted to a more reactive form, the acid chlorides, by reaction with thionyl chloride, with the release of HCl and SO_2 (Kikuchi 2018). The increased reactivity can be regarded as an advantage for two reasons. First, the subsequent acylation reactions can be carried out at lower temperature, with less expected harm to the polysaccharide material being modified. Second, the reaction can be expected to require less time, which is critical for many industrial processes. The reaction is shown in Scheme 9.



$$R'\overset{O}{\overset{\|}{C}}\text{-Cl} + ROH \rightarrow RO\text{-}\overset{O}{\overset{\|}{C}}\text{-}R' + HCl$$

Scheme 9. Reaction of an acid chloride with an –OH group of a polysaccharide-based substrate

Conditions that have been utilized for the surface-esterification of polysaccharides using acid chlorides are summarized in Table E. Two main categories of conditions have been employed in most of the reported work: non-aqueous solvents and gas-phase treatments. Aqueous media are generally avoided due to the high reactivity of acid chlorides with water. Various non-aqueous solvents have been used, including toluene (Freire *et al.* 2006; Pasquini *et al.* 2008; de Mesquita *et al.* 2012; George *et al.* 2016), dichloromethane (Mukherjee *et al.* 2013), dimethylformamide (Peng *et al.* 2016), pyridine (Tomé *et al.* 2011b; Balasubramaniam *et al.* 2020), and N,N-dimethylacetamide (Li *et al.*

2019b). Hastati *et al.* (2021) carried out the reaction with the addition of a cationic surfactant, cetyltrimethylammonium chloride, presumably to stabilize the acid chloride as an emulsion. Tomé *et al.* (2011a) used an ionic liquid as the solvent for treatment of bacterial and vegetable cellulose specimens with hexanoyl chloride. Gas-phase reactions also have been widely studied (Berlioz *et al.* 2009; Fumagalli *et al.* 2013; Wulz *et al.* 2021).

As shown in Scheme 9, the esterification reaction again gives off one mole of HCl, which is potentially corrosive and which potentially may hydrolyze the glycosidic bonds of the material (Cabiac *et al.* 2011). Such acidity can be dealt with in various ways. For instance, in gas-phase reactions, a stream of inert gas can be used to dilute the vapors and carry them away (Berlioz *et al.* 2009). When the esterification is carried out in nonaqueous solvent, an alkaline co-solvent such as pyridine may be included (Freire *et al.* 2006; Corrales *et al.* 2007; Cunha *et al.* 2007c; Pasquini *et al.* 2008; Tomé *et al.* 2011b; Mukherjee *et al.* 2013; George *et al.* 2016; Li *et al.* 2019b; Balasubramaniam *et al.* 2020).

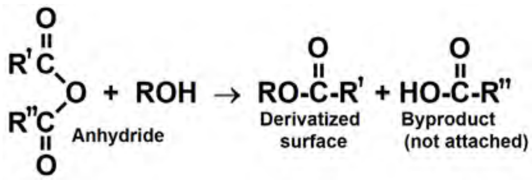
While the studied contact angles of a majority of cellulosic substrates treated with acid chlorides ranged from 55.5° to 136° upon the application of a polar liquid (Freire *et al.* 2006; George *et al.* 2016; Tomé *et al.* 2011b; Li *et al.* 2019b; Tomé *et al.* 2011a; Cunha *et al.* 2007c; Balasubramaniam *et al.* 2020; Wulz *et al.* 2021), one study presented noticeably lower numbers in comparison. Hastati *et al.* (2021) treated nanofibrillated cellulose in oil palm empty fruit bunches (NFC-OPEFBs) with a sustainable cationic surfactant, cetyltrimethylammonium chloride, derived from renewable palmitoyl alcohol (CTAC-PA), which also happens to be degradable. This was one of the first studies exploring the use of CTAC-PA in hydrophobic performance enhancement on polysaccharide surfaces. One of the differences between this experiment and other treatments with acid chlorides was the use of sulfuric acid as pre-treatment in the isolation process of NFC, which is claimed to increase the negative surface charges, remove any residues, such as hemicellulose, lignin or extractives, and reduce energy use thanks to shorter reaction times. However, the resulting water contact angles ranged from 25° to 40°, displaying a significant difference from the rest of studied cases. While the treatment did increase the hydrophobicity of the NFC-OPEFB surface, the modified substrate can hardly be called hydrophobic. These low contact angle results can be potentially explained by the fact that large quantities of cationic surfactant are normally required to carry out the reaction, and as the exact amount of CTAC-PA used in the experiment is unknown, it is difficult to determine if the quantity used was sufficient to achieve full hydrophobicity. Additionally, any impacts of the natural origin of the surfactant used are unknown (Hastati *et al.* 2021; Law 2015; Kamel 2007).

Anhydrides

Another way to increase the reactivity of a carboxylic acid compound is to dehydrate it, thus forming an anhydride. Scheme 10 shows the basic reaction to form an anhydride, as well as a subsequent reaction if and when the anhydride is used for the treatment of a substrate having available –OH groups. As is evident from the scheme, each reaction to form an ester involves simultaneous production of a carboxylic acid moiety (or its corresponding salt form). This detail is highly relevant in the context of hydrophobic treatments, since the leftover carboxylic acid group will be highly hydrophilic. Depending on the reaction conditions, carboxylic acid compounds sometimes pass through an anhydride form on their way to forming esters; thus, it may be possible for such reaction sequences to continue, with anhydrides formed between pairs of carboxylic acids, followed by esterification, until most of the reagent has been converted to ester species (Held *et al.*

2008). In other cases, the leftover carboxylic compound may be expected to act as a hydrophilic site, having the opposite of the sought effect as a hydrophobizing treatment (Chai *et al.* 2004).

$$2\ RCOOH \rightarrow (RCO)_2O + H_2O$$



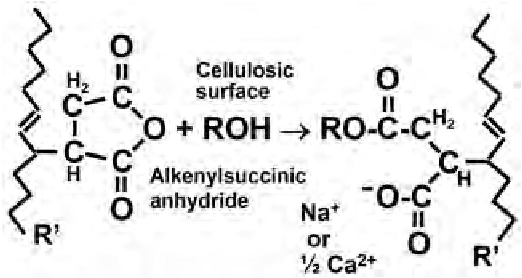
Scheme 10. Main reactions for the preparation of carboxylic acid anhydrides and their subsequent reaction of polysaccharide surfaces

Simple alkyl carboxylic acid anhydrides are the clearest examples that are well described by Scheme 10. Thus, acetic anhydride has frequently been used for the hydrophobic treatment of polysaccharide surfaces (Bledzki *et al.* 2008; Jonoobi *et al.* 2010; Hu *et al.* 2011; Ashori *et al.* 2014; Liu *et al.* 2021b). Yuan *et al.* (2005) and Cunha *et al.* (2006, 2007a,b) carried out essentially the same derivatization, using a trifluoromethyl version of acetic anhydride. Such reactions often have been carried out in non-aqueous solvents (Cunha *et al.* 2006, 2007a,b; Bledzki *et al.* 2008; Sehaqui *et al.* 2014; Peng *et al.* 2016; Liu *et al.* 2021b). Ionic liquid medium was used by Tomé *et al.* (2011) for acetic, butyric, and hexanoic esterification. In addition, so-called "solvent-free" (100% active reagent) treatment has been conducted in glacial acetic acid with pyridine as a catalyst at 100 °C for 4 h (Jonoobi *et al.* 2010; Ashori *et al.* 2014). Hu *et al.* (2011) acetylated bacterial cellulose with acetic anhydride, to which iodine was added as a catalyst. Gas-phase esterification, using anhydrides, also has been reported (Yuan *et al.* 2005; Wulz *et al.* 2021).

The effect of alkyl chain length of anhydrides was studied by Sehaqui *et al.* (2014). The cited authors found a strong increase in the water contact angle with increasing alkyl chain length (in the range 2 to 16 carbons). This was despite the fact that the degree of substitution obtained in the reaction fell strongly with increasing alkyl chain length. This observation suggests that the higher-mass alkyl analogues may have been better retained on the outsides of the treated substrates. Alternatively, the different results might be attributed to a greater effectiveness of longer alkyl chains. Tomé *et al.* (2011) found an analogous increase in hydrophobicity with increasing alkyl chain length when comparing systems under the same reaction conditions. Wultz *et al.* (2021) reported effective hydrophobization of paper following gas phase treatment with palmitoyl chloride. Linear alkyl chains having a length longer than about twelve are known to have a strong tendency to self-associate, thus forming highly hydrophobic monolayer films (Hubbe *et al.* 2020).

Alkenylsuccinic anhydride (ASA)

A representative of the cyclic anhydride class of compounds, alkenylsuccinic anhydride (ASA), is extensively used as a hydrophobic sizing agent for the preparation of paper products, especially printing paper (Dumas 1981; Hubbe 2007). A distinctive feature of ASA is that the anhydride is formed by the closing up of a five-membered ring within single molecules that have two carboxylic acid groups. The alkyl chains, which typically contain one unsaturated linkage, usually have overall lengths in the range of 16 to about 22 carbons (Gess and Rende 2005). In current production, the alkenyl chains are obtained from petroleum fractions; however, it is also possible to prepare effective ASA compounds from plant-based fatty acids (Lackinger *et al.* 2012). In either case, strain within the succinic anhydride group is expected to contribute an extra degree of reactivity to the system (Martorana *et al.* 2010). A reaction scheme is given in Scheme 11.



Scheme 11. Main reactions for the preparation of alkenylsuccinic anhydride and its subsequent reaction of polysaccharide surfaces

In the widely used systems for ASA sizing in the paper industry, the first step is to emulsify the ASA, which is an oily liquid at room temperature, with a cooled solution of cationic starch or an optimized cationic acrylamide copolymer (Dumas 1981; Hubbe 2007; Ashish *et al.* 2019). The polymers stabilize the oily droplets of ASA with a hydrophilic layer, keeping them from colliding and coalescing. In addition, the cationic charge favors efficient retention on the generally negatively charged cellulosic fibers during the formation of the paper sheet. To minimize the undesired hydrolytic decomposition of the ASA, the emulsion is typically used immediately, as soon as it has been continuously prepared. In some academic research, ASA has been emulsified in water without any stabilizer, then used immediately (Yuan *et al.* 2006; Nypelö *et al.* 2011).

Another approach demonstrated in academic research, presumably aimed at specialty applications, is to use nonaqueous media. Such an approach minimizes the unproductive reaction between ASA and water. Typically, researchers select media that cannot react with ASA, such as toluene or tetrahydrofuran (THF) (Kisonen *et al.* 2015) or N-methyl pyrrolidone (Sato *et al.* 2016). An ionic liquid also has been shown to be an effective medium for ASA esterification of bacterial and vegetable cellulose (Tomé *et al.* 2011).

Gahruie *et al.* (2019) carried out an aqueous-phase reaction between basil seed gum-based films and octenyl succinic anhydride (OSA). The OSA was preliminarily dissolved in ethanol to facilitate its addition to a stirred aqueous suspension. The reaction was carried out at 40 °C for 90 minutes. Ester groups were detected, and hydrophobic effects were observed. Notably, Shah *et al.* (2018), Gahruie *et al.* (2019) and Venkateshaiah *et al.* (2021) employed ethanol as the medium for dissolution of the ASA and reaction with the polysaccharide substrate; it is not clear from the articles whether or not significant reaction took place between the ethanol and the ASA.

Gas phase application of ASA is also possible (Zhang *et al.* 2007; Cunha and Gandini 2010a,b; Khoshkava and Kamal 2013). Success of such treatments can be attributed to the thermal stability of melted and vaporized forms of ASA in the absence of water (Zhang *et al.* 2007). In the cited work, in which the vapor needed to travel only about 0.2 mm, the temperatures and time of treatment were 100 °C and 20 min. In other tests, a film composed of cellulose nanocrystals (CNC) was treated with ASA vapor at 145 °C for

1 to 3 h. In neither case were any tests carried out to determine whether lesser temperatures or times would have achieved equivalent results in terms of hydrophobicity or other outcomes.

Alkylketene dimer (AKD)

AKD likewise has a long history of widespread usage in the paper industry (Dumas 1981; Hubbe 2007; Lindström and Larsson 2008). It is used especially in the production of the paperboard for milk cartons and related products. Unlike ASA, which is usually an oily liquid before emulsification, the common form of pure AKD is a waxy solid at room temperature. Though the reactive group is unique, it bears some similarity to anhydrides. In general terms, AKD is much less reactive than ASA. As a consequence, it is practical to pre-emulsify the AKD wax in a solution of a suitable cationic polymer to act as a stabilizer. The solution is warmed above the melting point of the AKD for the emulsification, and then the mixture is immediately chilled to minimize the rate of the unwanted reaction of AKD with water.

Reactions of AKD are as shown in Fig. 17 (Bottorf 1994). For purposes of hydrophobization, the most favorable reaction results in the formation of a β-keto ester bond with the substrate. When the AKD reacts with water, the initial product has been shown to be a beta-keto acid, which is unstable. The β-keto acid decomposes on its own to form a ketone. Though the ketone is highly hydrophobic, it lacks any way to become bound to a polysaccharide-based surface, which makes it ineffective as a hydrophobic sizing agent. Another undesired reaction is when the AKD decomposes with the formation of oligomeric species (Bottorf 1994). Though the decomposition appears not to hurt the sizing effect, it is using up some of the reagent that could have been reacting with the surface –OH groups. A further complicating factor, especially from the standpoint of commercial papermaking, is that unreacted AKD may remain on the surface after an intended reaction, *e.g.* after a sheet of AKD-treated paper has been dried (Bottorf 1994).

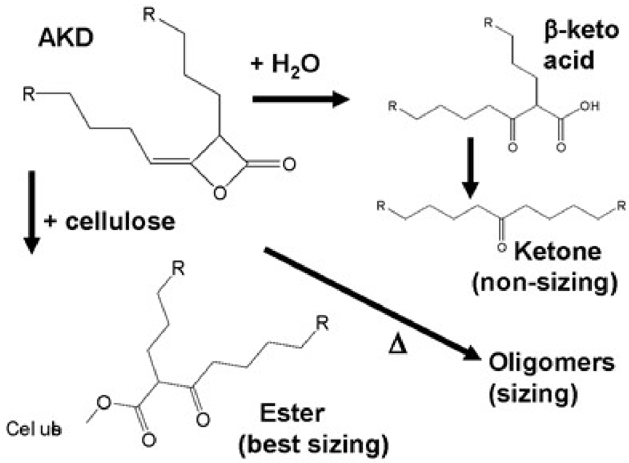


Fig. 17. Main reactions for the reactions of AKD: with polysaccharide surfaces, with water, and decomposition reaction

In preparation for the industrial hydrophobic sizing of paper, the AKD generally is first emulsified in a solution of cationic polymer (Dumas 1981; Bildik Dal *et al.* 2020; Korpela 2021), which is similar to what is done in the case of ASA. The difference is that the lower reactivity of AKD makes it practical to prepare the stabilized AKD dispersion at a centralized factory and to ship the formulation to paper manufacturing sites. The cationic charge of the polymer helps to retain the particles onto cellulosic fibers during the formation of the paper.

For laboratory investigations, distribution also can be conveniently achieved by dissolving the AKD in a non-polar liquid (Benkaddour *et al.* 2014; Bildik *et al.* 2016; Yuan and Wen 2018). Another option is to use a supercritical solvent, such as compressed CO_2 (Adenekan and Hutton-Prager 2019).

Heating is usually used to drive the sizing reaction of AKD with polysaccharide-based substrates (Lindström and Larsson 2008; Benkaddour *et al.* 2014; Yuan and Wen 2018; Iriani *et al.* 2020). Yan *et al.* (2016) used ethyl acetate as a solvent to distribute AKD onto microfibrillated cellulose. After drying, the mixture was heated to 130 °C for 24 hours, leading to high levels of hydrophobicity. Iriani *et al.* (2020) hydrophobically treated cassava starch by heating it under compression with AKD powder at 180 °C for five minutes.

Though most researchers have assumed that heating of an AKD-treated system is needed to achieve hydrophobicity, some exceptions to this rule have been found. Tarres *et al.* (2018) vacuum-dried an AKD-containing coating applied to a paper sheet at 23 °C and 50% relative humidity. The resulting contact angles were increased from the range 16° to 39° degrees to the range 103° to 115°, with higher values corresponding to the use of nanofibrillated cellulose in the coating formulation. Bildik *et al.* (2016) deposited AKD from heptane solution onto filter paper. Some of the specimens were heated after drying and some were not. Almost as great resistance to water penetration was observed when testing sheets that had not been heat-cured. Werner *et al.* (2010) achieved superhydrophobicity by airblasting AKD powder onto paper samples. Supercritical hydrophobic treatment of cellulose substrates with AKD also was carried out without heating (Adenekan and Hutton-Prager 2019). Such results suggest that the hydrophobic character of AKD can express itself merely by being distributed onto a surface at a sufficiently high amount, even without significant reaction having taken place.

Attempts have been made to achieve vapor-phase hydrophobization with AKD, but such efforts mainly have been unsuccessful (Zhang *et al.* 2007; Lindström and Larsson 2008). It has been shown that pure AKD, when heating, breaks down to form a tar-like oligomeric structure (Bottorf 1994). Limited success in gas-phase distribution of AKD, leading to hydrophobicity, has been demonstrated when the distance of gas-phase transport was about 0.2 mm (Zhang *et al.* 2007). Shen *et al.* (2002) showed that the ketone breakdown product of AKD decomposition tends to block the surface-migration and spreading of heated AKD.

In terms of achieving hydrophobic performance, AKD treatments have shown consistently high contact angle values in comparison with other esters. The contact angles of most AKD-treated samples studied were >90°, making them highly hydrophobic (Benkaddour *et al.* 2014; Bildik *et al.* 2016; Yuan and Wen 2018; Korpela 2021; Yan *et al.* 2016; Tarres *et al.* 2018; Werner *et al.* 2010; Adenekan and Hutton-Prager 2019; Zhang *et al.* 2007; Shen *et al.* 2002; Yang *et al.* 2012; Law 2015). Fang *et al.* (2008) explored the mechanisms behind AKD-induced surface water repellency, which included the formation of fractal surface, and found that the application of this dimer can enable substrates to also easily reach levels of superhydrophobicity. Heat has a major impact on hydrophobic performance of the AKD-treated surface, as even subtle increases in the temperature of the reaction magnify its hydrophobic benefits (Fang *et al.* 2008).

