

How to Make