Lastly, while AKD for hydrophobic performance has been successfully used in papermaking for some time now, the main needs for technology advancements are currently related to process. In the papermaking industry, while traditionally added on the wet-end directly to the pulp slurry, AKD dispersions can also be applied at the size press to achieve strictly surface-level performance. As one of the future challenges, there is a need to develop methods of application that would result in higher levels of reaction without as big of an input of AKD (Roberts 1996; Yang *et al*. 2012).

Transesterification

The term transesterification can be used when an ester is the reagent, and the goal is to form a different ester. Dankovich and Hsieh (2007) employed such an approach when treating cotton cellulose with plant triglyceride fats. The concept is that the fatty acid groups are released from the triglyceride compounds and react with the –OH groups of a polysaccharide surface. The byproducts of the reaction may include glycerol molecules or partially esterified glycerol (*e.g.* diglycerides). The reaction was carried out in an ethanol or acetone medium with heating in the range 110 to 120 °C. Wei *et al.* (2017) carried out analogous treatments using canola oil fatty acid methyl ester. The temperatures of curing were the same as in the previously cited work (110 to 120 °C) and the curing times were 4 to 30 h. Zhang *et al.* (2020) carried out related treatment of hemicelluloses by vinyl laurate in an ionic liquid. Treatments were carried out in the range 60 to 100 °C; water contact angles above 100° were achieved throughout this range.

Though the esters used in the work cited above can be expected to be less reactive towards polysaccharide-based surfaces compared to such agents as anhydrides and acid chlorides, there can be some inherent advantages. In particular, the ester form of the reagent means that it will have relatively high chemical stability during storage before the treatment. In addition, the plant triglycerides are relatively cheap and eco-friendly. The sustainable appeal of fatty acid esters is not only due to their biobased origin, but also due to the additional benefit of biodegradability. The feedstocks used to produce fatty acid esters can also come from tall oil fatty acids (TOFA), which are a by-product of the pulping industry (Kulomaa *et al.* 2015). Onwukamike *et al.* (2018) carried out transesterification of cellulose using high oleic sunflower oil, resulting in esters that are soluble in most organic solvents and show good mechanical properties. Simultaneously, the homogenous route used rendered the synthesis more sustainable, eliminating the additional step of derivatization, and minimizing potential waste (Onwukamike *et al.* 2018). However, further research is needed to determine whether such approaches can be carried out at high speed, which presumably implies a very short time of heating in a temperature range that does not damage the substrate.

Enzymatic hydrophobization

Enzymatic treatment provides an alternative approach to carrying out esterification reactions under relatively low temperature conditions in aqueous media. Saastamoinen *et al.* (2012) used laccase to catalyze the esterification of unbleached nanofibrillated cellulose (NFC) with dodecylgallate. The treated NFC was coated onto paper surfaces, yielding decreased hydrophilicity. Kudanga *et al.* (2010) used laccase to couple fluorophenols to wood veneers, thus providing hydrophobicity. Yin *et al.* (2020) used lipase to catalyze the esterification of cellulose nanocrystals (CNC) with laurate alkyl chains. The initial water contact angle was above 100°, and the treated CNC was more effective for increasing stress and strain maximum values when formulated into a poly(lactic acid) matrix. Though the reactions described in the work cited in this paragraph tend to be relatively slow, compared to what might be needed for the industrial production of packaging papers or films, they might be considered for the surface treatment of cellulose fibers or nanocellulose in suspension.

Enzymatic hydrolysis has also been used to impact nano- and micro-scale roughness to the surface of cellulosic materials, thereby enhancing hydrophobicity of the substrate. Rahman *et al.* (2020) used *Aspergillus niger* to achieve surface roughness through enzymatic hydrolysis on cotton and lyocell textile samples, following the treatment with dip-coating the sample with polydimethylsiloxane (PDMS). Focusing solely on the enzyme hydrolysis component, as the temperature and enzyme concentration increased, nano-scale roughness and crystallinity also increased. The nano-scale structure on the surface spurred the formation of air pockets, which resulted in the contact angle increase. The presented treatment suggested a more environmentally friendly and affordable process that is free of fluorine and nanoparticles (Rahman *et al.* 2020).

Amides

An earlier review article provides basic information about amide modification of cellulosic surfaces (Hubbe *et al.* 2015b). Here the emphasis will be on treatments that render polysaccharide surfaces hydrophobic.

Formation of an amide bond at the surface of a polysaccharide-based substrate requires the presence of carboxylic functions. Though typical cellulosic materials, such as conventional papermaking pulps, contain various amounts of carboxylic acid groups, a higher level may be needed to achieve a high level of amidation. Thus, Isogai *et al.* (2011) and Fathi *et al.* (2017) described the use of TEMPO oxidation to convert surface-bound –OH groups first to aldehyde form and thereafter to –COOH. Johnson *et al.* (2011) carried out amidation of TEMPO-oxidized nanocellulose using octadecylamine. The reaction was carried out in a 4:1 water:dimethylformamide solution that contained 1-ethyl-3-(3-dimethyl-aminopropyl) carbodiimide (EDC) and N-hydroxysuccinimide (NHS). The mixture was reacted at 50 °C for 24 h. Initial water contact angles above 110° were obtained. Benkaddour *et al.* (2014) reported a similar amidation. However, the reaction was reported to have been carried out in aqueous solution at pH 5 and room temperature for 30 minutes. Amide bonds were confirmed by FTIR spectra. Increased hydrophobicity was reported. Shrestha *et al.* (2019) reported a two-step process in which tannic acid was used as a primer for nanofibrillated cellulose, followed by treatment with hexadecylamine. The reaction was carried out in aqueous media at a pH of 8 for 12 h under stirring. The particles, which had been rendered hydrophobic, floated to the top of the solution.

Ethers

Ether derivatives of polysaccharides can be readily prepared by treatment under highly alkaline conditions using β-hydroxy chloro species (Mohanty *et al.* 2001). Such reactions are widely used for the preparation of cationic starch and related products. However, there is potential to use the same approach for hydrophobization of polysaccharide surfaces by employing analogous agents having hydrophobic groups. Accordingly, Balan *et al.* (2014) reported the preparation of 3-chloro-2-hydroxypropyl stearate by reaction of epichlorohydrin with stearic acid. The product was then reacted with cotton fabrics at 60 to 100 °C, rendering them hydrophobic. Water contact angles as high as 150° were observed, depending on the treatment concentration and on the type of reactive dye that was simultaneously being used for preparation of the cotton fabric. Shao *et al.* (2001) used epoxychloropropane to modify hemicellulose, thus rendering it more hydrophobic. Solala *et al.* (2018) treated porous cellulosic membranes with C14-alkyl epoxy groups. Water contact angles were increased from about 25° to about 50°, while having relatively little effect on the water vapor permeability of the porous films. Borjesson *et al.* (2019) enhanced the etherification of arabinoxylan by initially oxidizing the surface, thereby increasing the number of OH groups that could be etherified with hydrophobic alkyl chains.

Urethanes

Urethane linkages can be created by reaction of isocyanate moieties with the –OH groups on polysaccharide-based substrates. For example, Missoum *et al.* (2012) grafted nanofibrillated cellulose with long-chain aliphatic isocyanate chains. The reaction was conducted in toluene suspension at 105 °C for 2 h. Stable water contact angles in the range 79° to 90° were observed. de Souza *et al.* (2020) prepared hydrophobic eucalyptus pulp fibers in a solution of blocked diisocyanate. Liu *et al.* (2019) employed toluene diisocyanate as a component in the preparation of superhydrophobic cellulose membranes. The reaction was conducted in boiling toluene solution for 5 min. The solids subsequently were heated for 10 minutes at 100 °C. Related work is described by others (Siqueira *et al.* 2010; Shang *et al.* 2013; Zhou *et al.* 2020), as summarized in Table M. To summarize, the literature reports indicate successful hydrophobization of various cellulose substrates in the presence of solvent (usually toluene or acetone), usually with heating, and usually with many hours of reaction.

Acrylic and Related Systems

Acrylic systems have widespread use not only in polymer synthesis but also in grafting reactions. Li *et al.* (2016) used methyl methacrylate and a free radical initiator to modify cotton stalk fiber under alkaline conditions. Alipoormazandarani and Fatehi (2020) used the same reagent to modify kraft lignin in a water-dimethyl sulfoxide solvent mixture, increasing the hydrophobic character of the lignin. Liu *et al.* (2021a) carried out a similar reaction of methyl methacrylate to treat cellulosic paper, except that they used a trifluoroethylacrylate co-monomer. A high level of water repellency was achieved. Bayer *et al.* (2011) and Ayadi *et al.* (2013) dipped paper sheets into solutions of ethyl cyanoacrylate monomer, rendering the material hydrophobic. Qi *et al.* (2020) used a fluorinated acrylic monomer and polymerization as a means of achieving highly hydrophobic nanocellulose films. Related “living polymer” versions of free-radical acrylic chemistry also have been reported for rendering cellulose hydrophobic (Arteta *et al.* 2017). Other related work, involving surface treatment of lignin with abietic acid moieties, was reported by Wang *et al.* (2011).

Other Plasma Hydrophobic Treatments

Certain plasma treatments already were considered in the section devoted to silane chemistry. As discussed in that context, the use of a plasma opens up the possibility to covalently attach a wide range of chemical moieties that otherwise would not be reactive (Siow 2018). In general, the activated species are short-lived, and the reaction rates are sometimes suitable for continuous processing. Issues of concern include the uniformity of the treatment and the ability to control the level of treatment. Gorjanc and Gorensek (2010) reviewed various plasma treatments of cotton, which resulted in a wide range of surface properties, including both hydrophilic and hydrophobic. Samanta *et al.* (2012) used plasma treatment with 1,3-butadiene to treat cellulose. A high level of hydrophobic character was achieved. Song *et al.* (2013b) used atmospheric cold plasma to treat paper surfaces with various acrylates. Sahin *et al.* (2002), Sahin (2007), and Follain *et al.* (2015) describe cold plasma treatment of sunflower pith with tetrafluoromethane. Kong *et al.* (1992) used plasma treatment with octofluorocyclobutane to hydrophobize porous nitrocellulose membranes. Superhydrophobic systems also have been achieved by plasma treatments involving perfluorocarbon compounds (Zhang *et al.* 2003; Toriz *et al.* 2008; Mirvakili *et al.* 2013).

Click Chemistry

The subject of click chemistry has been considered in an earlier review (Hubbe *et al.* 2015b). Some recent work involving hydrophobic treatment of polysaccharide surfaces can be mentioned. Krishnamurthy *et al.* (2020) used click chemistry to treat bacterial cellulose, rendering it hydrophobic. As described earlier by Tingaut *et al.* (2011), the first step involved a trialkoxysilane compound, the reaction of which was discussed earlier in this review. Nongbe *et al.* (2018) derivatized paper with azide groups, thus enabling their hydrophobic transformation by click chemistry using cholesterol. Wu *et al.* (2021a) more recently prepared highly hydrophobic filter paper with click chemistry, again starting with a trimethoxysilane treatment of a cellulosic surface.

Adsorbed Hydrophobic Compounds

Ion-pair association

Cationic surfactants are known to have enhanced affinity when adsorbing on the generally negatively charged surfaces of cellulosic materials from aqueous solution. Such cases were documented in an earlier review (Hubbe *et al.* 2015b). Hydrophobic effects were achieved in such a system by Aarne *et al.* (2013), who used a diblock copolymer of polystyrene (hydrophobic) and poly(N-methyl-4-vinyl pyridinium iodide) (cationic).

The potential importance of ion-pair structures in the hydrophobic treatment of polysaccharide-based substrates was revealed most clearly in a study by Johnson *et al.* (2001), which already was cited earlier when discussing the formation of amides. These authors showed that an ammonium salt ionic association could be used to anchor monolayers of long-alkyl-chain amines to TEMPO-oxidized cellulose. The reactions were carried out in a 4:1 water:dimethylformamide mixture for 24 h at 50 °C. It is notable that the cited authors reported similar performance of the treated cellulose in comparison to parallel experiments in which covalent amide bonds were formed from the same materials. In fact, the water contact angles achieved by use of this non-covalent system were much higher (*e.g.* 117°) than those obtained in the same study by forming amide bonds (*e.g.* 108°). Hu *et al.* (2017) likewise carried out a two-step treatment, starting with tannic acid adsorption onto cellulose nanocrystals (CNC). These were reacted with decylamine at room temperature for 3 h, yielding increased hydrophobicity. The mild conditions of treatment suggest that the decylammonium salt of the anionic CMC particles was formed, rather than the formation of amide bonds. Syverud *et al.* (2011) applied cetyltrimethylammonium bromide (CTAB) onto a TEMPO-oxidized surface to achieve increased hydrophobicity.

Izadyar *et al.* (2020) elucidated the functionalization of cellulosic fibers with palmitic acid, in combination with zinc ions. Such association of metal ions with polysaccharide-based surfaces can be increased by oxidation, such as with use of the 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) radical species (Isogai *et al.* 2011). Thus, Benkaddour *et al.* (2014) were able to increase the ability of cellulose gel to bind with stearylamine and develop hydrophobicity. Though the cited authors used the term "amide" to describe the products of the interaction, the conditions of treatment suggest that amide groups had not formed; rather, the findings are consistent with the formation of ammonium salt-carboxylate ionic associations. The same mechanism can explain the findings of Salajkova *et al.* (2012) and Shimizu *et al.* (2014), the latter of whom treated TEMPO-oxidized cellulose nanocrystals with tetra(n-butyl)ammonium hydroxide and achieved hydrophobicity. Soboyejo and Oki (2013) cationized cotton by use of a combination of cationic surfactant and oxidized carbon nanotubes, again taking advantage of opposite charges to achieve the binding interaction.

Though the mechanism appears not yet to be fully explained, results reported by Saastamoinen *et al.* (2012) and Cusola *et al.* (2015) may involve ionic association of hydrophobic groups at cellulose surfaces. Cusola *et al.* (2015) showed that the hydrophobicity of the treated cellulose increased with increasing alkyl chain length of enzymatically oxidized alkyl gallates. The chemical structures created by oxidation of gallates have been studied by Kusano *et al.* (2007). The association of gallates with metal ions also has been established (Hyung *et al.* 2013). On this basis, a possible mechanism of attachment of oxidized alkylgallates to cellulosic surfaces may involve bridging by divalent ions such as calcium present in the media (Walther *et al.* 2004).

Self-assembly

Self-assembly is another factor that can help in the formation of an effective hydrophobic layer, based on adsorption of surfactants at polysaccharide-based surfaces. Fan *et al.* (2019) showed that the driving forces favoring such association increase with increasing length of saturated fatty acid alkyl chains. Such interactions likely contribute to the effects observed by Dankovich and Hsieh (2007), who used plant triglycerides to render cellulose surfaces hydrophobic. The system was heated to 110 or 120 °C for 60 min. Cusola *et al.* (2015) observed a large increase in hydrophobicity when oxidized gallate monolayers on cellulose were subjected to 150 °C heating for 30 minutes. The effect, which was attributed to alignment of the hydrophobic tails outwards from the surfaces, is consistent with self-assembly among those tails as a contributing factor. Similar effects were reported by Aarne *et al.* (2013). Further evidence of the importance of self-assembly was provided by Bildik *et al.* (2016), who showed that hydrophobic effects of AKD treatment of paper could be achieved even without heating of the paper during its drying, thus ruling out covalent bonding as a main contributor to the observed effects. Oh *et al.* (2011) invoked the self-assembly mechanism to account for the self-organization of perfluorodecyltrimethoxysilane at paper surfaces. Related effects have been observed in systems having hydrophobic nanoparticles. Benavente *et al.* (2010) modified a regenerated cellulose membrane with the addition of lipid nanoparticles and layers, and the results were consistent with self-assembly of a monolayer at the surface.

Adsorbed Polymers

In comparison to the surface modification system already described in this review article, polymeric treatments can be expected to deviate more greatly from the stated ideal goal of monomolecular coverage. Polymers are more likely to have tails, loops, and layers of segments extending outwards from a substrate. On the other hand, some water-soluble polymers can be applied very easily onto polysaccharide-based systems from aqueous solution, making them very worthy of consideration. The general topic of polyelectrolytes adsorption from aqueous solution as a means to modify surface characteristics of cellulose has been reviewed (Wågberg 2000; Hubbe *et al.* 2015b).

Chitosan

Much attention has been paid in recent years to chitosan as a naturally renewable polymer that can be obtained from the shells of crustaceans (Rinaudo 2006). The chitin present in such shells can be converted to chitosan by treatment in strong base in hot aqueous solution. Chitosan, which can be regarded as the only strongly cationic natural polymer, has an identical molecular structure to cellulose, with the exception of amine groups attached to the C2 carbons of the anhydroglucose units. Despite the presence of inherently hydrophilic amine and –OH groups, films of chitosan exhibit hydrophobic character when they are prepared by evaporation in air of the corresponding aqueous solutions (Cunha *et al.* 2008; Vikele *et al.* 2017). This tendency has been attributed to orientation of the macromolecular chains at the interface, such that a non-polar side faces outwards (Hubbe 2019). However, as noted by Elsabee *et al.* (2009), the hydrophobic character of such films can be described as “weak,” since there are no distinctly hydrophobic segments of the polymer.

Blending with chitosan has been reported to increase the hydrophobic character of polysaccharide-based materials. For instance, Deng *et al.* (2017) showed that chitosan contributed to water resistance and antibacterial properties of food packaging films prepared for nanofibrillated cellulose. Gao *et al.* (2020) prepared hydrophobic films by combining aqueous chitosan with microfibrillated cellulose and drying the films. The films were oxidized with ferric chloride and then treated with pyrrole. Ni *et al.* (2018) achieved a strong resistance to wetting when combining starch, ZnO nanoparticles, and a final treatment with chitosan in an aqueous system. When this mixture was applied to filter paper and dried, the resulting water contact angles were as high as 120°.

Synthetic copolymers

Various amphiphilic copolymers are widely used in the paper industry to achieve hydrophobic effects when they are added with dissolved starch to the paper surface at a size press. Such systems were reviewed recently (Bildik Dal and Hubbe 2021). Examples include styrene-maleic anhydride copolymers. As described in the cited article, the copolymers appear to migrate to the air interface, during drying, in such a way that hydrophobic groups tend to be facing outwards.

Naturally Hydrophobic Substances

There are numerous hydrophobic natural products that can be considered as candidates for surface treatment of eco-friendly films. For example, rosin compounds and fatty acids are routinely obtained as byproducts (tall oil components) during the alkaline pulping of softwood (Dogaris *et al.* 2019). Other options include some lignin products, natural waxes, tannins, protein, suberin, and chitosan, which are considered in more detail below.

In the Introduction section of this article it was hypothesized that especially promising hydrophobization systems are likely to involve approximately monolayer coverage of the polysaccharide-based substrate. However, the natural products listed above all have a tendency to phase-separate from neutral water. This tendency needs to be overcome in some way when the goal is to achieve the desired hydrophobic effects with a near-monolayer coverage of the surface.

Rosins

Rosins products will be considered first. Among the natural products, rosin has the longest history of usage as an agent for hydrophobic sizing of paper. Two contrasting strategies are used by papermakers to achieve relatively uniform distribution of rosin within the fiber furnish before the formation of paper. The older technology, dating back at least to about 1805 (Garlick 1986), involves saponifying the rosin with alkali, thus forming a soap. When added to the furnish, the rosin soap will be present as micelles (Ehrhardt and Leckey 2020). To precipitate (or "set") the rosin soap onto the surface of fibers, a solution of papermakers' alum (*i.e.* aluminum sulfate) is added. Particles of aluminum abietate (and other related compounds) become insolubilized and deposit onto the fiber surfaces. Contrary to the goal statement in the Introduction to this article, the precipitated rosin is unlikely to resemble a molecular monolayer. Rather, particles of precipitated rosin soap are initially very small (*e.g.* 25 nm), but they can agglomerate and increase in size (*e.g.* 150 nm) (Stryker *et al.* 1973). Both rosin soap and alum are relatively inexpensive. Thus, despite its inherent inefficiency, the rosin soap sizing system is often preferred for internal sizing of paper when the pH of the operation is in the range from about 4.0 to 5.0 (Ehrhardt and Leckey 2020).

The other common strategy for distributing rosin in paper, during its formation, involves heating up the rosin until it melts, then emulsifying it by applying hydrodynamic shear in the presence of a solution of a cationic polymer (Ehrhardt and Leckey 2020). The polymer acts as a stabilizer for the emulsified rosin, in its protonated form. During formation of the sheet, the cationic polymer coating each emulsion droplet helps to retain them onto the fiber surfaces. Spreading of the rosin onto the paper surfaces occurs when the paper is being dried, *i.e.* when the temperature is not far from the boiling point of water. The molecular distribution of the water molecules over the surface is likely to involve both surface migration and vapor-phase transport. As such, there is potential for the resulting treatment to more closely approach the ideal goal of molecular monolayer coverage. Due to the high temperatures in the dryer section of the paper machine, the following reaction is expected to take place at the paper surface, as depicted in Scheme 12.

$$\text{Paper-Al(OH)} + \text{Rosin-COOH} \rightarrow \text{Paper-Al(OH)-OCO-Rosin} + H_2O$$

Scheme 12. Generalized reaction of rosin acid with hydroxylated aluminum groups at a paper surface during evaporative drying

In Scheme 12, "Al(OH)" represents part of an alum precipitate that is associated with a hydroxyl group on the surface, and "Rosin-COOH" represents the protonated form of rosin. Thus, the hydrophobic material becomes anchored at the paper surface. It is worth noting that the end product represented in the scheme has a lot of similarity to the aluminum rosinates that form in solution when alum is added to a system that contains rosin soaps. A key difference is that rosin soaps are able to directly combine with dissolved aluminum species, forming the aluminum abietate, which quickly precipitates onto fiber surfaces as tiny particles, even before the paper is dried.

Moriam *et al.* (2021) reported high levels of hydrophobicity when treating textile surfaces with higher molecular mass compounds related to rosin. Specifically, betulinic acid is a terpene-type compound having five unsaturated hydrocarbon rings and a single carboxylic acid group, giving it high hydrophobic character. The compound was applied to cellulose by dissolution in an ionic liquid.

Fatty acids, triglycerides. and oils

Fatty acids, which are an important component of the extractives present in wood species, were already considered in the context of esterification of polysaccharide surfaces. Depending on such processes as enzymatic hydrolysis and oxidation, there is an expected shifting of the ratio between triglycerides and free fatty acids that are present in wood, depending on the season of harvesting, weather conditions, and other factors (Back and Allen 2000; Blazey *et al.* 2002). Whereas the triglyceride forms are the most hydrophobic, it is well known that the carboxylate form of free fatty acids can, when anchored by certain aluminum ions, serve as effective hydrophobic sizing agents in paper (Ehrhardt and Leckey 2020).

He *et al.* (2013) dissolved stearic acid in ethanol solutions and then exposed cellulose gel sheets to the solutions. The sheets were then hot-pressed at 90 to 100 °C at about 0.1 MPa pressure. High hydrophobicity was attributed to a highly rough surface composed of oleophilic material. Chen *et al.* (2020) describe the direct treatment of either microcrystalline cellulose or nanocellulose with an ethanol solution of stearic acid. The system was dried and cured at 50 °C for 24 h. Another group of researchers (Chen *et al.* 2021) used vapor-phase deposition to treat anisotropic cellulose films with myristic acid. Not only were the surfaces rendered hydrophobic, but the materials were completely biodegraded in soil after 102 days. Because the systems described in this paragraph involved heat-curing in air, it is reasonable to expect that the fatty acid molecules became oriented mainly with their hydrophobic tails facing outwards (Fischer *et al.* 1997). In the presence of aluminum or calcium ions, fatty acids have been found to form stable, oriented salts at the surface to which they are adsorbed (Mihajlović *et al.* 2013).

Several authors have described the addition of plant-derived oils as a means of rendering polysaccharide-based surfaces more hydrophobic. These oils have included vegetable oils (Samyn *et al.* 2013); soybean oil (Dong *et al.* 2013), epoxidized soybean oil (Huang *et al.* 2017), tung oil (Shen and Kamdem 2015; Kick *et al.* 2017), castor oil (Shang *et al.* 2018), betulin from birch bark (Huang *et al.* 2019), sunflower oil (Ghiasi *et al.* 2020; Nehchiri *et al.* 2021), and essential oil (Gohargani *et al.* 2020; Syahida *et al.* 2020). The study by Samyn *et al.* (2013) involved incorporation of nanoparticles (hybrid styrene maleimide), which apparently was intended to provide a high level of fine-scale roughness, which is known to enhance the differences between hydrophilic and hydrophobic surfaces (Song and Rojas 2013). Compared to systems involving molecularly anchored monolayers of hydrophobic monomers, the described systems involving oils (often with a main component of triglyceride fats) can be expected to require higher amounts of material to achieve the sought hydrophobic effects. This is because of the lack a means of anchoring and orientation of individual molecules and because of a strong tendency for growth of droplets due to collisions and coalescence.

Waxes

Depending on factors such as molecular mass, degree of unsaturation, and especially temperature, many oleophilic materials may be waxes rather than oils under the conditions of usage. Stearic acid, when relatively pure at room temperature, is waxy. Chen *et al.* (2020) and Cai *et al.* (2021) rendered a starch film hydrophobic by dipping it in a suspension of fine stearic acid particles in ethanol. After the treatment, the system was heated to 80 °C for 8 h, which presumably allows the waxy material to melt, spread, and molecularly orient. When drying stearic acid at an air interface, one can expect that the non-polar ends of the molecules will face the air, thus decreasing the interfacial free energy.

Such orientation favors greater hydrophobicity, at least until the molecular orientation has time to adjust to the new environment. Related work, in which stearic acid was used to hydrophobize a regenerated cellulose surface, was reported by He *et al.* (2013). Similarly, Xu *et al.* (2019) increased the hydrophobicity of wood surfaces by treatment with glycerol stearate, followed by oven drying.

Paraffin wax has been shown in various studies to impart reliable hydrophobicity (Chitnis and Ziaie 2012). The cited authors carried out laser surface ablation, following a pattern, to enhance resistance to surface wetting by water. Khwaldia (2010) applied molten paraffin wax to paper surfaces after their treatment with sodium caseinate protein. Yadav *et al.* (2014) applied epicuticular wax to paper from various solvents. Gustafsson *et al.* (2012) achieved related effects by deposition of emulsified paraffin particles onto cellulose fibers. Indriyati *et al.* (2020) carried out similar work with emulsification of beeswax in aqueous suspension in the presence of bacterial cellulose. Syahida *et al.* 2020) applied palm wax, along with lemongrass essential oil to enhance barrier layers for paper packaging. Hutton-Prager *et al.* (2021) applied a variety of waxes (beeswax, carnauba was and vegetable wax) into paper by means of supercritical carbon dioxide. Li *et al.* (2021) enhanced the hydrophobicity of coating intended for packaging of blood-related materials by sprinkling of fine particles of carnauba wax. Liu *et al.* (2019) applied combinations of wax, AKD, and other additives by dissolution in various solvents. Films prepared from nanofibrillated cellulose were exposed to the treatment solution, with boiling, followed by evaporative drying. Spence *et al.* (2010) discovered that application of a relatively low amount of wax was effective for essentially plugging up minor defects within films of microfibrillated cellulose, leading to high levels of barrier performance. Though none of these systems can be expected to form monomolecular films, the application can be simple and the materials are inexpensive.

Lignin

Of the three main chemical components of ordinary wood, the lignin is the most hydrophobic in its natural state. Various forms of lignin are available as products of alkaline pulping (Vishtal and Kraslawski 2011) or from the enzymatic digestion of cellulosic materials (Cao *et al.* 2019). The pulping processes, in particular, change the chemical composition and decrease the molecular mass of the lignin. However, the material still can be described as macromolecular and insoluble in neutral aqueous solutions. As such, it is perhaps unreasonable to expect lignin to form a true molecular monolayer that is well anchored to a paper-like surface. In addition, by leaving the lignin present within wood-based material, it is practical to prepare nanofibrillated cellulose having a more hydrophobic character (Spence *et al.* 2020). Ferreira *et al.* (2020) prepared dry foams from lignocellulosic fibers and attributed their hydrophobic natural at least in part to the presence of lignin.

Several researchers have employed lignin-based products as hydrophobic coatings. For example, Rukmanikrishnan *et al.* (2020a) used solution casting to form a layer of kraft lignin as a composite film with K-carrageenan. The lignin was initially dissolved in ethanol, and then it was added to an aqueous solution of glycerin and carrageenan. Water contact angles were achieved in the range of about 64° to 78°, in comparison to about 59° for the pure carrageenan film. Similar results were achieved with incorporation of lignin into films of gellan gum and 2-hydroxyethyl cellulose (Rukmanikrishnan *et al.* 2020c). It is worth noting that both of these examples failed to meet the present goals of molecular treatment of the surfaces; rather the cited authors formed composite films. The fact that those films were hydrophobic might be attributed to a mechanism of migration of the lignin to the air-solid interfaces in the course of the forming and drying processes (Bildik Dal and Hubbe 2021).

Molecular distribution of a lignin-based product over a surface might be better achieved by employing a water-soluble lignin byproduct. Thus, Li *et al.* (2011) employed lignosulfonate, which is a product of the sulfite pulping process. Due to the presence of the anionic sulfonate group, the lignosulfonates are soluble in water. The cited authors used divalent copper ions, together with a layer-by-layer deposition technique, to apply multilayers of the hydrophobic material onto quartz slides or cellulose fibers. This is a slow process, which can raise concerns regarding whether such a procedure would be suitable for industrialization. However, there are many related approaches that could be considered, such as the treatment of paper with alum, followed by surface application of lignosulfonate.

Tannins

Tannins are polyphenolic compounds present as a component of the extractives of woody materials, especially bark (Pizzi 2008). As shown by the representative structures in Fig. 18, tannins are often present as condensed structures. In addition, they are often covalently bound to polysaccharide structures (Pizzi 2008). There are various reports of using tannins for the hydrophobic treatment of polysaccharide-based materials. Missio *et al.* (2018) used a simple one-step procedure in which condensed tannins were combined with nanofibrillated cellulose during the hydrodynamic shearing treatment. Films formed by drying the aqueous suspension exhibited high hydrophobicity. Shrestha *et al.* (2019) carried out a similar procedure, but then applied hexadecylamine, thus making the material more suitable as a filler for epoxy resin. Zhang *et al.* (2021) used electrospinning to prepare films that incorporated tea polyphenolics with starch. The components were dissolved in tetrahydrofuran (THF), which was heated to 70 °C. Hydrophobicity of the films increased with increasing time of subsequent cross-linking with glutaraldehyde. Ji *et al.* (2020) started by treating kraft pulp fibers with periodate to convert them to their dialdehyde cellulose form. This was reacted with tannin, yielding hydrophobic character.

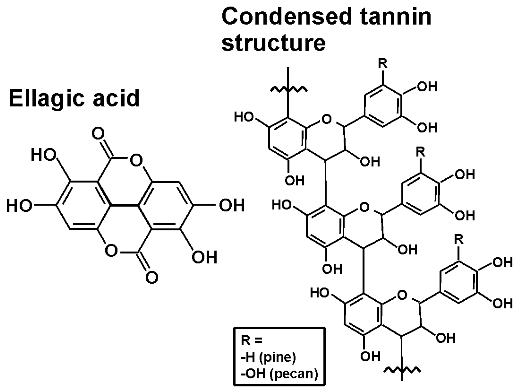


Fig. 18. Representative structures of tannins

Proteins

Natural proteins differ in their degree of hydrophobic character, and such effects can be altered by denaturation and folding (Sarkar and Kellogg 2010). Song *et al.* (2013a) showed that zein protein emulsion can be used to increase the water resistance properties of paper. Surface treatment involved spreading of the emulsion with a wire-wound bar, followed by drying overnight at 75 to 80 °C. Wan *et al.* (2017) used the term self-assembly to account for increased hydrophobicity when bacterial cellulose and zein protein were heat-dried. Notably, the highest hydrophobicity was achieved at partial coverage of the surface, leading to greater roughness than at higher coverage of the surfaces with the protein.

Suberin

Suberin is the hydrophobic and elastomeric component of cork, which can be obtained from the bark of the *Quercus suber* (cork oak) tree and, at lesser concentrations and amounts, from many other barks (Vishwanath *et al.* 2005). Suberin molecules contain a combination of polyaromatic and polyaliphatic domains, which naturally contribute to the flexibility and hydrophobicity needed for a sealing material such as a cork (Schreiber 2010). The polyaliphatic domains have been characterized as polyesters of fatty acids that are linked both head-to-tail (primary esters) and head-to-side (secondary esters) (Pollard *et al.* 2008). A representative structure of suberin is shown in Fig. 19 (Gandini and Belgacem 2013). Dou *et al.* (2021) found that willow bark, after a high degree of mechanical shearing, could be formed into nanofibrillated cellulose, which had high barrier performance for moisture as well as oxygen. Korpinen *et al.* (2019) extracted suberin fatty acids from the bark of *Betula pendula* Roth (silver birch); impregnation of paper sheets with suberin fatty acid monomers exhibited hydrophobicity, especially after during with maleic anhydride, applied in ethanol solution.

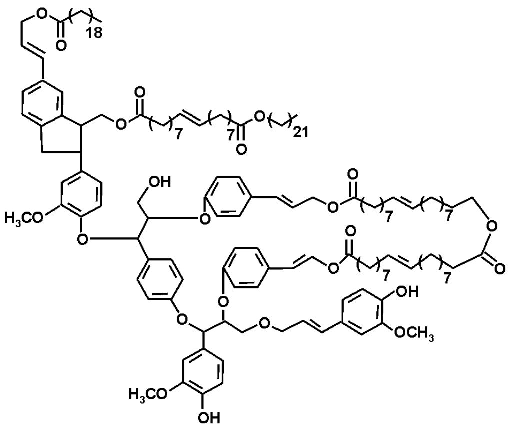


Fig. 19. Representative structure of suberin (redrawn based on Pollard *et al.* 2008)

Superhydrophobic Systems

The topic of superhydrophobic systems already has arisen in the foregoing discussions when considering some of the detailed findings of studies in which hydrophobic treatments of polysaccharide-based substrates were being discussed. Superhydrophobicity can be defined as a system providing an advancing contact angle of water greater than 150° and a sliding angle less than 10° (Song and Rojas 2013). Because this is an area of strong research interest, this section will focus on such findings. Background to this area has been provided in review articles (Samyn 2013; Song and Rojas 2013; Teisala *et al.* 2014; Li *et al.* 2016; Milionis *et al.* 2016).

As explained in these sources, superhydrophobic (and also superoleophobic) systems generally require a combination of two factors: high multiscale roughness and low free energy of the surfaces. These two factors are considered in the next subsections. Table 3 summarizes some main conditions and findings of studies in which superhydrophobic treatments were applied to polysaccharide-based substrates or particles.

Table 3. Reported Superhydrophobic Systems Applied to Polysaccharide-based Substrates

Roughness treatment	**Surface energy treatment**	**Substrate**	**Citation**
Likely due to silane effects	Chlorodimethylsilane	Microfibrillated cellulose	Andresen *et al.* 2006
Pickering emulsions with silicate particles	Cyclosiloxanes in water	Cellulose nitrate	Bayer *et al.* 2009
Montmorillonite clay (bentonite)	Alkyl-ammonium surfactant treatment of the bentonite	Bleached softwood kraft fibers	Chen and Yan 2012
Tetraethoxysilane	Perfluorodecyl triethoxysilane	Cellulose fibers	Cunha *et al.* 2010a
Ag nanoparticles *in-situ* generated	Octyltriethoxysilane	Cotton	Khalil-Abad & Yazdanshenas 2010
Tetraethoxysilane	Dodecyl triethoxysilane	Nanocellulose-silica film	Le *et al.* 2016
Titanium dioxide nanoparticles	Octyltriethoxysilane	Nanofibrillated cellulose	Li *et al.* 2010
Pyridine reaction with excess chlorosilane	Chlorosilane	Cotton fabric	Li *et al.* 2007
Polycondensation	Potassium methyl siliconate; polymethyl silsesquioxane	Cotton fabric or paper	Li *et al.* 2008
Silica hydrosols	Fluorotetradecyl trimethoxysilane	Cotton fabric	Liang *et al.* 2013
Tetraethoxysilane	Triethyoxysilylpropyl succinic acid anhydride	Cotton	Schramm and Amann 2019
Electrospun cellulose acetate & silica nanoparticles	*In-situ* polymerized fluorinated polybenzoxazine	Electrospun cellulose acetate	Shang *et al.* 2012
Silica nanoparticles	Trimethoxyoctylsilane	Silica films	Tasleem *et al.* 2019
Silica nanoparticles	Dodecyltrimethoxy silane	Kapok fiber	Wang *et al.* 2012
Sonication and other details of preparation	Stearoyl chloride	Microcrystalline cellulose or cotton linters	Wang *et al.* 2015
Silica nanoparticles and ZnO nanorods	Dodecyltrimethoxy silane	Cotton fabrics	Xu *et al.* 2010
Silica nanoparticles	Stearic acid, perfluoro-decyltrichlorosilane	Cotton fabrics	Xue *et al.* 2008
Roughness was attributed to plasma	Plasma fluorocarbon	Cotton fabrics	Zhang *et al.* 2003

Morphology

As listed in Table 3, a variety approaches have been employed as means to achieve the desired multi-scaled roughness that is regarded as a necessary condition for achieving superhydrophobicity (Nurmi *et al.* 2010; Song and Rojas 2013). Perhaps the simplest approach to providing roughness to a surface is by deposition of nanoparticles. Thus, the particles deposited onto cellulosic surfaces have included montmorillonite clay (Chen and Yan 2012) and lysozyme aggregation (Li *et al.* 2021a). Fine-scaled roughness also can be achieved by air-blasting with abrasive particles, crystallizing from organic solvents, and spraying of supercritical solutions (Cunha and Gandini 2010a,b). Balu *et al.* (2008) showed that oxygen plasma could be used to etch amorphous cellulose domains away from cellulosic fibers; subsequent treatment of the surfaces with fluorocarbon provided superhydrophobicity. Chitnis and Ziaie (2012) achieved analogous results by use of laser surface micropatterning of wax paper surfaces.

Silane chemistry provides means of tailoring treatment conditions to achieve roughness at the nano scale. In particular, inclusion of tetraethoxysilane (TEOS) in the treatment scheme tends to result in highly structured, high surface area substrates (Mai and Militz 2004; Cunha *et al.* 2010a; Khalil-Abad and Yazdanshenas 2010; Cappelletto *et al.* 2012; Wang *et al.* 2012; Le *et al.* 2016).

As the second factor of superhydrophobic performance, the free surface energy has been successfully lowered in some studies on ester treatments. In Khanjani *et al.*'s (2018) study, nanocrystals (CNCs) were treated with 2H,2H,3H,3H-perfluorononanoyl chloride and 2H,2H,3H,3H-perfluoroundecanoyl chloride, which are known to reduce surface energy. The resulting fluorinated cellulose esters were used as nanospheres in superhydrophobic treatments on cellulosic paper (Khanjani *et al.* 2018).

Hydrophobic monolayers

The treatments to impart hydrophobic character to roughened surfaces, with the intention to achieve superhydrophobic character, are generally consistent with the reactive monolayer treatments already considered in this review. As shown in Table 3, the silane-based treatments have received a lot of attention, which is likely due to their simplicity and effectiveness. Also, when using alkoxysilane-based treatments, inclusion of some tetraethoxysilane (TEOS) or related compounds makes it feasible to achieve both hydrophobicity and fine-scale roughness in a single step (Mai and Militz 2004; Cunha *et al.* 2010a; Le *et al.* 2016; Schramm and Amann 2019; Tasleem *et al.* 2019).

Additionally, there have been studies done on ester treatments. These treatments, which specifically focused on nanoprecipitation, resulted in superhydrophobicity when applied to cellulosic base layers. Nanoprecipitation is a simple and energy-efficient method of converting polymers into nanoparticles. In Geissler *et al.*'s (2014) experiment, cellulosic paper was treated with cellulose stearoyl esters (CSE), resulting in hydrophobicity, then spray-coated with CSE nanoparticles obtained via nanoprecipitation, which rendered the paper superhydrophobic with contact angles of >150°. Additional benefits of the treatment included self-cleaning and thermo-responsive character of the treated surface, which could be especially useful in packaging applications (Geissler *et al.* 2014).

In Khanjani *et al.*'s (2018) study, nanoprecipitation was also used to disperse nanospherical fluorinated cellulose esters on paper via spin-coating, resulting in contact angles of >150°. The authors also successfully tested the method not only on cellulosic paper, but also on spin-coated textiles, further expanding the flexibility of the process into a wider range of substrates. Some of the benefits of this method include the flexibility and industrial scalability of the process, which is of utmost interest in packaging hydrophobic treatment applications. However, both per- and polyfluorinated substances have come under scrutiny in recent years due to their toxicity and persistence in the environment. Long-chain perfluorinated compounds have mostly been banned, and more research has been focused on the less harmful short-chain substances.

Practical considerations for superhydrophobic systems

Though the articles cited in Table 3 show that there has been substantial progress in achieving superhydrophobic effects, there seems to have been insufficient attention to factors affecting the industrial and societal application of such systems. Because such systems resist wetting and adhesion, the surfaces cannot subsequently be coated or painted, especially by means of aqueous-based formulations. This can be an issue for cellulose-based systems, which often need protection from moisture and ultraviolet light. To overcome such issues, it would be logical to apply coatings to cellulosic materials and then, if deemed helpful, to apply the superhydrophobic treatments as a top layer.

Another area that needs attention relates to durability. Most theoretical work related to superhydrophobic systems assumes that the wetting liquid (often aqueous) contacts only the outermost points of roughness and that the valleys between those points are filled with air. However, over the course of time, the air within those spaces will tend to become dissolved in the liquid phase. It follows that, depending on the rate of gas solubilization, superhydrophobic properties are likely to disappear. Another point of vulnerability is when moisture or high humidity cause an underlying cellulosic or other polysaccharide substrate to swell (Lindström 1986), and such swelling has the potential to stretch and break part of a barrier film.

The assumed tendency of superhydrophobic properties to disappear with time might be seen as a benefit in applications intended to simultaneously biodegrade with the end of the product’s lifecycle. However, the reported high degree of substitution (DS) of some ester-based superhydrophobic treatments might be both an advantage and an obstacle in terms of the opposite performance needs of durability and biodegradability attributes. As an example, paper treated with nanoparticles of cellulose stearoyl ester (CSE) were found to have a very high DS of 2.99 (Geissler *et al.* 2014). There is often an inverse relationship between biodegradability and the extent of derivatization of polysaccharides (Buchanan *et al.* 1996; Frank *et al.* 2021).

RESEARCH NEEDS

Based on the research articles that have been cited in this review, it is clear that considerable progress has been achieved with respect to the development and characterization of hydrophobic treatments for polysaccharide-based surfaces. There are various related areas of technology that have tended to be neglected. These include the durability of various hydrophobic treatments, as well as issues related to cracks, pores, and other defects in barrier layers. Such issues, which can be the object of future research, will be considered in this section.

Durability

For a hydrophobic surface treatment to serve its intended function, it is generally not sufficient to consider just its initial behavior. The hydrophobic effect and barrier performance relative to transport of moisture (or sometimes also oily liquids) needs to persist as long as the longest typical usage of the item. The system may have to withstand moist or completely wet conditions, sometimes both inside and out. The temperature may be either cold (as in refrigerated items) or very warm. The package may have to stand up to different levels of scuffing, abrasion, as well as puncture or tear stresses. In this section, three main categories related to durability will be considered: the vulnerability of the hydrophobic monomolecular layer itself, problems attributable to a polysaccharide-based substrate, and critical tests that might be employed in future research to address practical issues of durability. Teisala *et al.* (2014) and Milionis *et al.* (2016) reviewed progress with respect to the durability of superhydrophobic systems.

Vulnerability of hydrophobic layer

An ideal barrier layer hydrophobic treatment, as envisioned in this article, will have a challenging assignment. It needs to serve essentially the same role as might otherwise be filled by the use of a three-dimensional phase material, such as glass, foil, or a macroscopic layer of plastic. The hypothesis here is that, for a range of food packaging applications, these three-dimensional barriers can be replaced by essentially monolayers of suitably anchored and oriented monolayers. Whereas a three-dimensional layer, *i.e.* a phase, will have a certain redundancy of its barrier function, a monolayer would be required to achieve its function at every point of the interfacial area.

Debonding of molecules comprising a hydrophobic monolayer is one of the ways in which such a barrier structure might fail. For example, ester and amide bonds are subject to hydrolytic cleavage under ambient conditions. Such cleavage tends to be promoted by moisture, increased temperatures, and sufficiently strong acidic or basic conditions (Patrick 2004). In addition, such bonds are susceptible to enzymatic attack (Bornscheuer 2002; McKinney and Cravatt 2005). On the other hand, authors such as Muresan *et al.* (2013) and Balan *et al.* (2014) have used the term “durable” when referring to, for instance, stearic ester monolayers on cotton fabrics; presumably such monolayers are more durable compared to physically adsorbed monolayers. Leal *et al.* (2020) touted the durability of hydrophobic modification of bacterial cellulose by oxygen plasma treatment and chemical vapor deposition. Likewise, Yang *et al.* (2018) used the word “durable” when describing cotton fabrics that have been treated with atmospheric plasma and hexamethyldisiloxane. It is worth noting a point made by Cunha and Gandini (2010a,b); that is, the durability of systems even within a given class of hydrophobic treatment can span a wide range.

Molecular overturn represents another potential mechanism by which a hydrophobic monolayer can become less effective with the passage of time. As illustrated in Fig. 20, the time-dependent overturn of inadequately anchored amphiphilic molecules can be brought about by contact with liquid water. Such a change is especially of concern in cases where hydrophobic monomers are associated by physical linkages (Angelova *et al.* 1994; Belman *et al.* 2012). By contrast, more stable hydrophobicity is anticipated when the hydrophobic groups are held into position by covalent bonds, as in the case of AKD sizing (Lindström and Larsson 2008). Uchida *et al.* (1991) showed that although adsorbed monolayers of surface-active molecules are susceptible to changes in orientation, which can harm their hydrophobic effects, such problems can be overcome by polymerization. In the cited work, the monomers in a hydrophobic bilayer contained acrylic groups, which could be joined together *in situ* within the compressed film by free-radical polymerization.

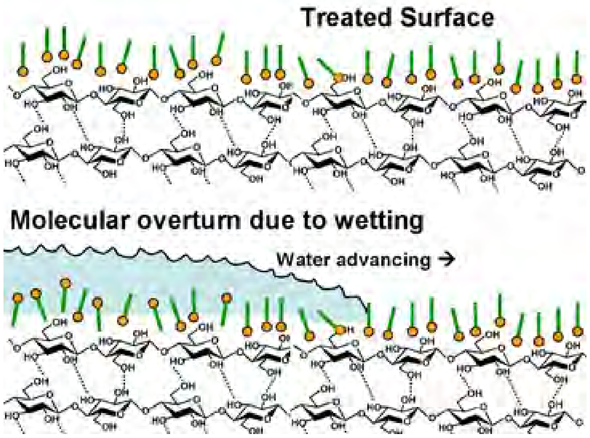


Fig. 20. Illustration of the possible overturn of amphiphilic molecules, assuming that the anchoring mechanism is somewhat reversible upon exposure to a water phase

Rubbing and abrasion potentially might be able to disrupt orientated monolayers of molecules (Zhang *et al.* 2003; Milionis *et al.* 2016; Schramm and Amann 2019). Most studies involving monomolecular hydrophobic treatments of polysaccharide-based substrates have not considered such effects. Clearly, this is an area where research is needed. As illustrate in Fig. 21, it is likely that the rubbing of a layer of amphiphilic molecules, if insufficiently anchored, will bring about their agglomeration into various micellar forms.

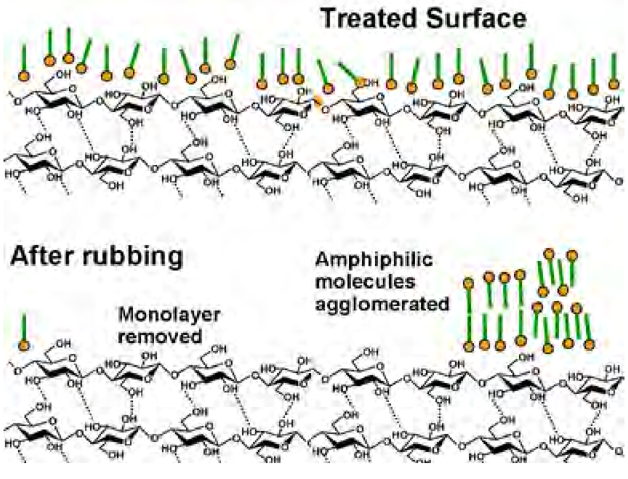


Fig. 21. Illustration of possible damage to a hydrophobic monolayer subjected to manual rubbing, with the likely formation of irregular agglomerated molecular assemblies

The word “fouling” can be used to denote problems resulting from deposition of contaminants on top of a surface. Thus, even if a molecular-based hydrophobic structure remains securely in place, there is a possibility that the hydrophobic effect may be overcome by substances added later. A mundane example is provided by the ability of soapy molecules to change the wettability characteristics of surfaces (Ivanova and Starov 2011). This is illustrated conceptually in the top portion of Fig. 22. Fouling by a variety of surface-active agents likewise is harmful to membrane distillation operations (Choudhury *et al.* 2019). The bottom portion of Fig. 22 considers a similar effect of a hydrophobic surface covered by miscellaneous matter, such that the wettability of the original substrate, and any hydrophobic system, no longer make any difference. Though such mechanisms appear likely to affect food packaging systems, no related research was found in the review of the literature.

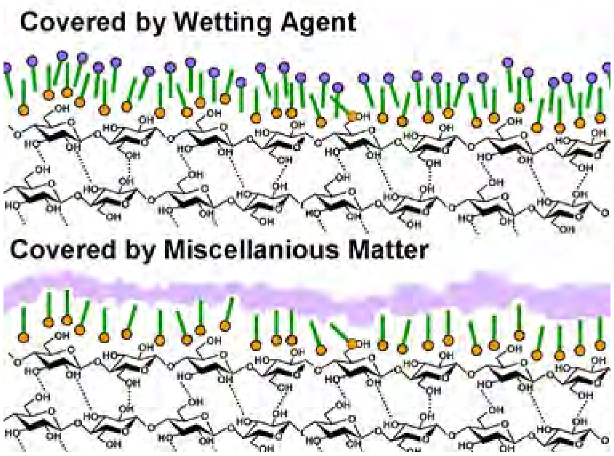


Fig. 22. Concepts of how effects of a hydrophobic treatment can be rendered ineffective, by either (A) the presence of wetting agents, or (B) fouling by miscellaneous materials that effectively cover up the nominal surface. In this figure, purple coloration indicates a hydrophilic nature, whereas orange coloration indicates an anchoring group that binds a hydrophobic group (green stick) to the substrate.

Problems attributable to the substrate

Even when it is protected by a hydrophobic molecular layer, as described in this article, an underlying polysaccharide-based film or paper-like structure may serve as a point of vulnerability and potential failure. Even if a hydrophobic monomolecular layer is assumed to be completely successful in preventing outright wetting, the underlying carbohydrate material will be susceptible to uptake of moisture content from the surroundings. In cases where no water is able to pass as a liquid through the hydrophobic layer, it is to be expected that water molecules can diffuse slowly through such a barrier as vapor (Bras *et al.* 2007). Some additional concerns include possible effects due to weakly adsorbed chemical species (*i.e.* weak boundary layers) on the carbohydrate-based substrate, problems due to excessive pore sizes within the substrate, inadequate strength and/or stretching ability of the substrate (leading to brittle failure and crack formation), and effects related to possible swelling of the substrate.

The concept of weak boundary layers has a long history as a way to account for low levels of adhesion between phases (Bikerman 1967; Stehr and Johansson 2000). Though a hydrophobic monomolecular layer is not a phase, it is proposed here that the same concept can be applied. For instance, many cellulose-based materials are likely to end up with a coating of natural waxy substances; these can be expected to migrate, over the course of time, toward air interfaces (Swanson and Cordingly 1956; Stehr and Johansson 2000). Extractives present on wood surfaces have been shown to decrease the strength of joints achieved with various adhesive resins (Nussbaum and Sterley 2002; Bockel *et al.* 2018). In systems depending on the effective anchoring of a selected hydrophobic compound, the presence of loosely bound oils or waxes, even if they are hydrophobic in character, could be expected to have a negative effect on the treatment results. Indeed, Sjöström *et al.* (2006) found that materials released into the water during preparation of kraft pulps tended to have an adverse effect on subsequent hydrophobic sizing of the paper by means of AKD emulsions added to the refined pulp slurry.

According to the Lucas-Washburn theory (Lucas 1918; Washburn 1921), the flow of liquid into a porous solid can be approximated by assuming a model of equal-sized, ideal cylindrical pores. The distance that the liquid can penetrate into such a system can be predicted by the interfacial tension, the angle of contact of the liquid with the surface, the viscosity of the liquid, and the pore diameter. A higher pore diameter makes it increasingly difficult for the porous material to resist entering flow of the liquid, even with a relatively high value of contact angle. It follows that, when an inherently porous material is to be used as a hydrophobic barrier, the pore sizes ought to be as small as can be practically achieved. For example, it is well known that the refining of cellulose fibers, in preparation for the forming of a paper sheet, will contribute to a smaller diameter of pores in the related structure (Forsström *et al.* 2003). When such paper is prepared with a hydrophobic sizing agent, the ability to resist penetration by water will be increased relative to that of paper made from less-refined pulp (Tufvesson and Lindström 2007).

Packaging materials can be subjected to a wide variety of stresses and strains during shipping, storage, and final usage by the consumer. Ideally, such stresses and strains would not adversely affect a hydrophobic molecular layer. However, the structure itself may fail if either the stresses or strains exceed the limitations that are inherent in the materials and structures themselves (Seth *et al.* 1982). Even before that happens, there can be a concern that the stretching of the substrate might create defects in a monomolecular film applied to the surface. It can be argued that the stretching of cellulose paper mainly will affect the gaps between fibrillar elements rather than the dimensions of the cellulosic fibrillar elements themselves. Thus, there is a likelihood that the hydrophobic character of monomolecular layers applied to the substrate will not be adversely affected by stretching. On the other hand, larger gaps might open up between the hydrophobically treated fibers or fibrils. It should be noted that papermakers can bolster the strength of the substrate not only by increased refining of the pulp, but also by usage of strength agents (Lu *et al.* 2020). When preparing paper materials for usage under moist conditions, wet-strength treatment can be used to achieve enhanced bonding that does not depend exclusively on hydrogen bonds (Espy 1995; Lu *et al.* 2020).

The swelling of a polysaccharide-based substrate can be a concern regardless of whether the package has been subjected to stresses. For example, Palasingh *et al.* (2021) evaluated the water-swelling of films prepared from a variety of polysaccharides. The degree of swelling was found to change depending on the compositions. In principle, such swelling can be mitigated by prior cross-linking reactions during formulation of the substrate (Ramaraj 2007a,b).

Critical tests

Regardless of the conceptual understanding of how the hydrophobic performance of packaging films might become degraded during storage and handling, there will be a need to assess durability relative to different kinds of conditions. Various durability-related tests have been reported in relation to hydrophobic molecular layers on polysaccharide-based substrates.

Milionis *et al.* (2016) reviewed the topic of durability, with particular attention to superhydrophobic systems. As stated in the cited article, “most superhydrophobic surfaces are very fragile (*i.e.* they will lose non-wettability if touched or rubbed by human hands)." Verho *et al.* (2011) describe a wide variety of self-developed tests that have been employed by researchers who were concerned about the effects of rubbing on the hydrophobicity of superhydrophobic surfaces. These have included rubbing the specimen with cloth, leather, or sandpaper with a specified load. Following such treatments, the specimens were evaluated again for their hydrophobic nature, *e.g.* by measuring the contact angle of water. Milionis *et al.* (2016) have published a set of recommended tests, including variations of conditions for the Taber abrasion test, a sand impact test, a jet/spray impact test, and exposure within an ultrasonic bath. Schramm and Amann (2019) used a Taber abrasion test to evaluate the durability of cotton specimens that had been rendered hydrophobic by treatment with alkoxysilane reagents. There is a need for future testing of this type on systems involving monomolecular hydrophobic treatment on polysaccharide-based substrates.

Tolerance of hydrophobic treatments to washing has been mentioned by various authors as a contributing factor in success (Dankovich and Hsieh 2007; Tomšič *et al.* 2008; Samanta *et al.* 2012; Vasiljević *et al.* 2013). Such tolerance can be evaluated by use of specified laundering conditions (Huang *et al.* 2011).

Having considered, in this subsection, publications related to durability of hydrophobic films, the main take-away message appears to be that relatively few scholars have been active in this area. A quick search of US patents yielded nothing relevant to the topic. In particular, further research is needed on the durability of monolayer hydrophobic treatments of polysaccharide substrates.

Biodegradability

Table 4 provides a listing of research articles in which terms related to "biodegradable" were used when referring to polysaccharide-based packaging materials. These materials are often contrasted to those based on synthetic plastics, such as polyethylene, which are very difficult to degrade under natural conditions. Greater biodegradability has been found when such synthetic plastics are replaced by certain bioplastics (Attallah *et al.* 2021). Poly(lactic acid) (PLA), which is most widely commercialized bioplastic, has been shown to be compostable under sufficiently high-temperature conditions, but not biodegradable under typical soil or ocean conditions (Emadian *et al.* 2017; Hubbe *et al.* 2021). Therefore, to achieve relatively rapid biodegradability and a minimization of adverse environmental effects, it would be advantageous to employ polysaccharide-based materials as the main substrates for packaging.

Despite the fact that all of the articles listed in Table 4 refer to biodegradability, only a few of them (*e.g.* He *et al.* 2013; Chen *et al.* 2021) describe experimental verification that the material still was deserving of that designation after hydrophobic surface treatment. Review articles by Rol *et al.* (2019) and Fotie *et al.* (2020) provide additional relevant references. One way to view this situation is that researchers generally do not take seriously the possibility that a mere monolayer (or so) of hydrophobic molecules would pose a problematic effect on the environment. Indeed, Shah *et al.* (2018) noted that researchers working with a type of alkenylsuccinic anhydride have claimed that such treatment would not affect biodegradability. However, to settle such questions, specific research is needed.

Table 4. Articles Using Terms such as Biodegradable for Polysaccharide-Based Substrates Treated with Hydrophobic or Oleophobic Monomolecular Layers

Hydrophobic agent	**Substrate**	**Details**	**Citation**
Fluorocarbon	Cellulose paper	Plasma, superhydrophobic	Balu *et al.* 2008
Stearic acid	Starch film	Solution immersion	Cai *et al.* 2021
Myristic acid	Cellulose film	Solvent evaporation	Chen *et al.* 2021
Chitosan, polypyrrole	Nanofibrillated cellulose	Aqueous cast films	Gao *et al.* 2020
Chitosan, essential oil	Composite film with whey protein	Aqueous formulation	Gohargani *et al.* 2020
Stearic acid	Cellulose film	From alcohol solution	He *et al.* 2013
Alkylketene dimer	Starch biofoam	Thermopressing	Iriani *et al.* 2020
Polydimethylsiloxane	Chitosan & collagen	Simple coating	Jing *et al.* 2021
Paraffin wax	Paper, casienate	Melt-coating	Khwaldia 2010
Alkenylsuccinic anhydride	Nanofibrillated cellulose & hemicell.	In DMF/pyridine solution	Kisonen *et al.* 2015
Silanized (2 methods)	Cellulose cryogels	Vapor & aqueous	Lazzari *et al.* 2017
Trichloromethylsilane	Bacterial cellulose	Oxygen plasma	Leal *et al.* 2020
Silicone polymer	As-is	Composting	Lehmann *et al.* 2001
Alkylketene dimer	Paper	Pickering emulsions	Li *et al.* 2021b
Polysiloxane	Paper coating	On a melamine primer	Li & Rabnawaz 2018
Linseed oil	Alginate films	Drying, oxidation	Nehchiri *et al.* 2021
Epoxy chloropropane	Hemicellulose films	Etherization	Shao *et al.* 2020
Butylacrylate	Nanocellulose	Monomer grafting	Song *et al.* 2014
Lemongrass oil, wax	Gelatin on paper	Coating & heating	Syahida *et al.* 2020
Alkenylsuccinic anhydride	Tree gum	Ethanol solution, dried, heated	Venkateshaiah *et al.* 2021
Long-chain fatty acid	Cellulose	Lipase esterification	Wang *et al.* 2017
Glycidyl methacrylate	Filter paper	Click chemistry	Wu *et al.* 2021b
Epicuticular wax	Paper	From various solvents	Yadav *et al.* 2014
Methyltrimethoxy silane, AKD	Nanofibrillated cellulose	Aqueous silane or AKD as emulsion	Yook *et al.* 2020
Methylene diphenyl diisocyanate	Filter paper	Acetone solution for surface reaction	Zhou *et al.* 2020

High-speed Application

Another aspect that is in continual need of research attention involves the scale-up of treatment concepts in the direction of high-speed application. Only a relatively few of the articles considered in this work explicitly involve scale-up features (Alf *et al*. 2010; Starostin *et al*. 2016). Alf *et al.* (2010) studied the roll-to-roll application of chemical vapor deposition films. Starostin *et al.* (2016) used a roll-to-roll format for testing plasma hydrophobization. In addition, Khwaldia (2010) applied coatings of caseinate and paraffin wax to paper at a speed of 6 m/s, which is faster than typical laboratory testing. Yu *et al.* (2019) applied gas-phase treatment to viscose rayon at a speed of 0.5 m/min. Zhang *et al.* (2018) reviewed plasma-based hydrophobic treatments and characterized them as suitable for high-speed applications. Many of the treatment options considered in this review article apparently have been studied only under laboratory conditions, so there is a great need for developmental work at higher application speeds.

CONCLUDING STATEMENTS

Based on the articles considered in this review, there appear to be several promising categories of molecular-type treatments of polysaccharide-based substrates that are capable of providing high levels of hydrophobicity and effective hold-out of aqueous fluids. Of particular note, in the context of preparing biodegradable food packaging materials, are systems based on silane chemistry, esters, and plasma treatments. Such systems, depending on the details, have been shown to achieve suitable high water contact angles and resistance to permeation.

Further published research work is needed in critical areas. In particular, studies are needed that focus on both the durability of hydrophobic effects and biodegradability. A lack of definitive studies in these areas appears to have its roots in the fact that current packaging systems routinely employ layers such as polyethylene, metal foil, or glass, *etc.* to effectively exclude the transport of water. Though hydrophobic systems based on the anchoring of monolayers of hydrophobic molecules on polysaccharide-based systems are well known, especially in the paper industry, such systems have not been called upon to function in the absence of plastic films or foils. Circumstances are changing, however, in light of the goal of achieving higher levels of biodegradability and recyclability of packaging materials.

In addition to the published research, which has been the main focus of the present review article, it is worth noting two important aspects that were not the prime focus of the present work. It is likely that a search of patent literature would reveal further progress in the implementation of workable systems related to the topics of this article. In addition, it is likely that some corporate research will have resulted in progress in barrier layers that goes beyond what has been published. Relatively low-cost, practical solutions would have the greatest chances to be implemented on a commercial scale. Practical success in commercialization may or may not be reflected in academic publications.

The subsections that follow summarize some key findings from the present review of the literature. First, it is possible to summarize some of the quantitative information that has been gathered. As was noted earlier, the variables of temperature and time can be critical when attempting to scale up various research findings to industrial production. High temperatures have limitations because of the thermal decomposition limits of the available polysaccharide-based substrates, such as paper, starch films, and the like. The times required for reaction are likely to place limits on rates of production in continuous web processing of packaging system. Second, based on the literature, it is possible to see some general trends in focus. Not only are the types of research studies evolving with time, but also the receptivity of industry to more eco-friendly packaging solutions appears to be increasing. Finally, there are many research opportunities in the general field of this article.

Summary of Findings

Time-temperature ranges

Figure 23 shows a plot of temperature (on the vertical axis) and time (on the logarithmic horizontal axis) for various classes of molecular hydrophobic treatment for polysaccharide-based substrates. The data, based on the conditions reported in articles cited in this work, are notably broad. The range of temperatures represented in the figure is generally not a concern in light of the thermal stability of polysaccharide materials. Hemicellulose, which has the lowest thermal stability among the main components of wood, thermally degrades within a temperature range of about 220 to 315 °C (Yang *et al.*

2007; Chen and Kuo 2011). In the case of starch, LeCorre *et al.* (2012) recommended that dry starch crystals can be used in processes lower than the range 150 to 200 °C to avoid melting. Thermogravimetric results reported by Averous and Boquillon (2004) show as much a 15% mass loss during heating of thermoplastic starch in the range 100 to 250 °C, above which there was major decomposition. On the other hand, Curvelo *et al.* (2001) report successful processing of starch, as a composite with montmorillonite clay, at 170 °C.

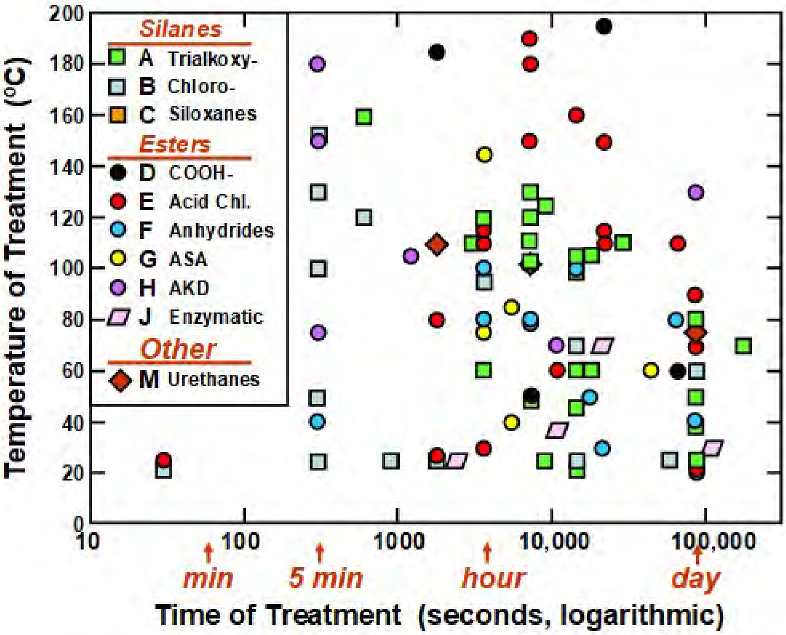


Fig. 23. Plot of the temperatures of treatment and durations of treatment in cases that such information was reported. The letters correspond to Tables A through M of the Appendix, where those results are given numerically.

The time information provided in Fig. 23 gives rise to concern. Ideally, one would want the hydrophobization process to take place as a web of paper or film is traveling at an industrially attractive speed through an exposure zone of limited size. The outer limit of practical exposure time would be in the range of a few minutes, which happens during the industrial drying of a web of paper. The plasma-based treatments, which seem especially suited for continuous processing, seem to have the most solid evidence supporting their suitability for scale up and usage under industrial conditions (Starosin *et al.* 2016; Zhang *et al.* 2018).

There is evidence within the points plotted in Fig. 23 that conditions of hydrophobic treatment had not been well optimized in the published studies. For example, it is well known to papermakers that alkenylsuccinic anhydride (ASA, yellow circles) is much more reactive than alkylketene dimer (AKD, purple circles). The ASA is usually fully cured before the size press on a conventional paper machine, whereas AKD often does not reach its ultimate effectiveness until after many minutes of residence time within a large reel of paper, before the product has been cut up into individual rolls or sheets. In this context it does not make sense that many of the points associated with AKD are further to the left (lower time) and to the bottom (lower temperature) than those associated with ASA. Likewise, it is well known that acid chlorides (red circles) are more reactive than carboxylic acids (black circles). So it is unexpected that so many of the red circles are towards the upper right of the plot (even though one such point is at the extreme lower left). Thus, it appears that many researchers have employed relatively hot, long-duration treatments as a matter of convenience, probably with the idea of leaving no doubt with respect to completeness of the reaction. It appears that minimizing the time of treatment has not been high on the priority list of a majority of researchers who have been studying these systems.

It is suggested here, as a hypothesis, that there may be ranges of conditions that have not yet been adequately explored in the mainly lab-based research that has been published so far. It is proposed the future studies can consider somewhat higher temperatures of exposure, paired with much lower exposure times, as a means of approaching industrially attractive conditions.

Results related to plasma treatments do not appear in Fig. 23. With just a few exceptions (Chen *et al.* 2017; Cerny *et al.* 2021; Ma *et al.* 2021), the researchers who have reported plasma-based hydrophobic treatments of polysaccharide-based substrates generally have not mentioned the time duration of treatment. Table 5 lists some typical periods of treatment employed in studies of plasma treatments to change the wettability properties of a variety of substrates. Notably, even the longest times listed in this table are towards the left-hand side of the plot in Fig. 23. On that basis, plasma treatments in general can be regarded as a promising path forward for relatively rapid treatment of surfaces.

Table 5. Studies Considering Treatment Times Needed for Plasma Treatments to Change the Wettability Characteristics of Various Substrates

Plasma type	**Substrate**	**Treatment time (s)**	**Citation**
O_2	Polydimethoxysilane	150	Amerian *et al.* 2019
Ar or O_2	Polyethylene	30 to 90	Ataeefard *et al.* 2009
Air	Polycaprolacone	60 to 300	Can-Herrera *et al.* 2016
Air & hexamethyldisiloxane	Cellulose fibers	900 to 5400	Cerny *et al.* 2021
Air & hexamethyldisiloxane	Poplar wood	75	Chen *et al.* 2017
Air & hexamethyldisiloxane	Polyester (PET)	13	Ma *et al.* 2021
CF_4	Nanocellulose films	60	Sahin *2007*

Practical issues

The ideal hydrophobic treatment technology should be reliable, safe, economical to run, and not overly expensive to set up the production equipment. The capital expenditure, when one considers the risk associated with new production schemes, is a matter of concern. As a starting point, let it be assumed that one is considering a continuous roll-to-roll application system. Thus, the main additional capital expenses may include such items as a vapor-phase exposure unit or a means to apply a liquid coating layer. In either case, it is likely that a heated drying or curing unit will be needed. These units need to be integrated with air processing systems to avoid discharge of harmful components to the environment and to achieve a safe working environment. Ideally, the exhaust air from vapor-phase application, perhaps after filtering or other treatments, can be circulated back to the intake of the vapor preparation system. Pure vapor-phase treatments and plasma-based treatments have the inherent advantage of not requiring evaporation, which can be expected to significantly increase the time and energy required for processing. On the other hand, aqueous-based coatings, with emulsified hydrophobic compounds and relatively high solids content, might be considered too. For example, an emulsion of alkenylsuccinic anhydride (ASA) or alkylketene dimer (AKD) may be applied with a stabilizing polymer solution, such as starch, at the surface of a polysaccharide-based web (*e.g.* paper or a barrier film on paper). Pilot-scale testing will be needed, in each case, to ensure that the extent and permanence of the hydrophobic treatment are sufficient for each application.

Shifting Focus of Industry

There is often a big gap between what can be achieved in the laboratory and what makes sense to operators or investors in industrial processes. On the other hand, more sustainable technologies are increasingly being considered by management of major corporations. A study by de Medeiros *et al.* (2014) considered how the gap between academic research and industrial scale-up can best be facilitated in the case of sustainable product manufacturing. Ketata *et al.* (2015) studied companies in Germany and came to the conclusion that most of them have inadequately trained staff to deal with the complexities inherent in efforts to achieve large advances in sustainability. Another factor contributing to likely widespread advances in sustainable production include regulations banning some uses of plastics in single-usage packaging (Steensgaard *et al.* 2017; Alfonso *et al.* 2021). Some of the technology needed to achieve more eco-friendly single-use packaging systems is relatively mature, though it has not been yet challenged with the assignment of acting on its own. For example, the hydrophobic sizing of paperboard in milk cartons has been just serving as a back-up for another water-barrier layer, extruded polyethylene.

Research Opportunities

In closing, there will be substantial opportunities for research in the coming years, both at the fundamental level and involving scale-up to industrial processing. Specifically, as discussed in earlier sections of this review, there is a need for research related to durability, including suitability for long exposure times, challenging temperature conditions, abrasion, and mechanical stresses. Researchers need to consider ways in which to overcome inherent vulnerabilities in systems that depend for their performance on the integrity of a single molecular layer of hydrophobic groups. For instance, the main barrier layer might be backed up by use of waxy materials in an underlying polysaccharide-based ply or film. High-speed application schemes need to be tested, thus pushing towards conditions that would be attractive for industrial production. Finally, there is a need for research to determine, in each case, whether or not the envisioned packaging system exhibits the desired rapid and thorough decomposition in the environment, while concurrently achieving the needed barrier properties to facilitate efficient shipping, storage, and delivery of food items.

ACKNOWLDGEMENTS

The authors thank the following volunteers who studied an earlier version of this document and provided useful corrections and suggestions: Jinwu Wang, US Department of Agriculture, Forest Product Laboratory, Madison, WI, USA; Tomasz Ganicz, Centre of Papermaking and Printing, Lodz University of Technology, Poland; Mona H. Abdel Rehim, Packaging Materials Department, National Research Centre, Cairo, Egypt; Soojin Kwon, North Carolina State University, Raleigh, NC, USA; and Lisandra Chacon, North Carolina State University, Raleigh, NC, USA.

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APPENDIX

The following tables are included in this appendix. All of the tables consider the hydrophobic treatment, the medium, the substrate, the water contact angles, important details, and the author-year citation.

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Table A. Tri-alkoxysilanes: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	Medium	Substrate	WCA	Details	Citation
Trimethoxy-silanes, *e.g*. C8	80/20 methanol/ water	Cellulose fibers	20 to 120	Prehydrolysis of trimethoxysilane at room temp; 2 h exposure; 2 d drying; heated 120 °C for 2 h; extracted by THF.	Abdelmouleh *et al.* 2002
Trimethoxy-silanes, amino, *etc*.	40:60 water/ ethanol	Banana fibers	-	5% treatment; pH 4 with acetic acid, 4 h, dried 80 °C for 24 h.	Alonso *et al.* 2019
Methyl tri-methoxysilane	Aqueous	Cellulose nanocryst.	100	Hydrolysis of MTMS at pH 3; CNC added; stirred room temp. 4 h, then heated to 70 °C for 4 h; dried 105 °C for 4 h.	Baatti *et al.* 2019
Vinyltriethoxy silane, *etc.*	Aqueous	Cellulose	-	0.05 M HCl for 30 min., then NaOH neutralized, 2.5 to 5 h; centrifuged; washed.	Beaumont *et al.* 2018
Glycidyloxy-propyl dimenthyl-ethoxy silane	Aqueous or ethanol	Nano-fibrillated cellulose	-	Acetic acid to pH=3; 4 h at 46 °C; in ethanol; refluxed for 4 h; vacuum oven drying at 120 °C.	Cabrera *et al.* 2020
Methyl methyoxysilanes	Aqueous	Paper	65 to 124	0.05 M HCl or NH_4OH; 4 h aged; dipped.	Cappelletto *et al.* 2012
Triethoxysilanes, various	Aqueous	Wood	79 to 115	0.05 M HCl, 4 h aged sols; wood had 12% moisture content; submerged; evaporated; heated 60 °C for 1 h; 1 or 2 layers.	Cappelletto *et al.* 2013
Triethoxysialines, cyano & MPS	Various organic	Cellulose fibers	100	Organic solvents or with some water added (heptane, dioxane, toluene/methanol 80/20; tetrachloroethane; then extraction)	Castellano *et al.* 2004
Perfluoro-octyl trimethoxysilane	Ethanol	Nano-cellulose films	80 to 130	The perfluorooctyl trimethoxysilane was added to ethanol and exposed to the nanopaper films for various times; the films were then washed with ethanol and dried at 130 °C for 2 h.	Chun *et al.* 2012
Triethoxysilanes, various	DMF	Cellulose fibers	140	Add the trimethoxysilanes to DMF, then stir for 5 h at 60 °C; modify the fibers over night;	Cunha *et al.* 2010a
Fluorosiloxane	Aqueous	Cellulose	130, 145	Layer-by-layer application, followed by siloxane hydrolysis, all at room temperature in air	Gonçalves *et al.* 2008
Aminopropyl trimethoxysilane	Ethanol/ water 4/1	Potato starch	-	Prehydrolysis at room temperature for two hours at pH=4 with acetic acid, then starch nanocrystals were dispersed by sonication; 2 h treatment; centrifuged and vacuum-dried.	Hao *et al.* 2019
Triethoxysilanes, various	Pyridine in CH_3Cl	Paper	141	Pieces of cellulose paper were inserted in 10% trimethoxysilane solution in chloroform/pyridine solvent system.	Hedeshi *et al.* 2020

Reagent	Medium	Substrate	WCA	Details	Citation
Azidopropyl triethoxysilane	Aqueous	Cellulose	-	11 mM NaOH with cellulose was treated with the 3-azido-propyl triethoxysilane for 4 h at room temperature. This was diluted and centrifuged, then washed.	Hettegger *et al.* 2016
Azidopropyl triethoxysilane	Aqueous	Cellulose	-	The cellulose was added to an acetone (32 mL) and water (4 mL) mixture, then treated; the bacterial cellulose film was dried and cured at 105 °C for 2 h.	Hettegger *et al.* 2015
Aminopropyl trimethoxysilane	1:9 water: ethanol	TEMPO Oxidized NFC	-	10% of the aminopropyl trimethoxysilane in a 10:90 water:ethanol mixture was added to a 1% TEMPO-oxidized nanocellulose suspension for 2 h at room temperature at controlled pH. Refluxed at 90 °C. Washed, vacuum dried, cured at 40 °C for 24 h.	Indarti *et al.* 2019
Chloropropyl trimethoxysilane	Water	Starch with PLA	-	The coupling agent was stirred vigorously with excess deionized water until the turbidity vanished, then dry starch was added. This was stirred at 50 °C for 2 h, then filtered and dried at 70 °C.	Jariyasakookroj & C. 2014
Perfluorooctyl trimethoxysilane	-	Etched paper TiO_2	154	The perfluorooctyl trimethoxysilane was self-assembled onto the titania ultra-thin film on the pre-coated cellulose nanofibers.	Jin *et al.* 2012
Octyltriethoxy silane	1:9 water: ethanol	Cotton textile	-	Dipping in a 3% solution of 1:9 water:ethanol mixture, and holding for 18 h at room temperature at pH 3.5 to 4, then soaking in HCl, rinsing in ethanol, and drying at 120 °C for 1 h.	Khalil-Abad & Y 2010
Aminopropyl trimethoxysilane	Aqueous	Alginate/ CMC gels	-	The CMC/alginate capsules were placed in an aqueous aminopropyl-trimethoxysilane solution. The pH was adjusted in the range 6 to 10.	Kurayama *et al.* 2010
Methyltrimethoxy silane	Aqueous	Cellulose cryogels	110 to 119	Method 1: The methyltrimethoxy silane was added dropwise to supernatent solution with stirring; this was aged at 70 °C for 2 h. Then cellulose suspension was added. The mixture was freeze-dried. Method 2: The cellulose was freeze-dried, then dipped into the silane on a screen and dried for 48 h at 70 °C.	Lazzari *et al.* 2017
Dodecyl triethoxysilane	Ethanol/ water	Cellulose film	-	Teraethoxysilane first was mixed with an ethanol water mixture, then anhydrous nanocellulose was added and stirred at 25 °C for 4 h to put particles on the surface. The dodecyltriethoxy silane and its mixtures with TEOS for added with stirring. A wet film was formed on filter paper. The material was pressed at 50 °C and dried in an oven.	Le *et al.* 2016
Heptadecafluoro trimethoxysilane	Alcohol	Cotton fabrics	82 to 155	The cotton was treated with a sol prepared form tetraethoxysilane, and then it was modified by heptadecafluoro trimethoxysilane, followed by heating.	Liang *et al.* 2013

Reagent	Medium	Substrate	WCA	Details	Citation
Aminopropyl & glycidoxypropyl trimethoxysilanes	Acetone	Microfibrillated cellulose	-	MFC was solvent-exchanged into ethanol and then acetone. The silanes were added at 0.3% of the final concentration and stirred 24 h. The treated MFC was filtered and dried at room temperature for 24 h, followed by 120 °C heating for 2 h in air.	Lu *et al.* 2008
Trifluoropropyl & perfluorooctyl trimethoxysilane	2:8 water: ethanol	MCC & paper	117 to 129	The silanes were prepared in the 2:8 water:ethanol solutions, which were added to 5% cellulose suspensions at room temperature for 2 h. The solids were centrifuged and heated for 2 h at 110 °C under vacuum.	Ly *et al.* 2009
Aminopropyl trimethoxysilane	5:95 water: ethanol	Rice husk	-	The silane was first hydrolyzed with a 5 mM solution of 5:95 water:ethanol solution, which was stirred for 5 min. The dried, extracted rice husks were treated, with stirring for 3 h and 60 °C, followed by drying for 1 h at 60 °C.	Park *et al.* 2004
Aminopropyl trimethoxysilane	Acetone & acetic acid, 19:1	Pine wood fiber	-	The aminopropyl trimethoxysilane was used to treat cellulosic fibers having a moisture content of 10%. The acetone was meant to swell the fibers to increase the area of cellulose treated.	Pickering *et al.* 2003
Aminopropyl trimethoxysilane	1:4 water: ethanol	Hemp fibers	-	The aminopropyl trimethoxysilane was hydrolyzed for 2 h at room temperature, then added to 5% hemp fiber suspension in the same 1:4 water:ethanol solution, with 2 h stirring at 120 °C. The solids were rinsed in fresh solvent mixture, extracted for 24 h (Soxhlet) in ethanol and dried.	Rachini *et al.* 2009
Methacryloxy-propyltrimeth-oxysilane	Aqueous citric acid pH 5.4	CNC	-	At pH 5.4 the CNC was placed into the citric acid buffer, followed by addition of the methacryloxy- propyltrimeth- oxysilane with stirring for 2 h at room temperature. The mixture was centrifuged; the solids were resuspended in deionized water. Alternate: 8 h annealing at 110 °C.	Raquez *et al.* 2012
Aminopropyl trimethoxysilane	Water; ethanol; mixture	Nanofibrillated cellulose	-	The aminopropyl trimethoxysilane was used to treat the NFC in three different media: water, ethanol, and their 50:50 mixture. The pH was adjusted to 5.5. The mixture was homogenized and held for 45 min, then filtered and washed with water. Curing was at 110 °C for 50 min in suspension. Films were formed at 100 °C.	Robles *et al.* 2018
Octadecyldimeth-yltrioxy silylprop-ammon. chloride	Aqueous	Composites with gum, SiO_2	52 to 68	The composites were cast from an aqueous mixture with glycerol with the silane added; After mixing, the temperature was raised to 55-60 °C, followed by casting on glass.	Rukmanikrishnan *et al.* 2020a
Aminopropyl trimethoxysilane	1:4 water: ethanol	Cellulose fibers	-	Hydrolysis was carried out in 1:4 water:ethanol solvent, followed by treatment at the same conditions at 25 °C.	Salon *et al.* 2005
Trialkoxysilanes, four of them	1:4 water: ethanol	Cellulose fibers	-	Hydrolysis was carried out in 1:4 water:ethanol solvent, followed by treatment at the same conditions at 25 °C. Alkaline *vs.* acidic conditions.	Salon *et al.* 2008

Reagent	**Medium**	**Substrate**	**WCA**	**Details**	**Citation**
Trialkoxysilanes, eight of them	Water-ethanol mixtures	Filter paper	-	Hydrolysis was done, then reactions were carried out at 25 °C. Acetic acid used for pH adjustment.	Salon & Belgacem 2010
Trialkoxysilanes, three of them	1:4 water: ethanol	Cellulose fibers	-	Acidic media were found to stabilize the hydrolyzed forms. After adsorbing to a cellulose surface, the product was thermally treated at 110 to 120 °C.	Salon *et al.* 2007
Glycidylpropyl trimethoxysilane	Aqueous	Cotton		Hydrolysis was for 3 h at room temperature; then boric acid or pyrogenic silica were added. The cotton was impregnated, then thermally treated at 160 °C for 10 min.	Schramm & Amann 2019
Silane structures Me_3Si-O-Si, etc.	Aqueous	Wood	60 to 145	Hydroxylation of oligoesterified wood was done at 80 °C for 3 h with catalyst. This was extracted and dried.	Sebe & Brook 2001
Methyltrimethoxy silane	Vapor	Cellulose attapurite aerogels	up to 161	In a sealed container, the reagent was placed in a beaker at 70 °C for 14 h.; curing was at 50 °C for 24 h.	Shang *et al.* 2021
Aminopropyl triethoxysilane	2:3 water: ethanol	Cellulosic fiber	-	The fibers were first mercerized. The aminopropyltriethoxy silane was added to ethanol/water mixture and kept for 2 h. The pH was adjusted to 3.5 to 4. The alkali-treated cellulose fibers were dipped for 1 h in the mixture, then dried in air at 60 °C.	Singha & Rana 2013
Isocyanatepropyl trimethoxysilane	DMF	CNC		The dry nanocrylstal suspension was added to the DMF. Then the isocyanatepropyl trimethoxysilane was added and kept for 8 h. Catalyst and water were added, with mixing for 30 min. The product was rotary evaporated to obtain nanocrystal powder.	Taipina *et al.* 2013
Trimethoxy octylsilane	Butanol & water	Glass or cellulose acetate	150	The silane was dissolved in butanol. It was condensed upon addition to water.	Tasleem *et al.* 2019
Dodecyl trimethoxysilane	Aqueous	Kapok fiber	116 to 151	Mixed with water, together with tetraethoxysilane for 1 h. then the bleached kapok fiber was added with stirring for 10 min and gradual addition of ammonia for 4 h. This was washed and oven-dried at 60 C. The coated fiber was added to ethanol solution of DTMS for 1 h and cured at 120 °C.	Wang *et al.* 2012
Hexadecyl trimethoxysilane	Aqueous	Wood	140	Wood was immersed in a suspension of silica nanoparticles, washed and dried at 80 °C. Then it was immersed in an ethanol solution of hydrolyzed hexadecyl trimethoxysilane for 1 h, dried at room temperature, then cured at 105 °C for 5 h.	Wang *et al.* 2013

Reagent	**Medium**	**Substrate**	**WCA**	**Details**	**Citation**
Hexadecyl trimethoxysilane	1:4 water: ethanol	Starch nanocryst.	70 to 120	The hexadecyl trimethoxysilane was pre-hydrolyzed in 1:4 water: ethanol at room temperature for 2 h at pH=4 with acetic acid. The starch was dispersed in ethanol, then added to the mixture at pH=4 and 2 h. The product was centrifuged and vacuum dried and heated at 120 °C for 2 h.	Wei *et al.* 2016
Dodecyl trimethoxysilane	Ethanol	Cotton fabrics	>150	The cotton fabric samples were placed in an ethanol solution of dodecyl trimethoxysilane for 24 h at room temperature. Then were washed in ethanol and dried in air, than cured at 120 °C for 1 h.	Xu *et al.* 2010
Perfluorooctyl trimethoxysilane	Vapor deposited	Paper	110 to 155	The paper was treated with poly-diallyldimethylammonium chloride. Then the dry paper was placed in a sealed chamber with the perfluorooctyl trimethoxysilane at 125 °C for 2.5 h.	Yang & Deng 2008
Perfluorooctyl trimethoxysilane	Vapor deposited	Filter paper, *etc*.	up to 146	Dodecyl trimethoxysilane and PFTS were placed in sealed chambers and heated to 100 °C for 4 h.	Yu *et al.* 2019
Methyltrimethoxy silane	Aqueous	Nanofibrillated cellulose	110 to 142	The methyltrimethoxy silane was diluted with deionized water. The pH was adjusted with HCl. Polysiloxane sol was added. Drying was under vacuum.	Zhang *et al.* 2015

Table B. Chlorosilanes: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	**Medium**	**Substrate**	**WCA**	**Details**	**Citation**
Perfluorinated C6 trichlorosilane	Heptane	Cellulose nano-crystals	Oils only	Tridecafluoro-1,1,2,2,-tetrahydrooctyl-trichorosilane in heptane was immersed for 15 min, followed by rinsing with heptane, then water. Vertically aligned pillars were formed.	Aulin *et al.* 2009
Trichloromethyl-silane	Vapor phase	Cellulose filter paper	125 to 136	Nitrogen gas was passed through a bath of the trichloromethylsilane. The treated gas was passed through the filter paper for various periods of time.	Cunha *et al.* 2010b
Trichloromethyl-silane	Vapor phase	Cellulose filter paper	125 to 136	Dry filter paper was humidified, then treated with a stream of trichloromethylsilane in nitrogen gas for various time periods (30 s and 30 min).	Cunha *et al.* 2007a
Trimethylsilyl chloride	Vapor phase	Polymers on glass	-	Poly(vinyl alcohol) and chitosan were adsorbed onto glass. Then the surfaces were exposed to the trimethylsilyl chloride vapors. A typical treatment time was 4 h.	Duchoslav *et al.* 2021
A wide range of alkylchlorosilanes	Toluene	Silicone wafers	80 to 110	The toluene solutions of the various alkylchlorosilanes were exposed to purified silicon wafers at 70 °C for 3 days. The treated wafers were rinsed with toluene and then and ethanol and dried at 120 °C for 10 min.	Fadeev & McCarthy 2000

Reagent	Medium	Substrate	WCA	Details	Citation
Fluoroalkyl trichlorosilanes	Vapor phase	Filter (R-F) paper	130, 152	The silanization was applied in a vacuum oven from a toluene solution at 95 °C and 30 mbar for 5 min.	Glavan *et al.* 2014
Isopropyldimethyl chlorosilane	Organic solvents	Microfibrillated cellulose	-	Toluene solution was used with 1% water content was used as the solvent for isopropyldimethyl chlorosilane, with imidazole to trap the evolved HCl. Reaction was at room temperature for up to 16 h. Rinsing was with THF.	Goussé *et al.* 2004
Trimethylchlorosilane	Vapor phase	Newspaper	136	At 35 to 65% relative humidity in a vacuum desiccator, the cellulose was heated with the trimethylchlorosilane vapors at 70 °C for 4 h.	Jin *et al.* 2015
Trichloromethyl silane	Vapor phase	Bacterial cellulose membrane	108-135	After oxygen plasma treatment, the surface of bacterial cellulose was silanated at 95 °C and reduced pressure for 60 min. The excess was removed by vacuum.	Leal *et al.* 2020
Trichloromethyl silane	Vapor phase	Cotton fabric	157	At 50 °C, the cotton fabric in a sealed chamber is exposed to the vapors of the trichloromethylsilane for 1 to 5 minutes.	Li *et al.* 2007
Dichlorodiethyl silane	Acetone, acetic acid	Pine wood TMP fiber	-	The fiber was equilibrated with air to give a moisture content of 10%; then dried in air, then heated to 60 °C for 24 h.	Pickering *et al.* 2003
Perfluorodecyl trichlorosilane	Toluene	Cotton textile	142, 168	Perfluorodecyl trichlorosilane or stearic acid or their mixture were used to treat cotton textile.	Xue *et al.* 2008
Dichlorotetra methyldisiloxane	Vapor phase	Release liners	115	After oxygen plasma treatment of the release liners, the dichlorotetramethyldisiloxane was applied by vapor in a closed chamber for 5 min at room temperature.	Zhao *et al.* 2020

Table C. Siloxanes: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	Medium	Substrate	WCA	Details	Citation
Hexamethyldisiloxane	Plasma (air)	Wood	-	Atmospheric pressure plasma jet with hexamethyldisiloxane was used for thin layer deposition on the wood.	Avramidis *et al.* 2009
Cyclosilanes	Water emulsion	Aluminum	120, 160	Pickering emulsions were sprayed onto the surfaces.	Bayer *et al.* 2009
Hexamethyl disiloxane	Plasma (air)	Cellulose fibers	140	Hexamethyl disiloxane was applied by means of low-pressure plasma. Treatment durations were 15, 30, 45, 60, 75, and 90 min.	Cerny *et al.* 2021
Hexamethyl disiloxane	Plasma (air)	Poplar wood	127, 130	Hexamethyl disiloxane was applied by low-pressure plasma discharge. Treatment duration was 75 s.	Chen *et al.* 2017

Reagent	**Medium**	**Substrate**	**WCA**	**Details**	**Citation**
Hexamethyl disiloxane	Plasma (oxygen)	Polished silicon, PET	-	Silicon oxide films (SiO_x) were deposited onto Si surface. The resulting surface was not intended to be hydrophobic.	Creatore *et al.* 2001
Hexamethyl disiloxane	Plasma (oxygen)	Polished silicon	-	Silicon oxide films (SiO_x) were deposited onto Si surface. The resulting surface was not intended to be hydrophobic.	Creatore *et al.* 2002
Hexamethyl disiloxane	Plasma (oxygen)	Polyethylene tere-phthalate	-	Hexamethyl disiloxane was reacted with the PET surfaces with pulsed low-pressure plasmas.	Deilmann *et al.* 2008a
Hexamethyl disiloxane	Plasma	Polyethylene tere-phthalate	-	Hexamethyl disiloxane was reacted with the PET sufaces with pulsed low-pressure plasmas.	Deilmann *et al.* 2008b
Potassium methyl siliconate	Aqueous	Cotton or paper	157, 158	Potassium methyl siliconate aqueous solution was used to soak the cellulose with stirring at pH=12.5. Carbon dioxide was used to reduce the pH to 7.5 to 8.5. After 1 min or more, the soaked fabric was washed and dried at 120 °C for 30 min.	Li *et al.* 2008
Poly(dimethyl siloxane) iso-cyanate	Acetone	Paper w/ melamine	120 to 132	The melamine-coated paper was dipped into the acetone solution of poly(dimethyl siloxane) isocyanate. The coated paper was dried, then heated to 120 °C for 1 h.	Li & Rabnawaz 2018
Hexamethyl disiloxane	Plasma	Polyethylene tere-phthalate	46	Hexamethyl disiloxane was applied with cold atmospheric plasma. The plasma discharge duration was 5 min, which corresponds to 13 s of plasma contact with each part of the substrate.	Ma *et al.* 2021
Silane – siloxane mixture	Heptane	Filter paper	130-160	Water-coated paper samples were treated with 7% solutions of silane in heptane.	Rutter & Hutton-Prager 2018
Poly(methyl-hydrogen siloxane)	Hexane	CNC	120 to 141	The poly(methylhydrogen siloxane) was reacted with the cellulose nanocrystals in a hexane medium with a catalyst at room temperature for 10 minutes.	You *et al.* 2019
Polysiloxane sol	Aqueous	NFC	112-145	The polysiloxane sol was separately prepared in aqueous solution at a pH of 4, then combined with the nanocellulose and kept at room temperature for 2 h, then frozen and freeze-dried.	Zhang *et al.* 2014

Table D. Esters of Carboxylic Acids: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	Medium	Substrate	WCA	Details	Citation
Oleic acid	Pyridine,	Nano-fibrillated cellulose	56-80	Reaction carried out at 50 °C for either 1 or 4 h. Toluene sulfonyl chloride was used as an activator.	Almasi *et al.* 2015
Acetic, hexanoic and dodecanoic acids	Pyridine, toluene sulfonic acid	Bacterial cellulose	75-133° (for C_2-C_{12} BC)	Reaction carried out at 50 °C for 2 h.	Lee *et al.* 2011
Hexanoic acid	Pyridine	Bacterial cellulose	-	Never-dried and freeze-dried BC samples were examined, showing that freeze-drying BC before the reaction was found to promote esterification. Reaction was carried out at 50 °C for 2 h.	Lee & Bismarck. 2012
1'1-carbonyldi-imidazole (CDI) activated carboxylic acids	DMSO	CNC	-	Acid anhydrides, acid chlorides, acid catalyzed carboxylic acids, and CDI activated carboxylic acids were evaluated in surface esterification of CNC. Acid anhydrides and CDI were the most applicable reagents for grafting. Reaction with CDI was carried out at 60 °C overnight, with N_2 gas flow to remove evolved CO_2.	Peng *et al.* 2016
Fatty acids	Water	Undried cellulose powder	60-90°	Cellulose esters were prepared using two methods: the solvent exchange method (which resulted in no reaction) and the emulsion method. For the latter, after the mixture was dried, it was heated to 195 °C for up to 6 h.	Peydecastaing *et al.* 2006
Linoleic acid	Pyridine	CNC	-	Toluene sulfonic acid was used as the activator.	Uschanov *et al.* 2011
Polylactic acid with long-chain alkyl fatty acids	Ethanol	11.9 wt % never-dried CNC	-	Reaction carried out in two different routes, at 180 or 190 °C for about 30 minutes.	Yoo and Youngblood. 2016

Table E. Esters of Acid Chlorides: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	**Medium**	**Substrate**	**WCA**	**Details**	**Citation**
SOLVENTS					
Lauroyl chloride, stearoyl chloride, palmitoyl chloride	Pyridine	Cellulose nanofibers (CNF)	104.61-120.98°	The CNF film was presoaked in a solution at 110 °C, then after application of fatty acid chloride and left overnight at room temperature.	Balasubramaniam *et al.* 2020)
Oleoyl chloride	Pyridine and dichloromethane	Jute fibers	-	Reaction carried out at 20 °C for both solvents, at 40 °C and 60 °C for dichloromethane and pyridine, then dried under vacuum at 90 °C for 24 h.	Corrales *et al*. 2007
Trichloromethyl-silane (TCMS)	Sodium hydroxide (NaOH)	Cellulose Whatman filter paper (FP)	98-136° for all samples except FPh1 - 40-43°	Four samples were prepared: FP_1 (no prehumidification, 0.5 min reaction time, 10 µL TCMS), FP_2 (no prehumidification, 30 min, 600 µL TCMS), FPh_1 (prehumidification, 0.5 min, 10 µL TCMS), FPh2 (prehumidification, 30 min, 600 µL TCMS). For FPh1 sample, the minimal extent of chemical modification was negligible, and therefore, results were reminiscent of the untreated substrate.	Cunha *et al.* 2007c
Undecanoyl chloride	Triethyl amine	Nonwoven fabrics	1 min, unheated	Viscose polyester fabric with hydrophobized and then subsequently treated with UV and further reagents.	Dan *et al.* 2021
Methyl adipoyl chloride (MAC)	Toluene	Chitosan and cellulose nanocrystals (CH-c-CNCs)	-	Reaction was carried out at room temperature, stirring for 24h.	de Mesquita *et al.* 2012
Fatty acyl chlorides	Dry toluene, pyridine, DMF	Industrial bleached kraft pulp fibers	55.5-87.5° (toluene); 69.0-92.8°(DMF)	The reaction with toluene, pyridine was carried out at 115 °C for 30 min, 1, 2, 4, and 6 h. The reaction with DMF was carried out at 115 °C for 6 h.	Freire *et al.* 2006
Fatty acids of intermediate chain length (C_6-C_{12})	Toluene, pyridine	Thermo-mechanical pulp (TMP)	~80-87°	The reaction flask was heated to 110 °C and investigated at one, two, four, and six hours. At the end, samples were dried at 80 °C for five hours.	George *et al.* 2016

Reagent	Medium	Substrate	WCA	Details	Citation
Cetyltrimethylammonium chloride derived from palmityl alcohol (CTAC-PA)	NaOH	Nanofibrillated cellulose in oil palm empty fruit bunches (NFC-OPEFBs)	35–45° (1 min) & 15–35° (10 min)	Reaction was carried out at 60 °C for 3 h, then modified NFC-OPEFB (modNFC) was dried at 40 °C for 12 h. WCA results obtained by applying drops of distilled water.	Hastati *et al.* 2021
10-undecylenoyl chloride and ethylenediamine-tetraacetic acid	N,N-dimethylacetamide, pyridine	CNFs from unbleached eucalyptus pulp	101°	The reaction was carried out at 80 °C for 1 h.	Li *et al.* 2019a
Acetic anhydride	Pyridine, dichloro-methane	Microcrystalline cellulose (MCC)	-	The reaction was kept at room temperature for 48 h, and at the end acetylated cellulose microcrystals were oven dried in vacuum at 70 °C for 24 h.	Mukherjee *et al.* 2013
Dodecanoyl chloride	Toluene, pyridine	Cellulose fibers	-	The reaction was carried out under reflux during 4 h, then modified fibers were dried at 40 °C. Cellulose fibers from organosolv/supercritical carbon dioxide pulping of sugar cane bagasse.	Pasquini *et al.* 2008
Acid chloride	N,N-dimethylformamide (DMF)	CNC	-	Acid anhydrides, acid chlorides, acid catalyzed carboxylic acids, and CDI activated carboxylic acids were evaluated in surface esterification of CNC. Acid anhydrides and CDI were the most applicable reagents for grafting. Reaction was carried out at 50 °C. Triethylamine (TEA) was added to capture HCl.	Peng *et al.* 2016
Hexanoyl chloride	Ionic liquids (2)	Bacterial and vegetable cellulose	105-110°	The reaction was carried out at 80 °C for 24 h. Tetradecyltrihexylphosphonium bis(trifluoromethylsulfonyl)imide [TDTHP][NTf2], N-Hexyl-4-(dimethylamino)pyridinium bis(trifluoromethylsulfonyl)imide ([C6N(CH3)2py][NTf2])	Tomé *et al.* 2011a
Fatty acid derivatives (hexanoyl and dodecanoyl chlorides)	Pyridine	Cellophane (regenerated cellulose)	75.5-94.0°(CellC$_6$-CellC$_{12}$)	Reaction was carried out at 30 and 50 min at 80 °C, which were optimum conditions in order to prevent membrane degradation	Tomé *et al*. 2011b

Reagent	Medium	Substrate	WCA	Details	Citation
GAS PHASE					
Palmitoyl chloride	Gas-phase	Tunicin whiskers & $scCO_2$ bacterial cellulose microfibrils	-	The reactions for both substrates were carried out for: 2 h (190 °C), 4 h (160 °C, 170 °C, 180 °C), 6 h (170 °C), 13 h (170 °C).	Berlioz *et al.* 2009
Palmitoyl chloride	Gas-phase	Cotton linter CNC (dried cellulose aerogel)	-	Reactions for all samples were carried out for 2 or 6 h at 150 °C.	Fumagalli *et al*. 2013
Palmitoyl chloride	Gas-phase	Bleached eucalyptus pulp paper	117°	The reaction was carried out at 180 °C for a period of 2 h.	Wulz *et al.* 2021

Table F. Esters of Anhydrides: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	Medium	Substrate	WCA	Details	Citation
Acetic anhydride	Pyridine	Kenaf bast cellulose nanofibers (CNFs)	75° after 1 s, 41° after 30 s	The reaction was carried out at 100 °C for 4 h.	Ashori *et al*. 2014
Acetic anhydride	Toluene	Flax fibers	-	The reaction was carried out at 60 °C for 1 to 3 hours, using small amounts of perchloric acid as the catalyst.	Bledzki *et al.* 2008
Trifluoroacetic anhydride	Non-aqueous solvent (pyridine, NaOH); toluene	Eucalyptus bleached kraft pulp fibers; pure cellulose filter paper	119-126°	Reactions were carried out at three different temperatures (20, 50, and 80 °C) and for three times (1, 5, and 20 h). *Eucalyptus globulus* industrial ECF bleached (DEDED) kraft pulp fibers; pure cellulose filter paper	Cunha *et al.* 2006, 2007b
Acetic anhydride	Iodine	Bacterial cellulose nanofibrils	76.7 - 112.1°	Samples were dried for 2 h at 80 °C. Then, mixture was heated to 60, 70, 80, 90 and 100 °C and left for 15, 30, 60, 120 min at 80 °C. Finally, samples were vacuum-dried 60 °C for 12 h.	Hu *et al.* 2011
Acetic anhydride	Pyridine, glacial acetic acid	Raw kenaf bast fibers	113-115° after 10 s	Extracted fibers were oven-dried overnight at 100 °C. Then, reaction was carried out at 100 °C for 4 h. The acetylated fibers were oven-dried at 100 °C overnight.	Jonoobi *et al.* 2010
Acetic anhydride	Non-aqueous solvent (NaOH)	*Sesbania cannabina endosperm*	101-107°	Galactomannan solids and distilled water were stirred at 50 °C for 6 h. Then the mixture was left to process for 5 h, and then dried at 50 °C.	Liu *et al.* 2021b
Acid anhydrides	Non-aqueous solvent (pyridine)	CNC	-	Acid anhydrides, acid chlorides, acid catalyzed carboxylic acids, and CDI activated carboxylic acids were evaluated in surface esterification of CNC. Acid anhydrides and CDI were the most applicable reagents for grafting. CNC/pyridine suspension was bubbled with N_2 gas overnight at 80 °C.	Peng *et al.* 2016
Acetic anhydride, butyric anhydr., hexanoic anhydr. & 2 dodecen-1-yl-succinnic anhydride	Acetone	Cellulose nanofibrils (CNF) film (nanopaper)	31.8-118.5°	The reaction was carried out in an oven at 80 °C for 2 h. The total time required to prepare isolated nanofibers into treated nanopaper was 1 week. The WCA increase was relative to the length of alkyl chains.	Sehaqui *et al.* 2014

Reagent	Medium	Substrate	WCA	Details	Citation
Acetic anhydride, butyric anhydride, hexanoic anhydride	Ionic liquid	Bacterial and vegetable cellulose	80-105°	The reactions were conducted at 30 °C for 6 h (acetic anhydride), 4 days (butyric anhydride) and 11 days (hexanoic anhydride).	Tomé *et al.* 2011
Hexamethyl-disilazane (HMDS); acetic anhydride/trifluoroacetic anhydride	Gas-phase	Bleached eucalyptus pulp paper	60-112°(TFAA/Ac2O); 35-108 °(HMDS)	The reaction was carried out at 40 °C for 24 h for HMDS, and 5 min for the TFAA/Ac2O. WCA measurement significantly increased with function of settling time to exposure time.	Wultz *et al.* 2021
Acetic anhydride	Phos-phoric acid	Cotton	-	A mixture of polyphosphoric acid and 85% phosphoric acid was prepared and combined with cotton cellulose at 1-3 °C with kneading, followed by reaction at 30 or 40 °C for 1 to 3 h.	Yan *et al.* 2013
Trifluoroacetic anhydride (TFAA) and acetic acid (AcOH) or TFAA and acetic anhydride (Ac_2O)	Vapor-phase	Commercial filter paper, tunicate cellulose	98.4-98.6°	Cellulose sample was dried for 1 h at 105 °C, after which reagent gases were introduced. Afterwards, samples were dried at 110 °C under vacuum. When TFAA/Ac2O-treated filter paper was immersed in water and redried, WCA was decreased significantly to 7.3°. TFAA/AcOH-treated paper remained hydrophobic.	Yuan *et al.* 2005

Table G. Esters of Alkenylsuccinic Anhydride (ASA): Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	**Medium**	**Substrate**	**WCA**	**Details**	**Citation**
Octenyl succinic anhydride (OSA)	Water	Basil seed gum-based films	46.6-71.9°	OSA was first dissolved in ethanol, reaction was carried out at 40 °C for 90 minutes.	Gahruie *et al.* 2019
2-Dodecen-1-yl succinic anhydride	Distilled water	Nanocrystalline cellulose (NCC) - pellets & films	24.8-34.4°	The reaction was carried out at 145 °C for 1h and 3h.	Khoshkava & Kamal 2013
Succinic anhydride	DMF, pyridine	NFC with O-acetyl-galac-toglucomannan (GGM) composite films	55-78° (at 1s)	Dispersion was heated at 80 to 85 °C, after which ASA was added and dispersion was kept for 1.5 h. While all CA values decreased over time, it was solely dependent on evaporation of applied water drop, as the wetting area remained constant and did not increase. Nanofibrillated cellulose (NFC)-Norway spruce O-acetyl-galactoglucomannan (GGM) composite films	Kisonen *et al.* 2015
ASA	Water	Nanofibrillated cellulose (NFC), paper	40-85° (NFC), 110-135° (paper)	The final dispersions were mixed for 5 min and sonicated for 2 min.	Nypelö *et al*. 2011
ASA (Hexadecenylsuccinic anhydride)	N-Methyl-2-pyrrol-idon; Dimethyl aminopyridine	Softwood kraft pulp (NBKP) cellulose nanofibers (CNF)	~70-105°	Once NMP and CNF were mixed in a mixer, water was evaporated under reduced pressure at 20 to 60 °C, then ASA was added and stirred for 1 h at 70 to 80 °C.	Sato *et al.* 2016
ASA	Ionic liquid	Bacterial and vegetable cellulose	90-100 °	The reaction was carried out at 80 °C for 15 days.	Tomé *et al.* 2011
Dodecenyl succinic anhydride	Distilled water	Gum konda-gogu/Cellul. nanofibers (CNF)	64.06-66.5°	Gum kondagogu was modified with DDSA, which were then prepared into hydrophobically modified gum kondagogu/nanocellulose (HMGK) films with different amounts of CNF, repeatedly stirred, and finally dried at 60 °C for 12 h.	Venkateshaiah *et al.* 2021

Reagent	Medium	Substrate	WCA	Details	Citation
Iso-octadecenyl & n-tetradecenyl succinic anhydride	Water	Tunicate cellulose whiskers	-	Emulsified without any stabilizer, then used immediately	Yuan *et al.* 2006
Commercial alkenyl succinic acid anhydride (ASA)	Gas-phase (NaOH)	Regen-erated cellulose film	-	Reaction was carried out for a few minutes at 100 °C.	Zhang *et al.* 2007

Table H. Esters of Alkylketene Dimer (AKD): Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	Medium	Substrate	WCA	Details	Citation
AKD, heptane	Supercritical CO_2	Filter paper	118-124°	CO_2 was pressurized to predetermined pressures of 50, 100, 150, 200 and 250 bar in a circulating loop, at constant temperature of 21 °C for 10 min. Then, filter paper was added, and after 15 min, CO_2 was released into the fume hood.	Adenekan and Hutton-Prager 2019
Alkyl ketene dimer AKD	Non-polar liquid (DMAC)	TEMPO-oxidized cellulose gel (TOCgel)	115° at first (but drops to 50° within 90 s)	Nanofibers were pre-swelled in DMAC solvent, then preheated at 70 °C and stirred for 20 min; then the mixture was stirred at 70 °C for 3 h. The cellulose was from commercial never-dried bleached kraft wood pulp	Benkaddour *et al.* 2014
Two different kinds of AKD waxes	Non-polar liquid (heptane)	Filter paper	19.08-116.17°	Sheets were dipped in AKD-heptane solution, then left to dry for 24 h. Then, four samples were subjected to varying conditions for 5 min (oven-drying at 75 °C, oven-drying at 150 °C, rotary drying at 105 °C, unheated at 25 °C). CA increased with amount of AKD used in the treatment.	Bildik *et al.* 2016
AKD	Water	Cassava starch	-	Various pulp samples with varying AKD contents were prepared to manufacture biofoam. Substrate was heated under compression with AKD powder at 180 °C for five minutes.	Iriani *et al*. 2020
AKD	Water	Bleached softwood kraft and hardwood CTMP paper	124-139°	The sheets were immersed in the sizing agent/water dispersion for 5 seconds, and at the end cured in an oven at 80 °C for 120 min. The cellulosic pulp types were bleached softwood sulfate pulp (NBSK) sheets & bleached hardwood chemi-thermomechanical pulp (CTMP) sheets	Korpela 2021
AKD	Heptane	Glass cover slip samples	60.6° (cured)	The reaction was carried out at 105 °C for 20 minutes.	Shen *et al*. 2002
AKD	Vacuum-dried	Paper sheet	103-115°	Vacuum-dried an AKD-containing coating applied to a paper sheet at 23 °C and 50% relative humidity.	Tarres *et al.* 2018
AKD	Supercritical CO_2	Commercial testliner type liner paper	145-175°	AKD powder was dissolved in supercritical CO_2 at 65 °C and 300 bar, and then airblasted onto substrate.	Werner *et al.* 2010
AKD	Ethyl acetate	Microfibrillated cellulose	110-140°	After drying, the mixture was heated to 130 °C for 24 hours.	Yan *et al.* 2016

Reagent	Medium	Substrate	WCA	Details	Citation
AKD	Non-polar liquid (toluene)	NFC hydrogel	86-114°	The reactions were performed at various temperatures (70 to 125 °C).	Yuan & Wen 2018
Commercial alkyl ketene dimer (AKD) wax sample	Vapor-phase (NaOH)	Regenerated cellulose film	-	Reaction was carried out for a few minutes at 100 °C.	Zhang *et al.* 2007

Table I. Transesterification: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	Medium	Substrate	WCA	Details	Citation
Plant triglyceride fats (coconut oil, soybean oil, olive oil, rapeseed oil, stearic acid)	Ethanol, acetone	4 types of cotton cellulose	15-80°	Reaction carried out at heating in the range 110 to 120 °C. WCA: 26.2-40.3° (cotton a. + stearic acid, ethanol); 47.4-72.6° (cotton a. + oils, ethanol); 15-80° (cotton + oils, acetone); 39 °(cotton b. + oils). The four types of cotton were: a) commercially bleached cotton, b) laboratory scoured cotton, c) microcrystalline cellulose powder, and d) cellulosic filter paper	Dankovich & Hsieh 2007
Canola oil fatty acid methyl ester (CME)	MeOH	Cellulose nanocrystals (CNC)	62°	Reaction carried out at temperatures of 110 to 120 °C and the curing times were 4 to 30 h.	Wei *et al.* 2017
Vinyl laurate	Ionic liquid	Hemicelluloses	>100°	Treatment carried out in the range 60 to 100 °C.	Zhang *et al.* 2020

Table J. Enzymatic Esterification: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	Medium	Substrate	WCA	Details	Citation
Fluorophenols, lignin model compounds, *Trametes hirsuta* lacasse (ThL)	Molecular oxygen	Wood veneer	60-89.6°	The coupling of fluorophenols onto wood veneer was carried out at 37 °C while shaking at 150 rpm with incubation for 3 h.	Kudanga *et al.* 2010
Dodecylgallate (DOGA), *Trametes hirsuta* lacasse (ThL)	Laccase	Unbleached nanofibrillated cellulose (NFC)	42-70°	Samples were stabilized for 40 min in room temperature, then ThL was added (except for with DOGA).	Saastamoinen *et al.* 2012
Laurate alkyl chains, lipase	Tert-butanol	Spray-dried cellulose nanocrystals (CNC)	114°	Immobilized lipase was used to catalyze formation of laureate ester groups on the surface of CNC. The reaction was carried out at 30, 40, 50, 60 and 70 °C for 6, 12, 18, 24 and 30 h. At the end, CNC-LAA powders were oven dried at 60 °C over 24 h.	Yin *et al.* 2020

Table K. Amides: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	Medium	Substrate	WCA	Details	Citation
Stearamine	Aqueous	TEMPO-oxidized cellulose	70 to 145	TEMPO-oxidized native cellulose fibers were subjected to high shear. The reaction with stearamine was at pH 8 with stirring for 3 h at room temperature. The product was freeze-dried. The authors used FTIR results to argue for formation of amide links. Ionic association only.	Benkaddour *et al.* 2014
Decylamine	Aqueous	CNC with tannic acid	74	The CNC suspension in the presence of hydroxyethyl-piperazineethylene sulfonic acid (HEPES) was combined with decylamine and mixed for 3 h. The produce was freeze-dried, then oven dried at 80 °C.	Hu *et al.* 2017
Octadecylamine	DMF	TEMPO-oxidized cellulose nanocryst	108	Coupling was achieved with ethyldimethylaminopropyl carbodiimide (EDC) and N-hydroxysuccinimide (NHS), following by addition of the octadecylamine under aqueous conditions. The reaction was for 12 h at room temperature and pH from 7.5 to 8.	Johnson *et al.* 2011
Hexadecylamine	Aqueous w ethanol	TEMPO-oxidized NFC	103	The tannic acid was added to the NFC suspension, followed by addition of hexadecylamine in ethanol, which was stirred for 12 h.	Shrestha *et al.* 2019

Table L. Ethers: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	**Medium**	**Substrate**	**WCA**	**Details**	**Citation**
2-chloro-2-hydropypropyl stearate	Aqueous	Cotton fabrics	150	Stearic acid was reacted with epichlorohydrin to form 2-chloro-2-hydropypropyl stearate, which under highly alkaline conditions (NaOH) formed an either with cellulose.	Balan *et al.* 2014
Butylglycidyl ether	Aqueous NaOH	Arabino-xylan	-	A ring-opening oxidation of a dialdehyde with subsequent reduction of the aldehydes to alcohol (to increase the number of –OH groups), followed by the etherification in strong NaOH and butylglycidyl ether stirred overnight at 45 °C.	Borjesson *et al.* 2019
Triphenylmethyl chloride	*N,N*-di-methyl acetamide	Microcry-staline cellulose	138	Dried MCC was suspended in *N,N*-di-methyl acetamide with addition of LiCl to dissolve the cellulose. The pyridine and triphenylmethyl chloride were added with stirring at 70 °C for 48 h.	Pour *et al.* 2015
Epoxychloro-propane	Aqueous NaOH	Hemi-cellulose	42 to 72	In 9.5% NaOH solution, the hemicellulose solution was reacted with the epoxychloropropane at 78 °C for 1 h. The product was precipitated with ethanol at a pH of 5.5, followed by centrifugation, washing, and freeze-drying.	Shao *et al.* 2020

Table M. Urethanes: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	**Medium**	**Substrate**	**WCA**	**Details**	**Citation**
Blocked di-iso-cyanate	-	Paper	144	Paper composed of eucalyptus pulp fibers was dipped in the blocked di-isocyanate solution.	De Souza *et al.* 2020
Toluene di-isocyanate	Toluene	Nanocell. membrane	>150	A patterned surface was induced on nanocellulose membrane and boiled for 5 min, followed by dabbing and oven-drying for 10 min.	Liu *et al.* 2019
Long aliphatic isocyanates	Toluene	Nanofib-rillated cellulose	80 to 92	After solvent exchange from acetone to toluene, the nanofibrillated cellulose was reacted with the long-chain isocyanates in the presence of n-butyltindilaurate as a catalyst at 105 °C for 2 h.	Missoum *et al.* 2012
Isocyanate-term-inated castor oil	Toluene	Cotton linters	85 to 95	Cotton linters were reacted with modified castor oil, that had terminal isocyanate groups due to reaction with toluene-di-isocyanate. The final reaction was at 75 °C for 24 h.	Shang *et al.* 2013
Octadecyl isocyanate	Toluene; acetone	Nano-cellulose	70 to 107	Both cellulose nanocrystals (CNC) and nanofibrillated cellulose (NFC) were treated with n-octadecyl isocyanate. Final reaction 110 °C, 30 min.	Siqueira *et al.* 2010
Methylenediph-enyl diisocyanate	Acetone	Filter paper	137	In acetone medium the methylenediphenyl diisocyanate was reacted with the filter paper in the presence of triethylamine catalyst. The reaction was at room temperature for variable time, followed by freeze-drying.	Zhou *et al.* 2020

Table N. Acrylics: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	**Medium**	**Substrate**	**WCA**	**Details**	**Citation**
Methylmeth-acrylate	Water/ DMSO	Kraft lignin	88	The lignin was dissolved in the water/DMSO mixture, initiator was added, and then methylmethacrylate for selected temperatures and times.	Alipoormazandarani & Fatehi 2020
Poly(lauryl or octadecyl) acrylate	Dichloro-methane	Filter paper	125 to 146	The ATRP system was used for living polymer modification of cellulose fibers with poly(lauryl) or poly(octadecyl) acrylates, with ethyl-2-bromoistobutyrate as an initiator.	Areta *et al.* 2017
Ethylcyano-acrylate	Toluene	Filter paper	125	Filter paper cellulose sheets were dip-coated in solutions containing ethylcyano-acrylate	Ayadi *et al.* 2013
Ethylcyano-acrylate and wax	Acetone	Filter paper	130 to 160	Filter paper sheets were either solution-cast or dip-coated with the solutions of ethylcyano-acrylate in acetone, with addition wax emulsion and of initiator and curing at room temperature overnight.	Bayer *et al.* 2011
Fluorinated poly-ether acrylic	Acetone	Filter paper	120 to 140	The paper was placed in a solution of the fluorinated poly-ether acrylic monomer and photoinitiator in acetone for 90 s, followed by UV irradiation and drying, followed by solvent extraction washing or Soxhlet.	Bongiovanni *et al.* 2011
Methylmeth-acrylate	Ethanol & water	Cotton stalk bark fiber	-	The cotton stalk bark fiber was added dry to the ethanol/aqueous mixture with methylmethacrylate and initiator with stirring at room temperature for 1.5 h, followed by drying at 105 °C for 2 h.	Li *et al.* 2016
Fluorinated acrylates & methyl acrylate	Aqueous	Filter paper	139 to 145	The filter paper, methacrylate and fluorinated acrylate monomers were added to water, then combined with hydrogen peroxide and kept at 60 °C for 30 min, then 80 °C for 30 min. After water wash, the solids were dried under vacuum at 60 °C.	Liu *et al.* 2021a

Table O. Other Plasma (non-silane): Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	**Medium**	**Substrate**	**WCA**	**Details**	**Citation**
Poly(tetrafluoro-ethylene)	Pulsed laser depos.	Cotton	151	Thin films of poly(tetrafluoro-ethylene) were deposited onto cellulose fibers by pulsed laser deposition.	Daoud *et al.* 2006
CF_4	Glow discharge	Sunflower pith	80 to 120	The discharged power, gas flow, and exposure time were varied.	Follain *et al.* 2015
Octafluorocyclo-butane	Plasma polymeri-zation	Cellulose nitrate films	100 to 120	The films were treated on both sides, creating a sandwich that was hydrophilic in the middle and hydrophobic on the outside.	Kong *et al.* 1992
Fluorocarbon	Plasma	Paper sheets	144 to 162	The handsheets were first exposed to oxygen plasma, then to fluorocarbon deposition plasma. The combination created etching, leading to superhydrophobicity.	Mirvakili *et al.* 2013
CF_4	RF plasma	Paper	-	Power, time, and gas pressure were varied. As little as 1 minute has a large effect.	Sahin 2007
CF_4	RF plasma	Paper	147	Radio-frequency plasma treatment of paper with the CF_4 gave rise to superhydrophobicity.	Sahin *et al.* 2002
1,3-butadiene	Atmos. He glow plasma	Viscose rayon fabric	142	The ratio of He to the 1,3-butadiene was varied. The treated rayon fabric was durable to soap washing.	Samanta *et al.* 2012
CF_4	Dielectric barrier discharge	Nanofibr. cellulose films	92	CF_4 or its mixture with oxygen was subjected to dielectric barrier discharge to treat nanofibrillated cellulose (NFC) films. Hydrophobicity was achieved with the CF_4 treatment alone, excluding oxygen.	Siro *et al.* 2013
Butylacrylate & ethylhexyl acrylate	Atmos. cold plasma	Paper	125	The paper handsheets were soaked in solutions of monomer or mixtures of monomer, then plasma-treated, dried at room temperature for 4 h, extracted at 60 °C and vacuum dried for 12 h.	Song *et al.* 2013b
Ethylene, meth-ane, chlorotri-fluoroethylene, hexafluoroprop-ylene	Atmos. dielec. barrier discharge	Wood	139 to 145	A parallel-plate dielectric barrier discharge reactor was used to expose the wood surfaces.	Toriz *et al.* 2008
Fluorocarbon (Scotchguard)	Audio frequency plasma	Cotton fabric	137	Audio frequency plasma was used to treat cotton fabric with fluorocarbon (perfluorooctanesulfonamide).	Zhang *et al.* 2003

Table P. Click Chemistry: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	Medium	Substrate	WCA	Details	Citation
Trialkoxysilane & click chemistry	Toluene	Bacterial cellulose	76 to 103	A trialkoxysilane derivative was used as the first step, followed by a click reaction to attach different aryl compounds.	Krishnamurthy *et al.* 2020
Trialkoxysilane & click chemistry	Ethanol-water	Microfibr-illated cellulose	-	Thiol or ene-type groups were applied to the microfilbrillated cellulose film surfaces, followed by click chemistry to confer hydrophobicity.	Tingaut *et al.* 2011
Glycidyl methac-rylate and silane	Ionic liquid	Cellulose in solution	128	A combination of ATRP and click chemistry was used to functionalize filter paper.	Wu *et al.* 2021b

Table Q. Adsorbed Compounds: Molecular Hydrophobic Treatment Conditions, Details, and Water Contact Angles

Reagent	Medium	Substrate	WCA	Details	Citation
Block poly-styrene poly(N-methylvinyl pyri-dinium iodide)	Aqueous	Bleached birch kraft fibers	130	The bleached elemental-chlorine-free birch kraft pulp was exchanged to the sodium form then treated with the block (cationic) polymer surfactant.	Aarne *et al.* 2013
Stearamine	Aqueous	TEMPO-oxidized cellulose	90 to 140	TEMPO-oxided native cellulose fibers were subjected to high shear. The reaction with stearamine was at pH 8 with stirring for 3 h at room temperature. The product was freeze-dried. The authors used FTIR results to argue for formation of amide links. Amines were also present.	Benkaddour *et al.* 2014
Alkylammonium surfactant	Aqueous	Bleached SW kraft fibers	160	Montmorillonite clay served as an anchor for the cationic surfactant, and perhaps also contributed to the scale or roughness required for superhydrophobicity.	Chen & Yan 2012
Oxidized gallates	Aqueous	Paper	130	The oxidized gallates, when adsorbed from aqueous solution, were proposed to form disorganized layers. Heating at 150 °C for 30 minutes gave high hydrophobicity, which was attributed to alignment of the hydrophobic tails outwards from the surface.	Cusola *et al.* 2015
Palmitic acid with Zn and Al hyroxides	Aqueous	Bleached hardwood pulp fibers	140	Layered double zinc and aluminum hydroxides were used as the anchor for palmitate layers on the fibers, which were formed into handsheets.	Izadyar *et al.* 2020

Reagent	**Medium**	**Substrate**	**WCA**	**Details**	**Citation**
Octadecylamine	Aqueous	TEMPO-oxidized nano-celluloses	117	Remarkably, greater values of water contact angle were achieved in comparison with amidation, using the same main components.	Johnson *et al.* 2011
Dodecylgallate	Aqueous	Nanofib-rillated cellulose	50 to 70	Laccase was used to catalyze the polymerization of dodecylgallate, which increased the hydrophobicity of NFC when coated on paper.	Saastamoinen *et al.* 2012
Quaternary ammonium with alkyl, phenyl, Glycidyl, diallyl	Aqueous	TEMPO-oxidized CNC	71	The C18 alkyl quaternary ammonium compound was the most effective for modifying the cellulose nanocrystal (CNC) surfaces.	Salajkova *et al.* 2012
Quaternary alkyl ammonium carbonates	Aqueous	TEMPO-oxidized NFC	100	Transparent hydrophobic films were prepared from the mixtures of nanofibrillated cellulose (NFC) and quaternary alkylammonium carbonates, which were dried on Petri dishes at 40 °C.	Shimizu *et al.* 2014
Epoxypropyltri-methylammonium chloride	Aqueous	Cotton & carbon nanotubes	123 to 136	TEMPO-oxidized carbon nanotubes provided the main anchor for adsorption of the cationic surfactant on the cotton.	Soboyejo & Oki 2013
Cetyltrimethylammon-ium bromide (CTAB)	Aqueous	TEMPO-oxidized NFC	70 to 76	The nanofibrillated cellulose (NFC) was formed into films by papermaking and dried. The CTAB was applied from aqueous solution at 4X the critical micelle concentration.	Syverud *et al.* 2011
Cationic surfactant	Aqueous	TEMPO-oxidized NFC	103	Layered double hydroxides were used to pretreat the tempo-oxidized nanofibrillated cellulose (NFC) and serve as the anchor for adsorption.	Wu *et al.* 2019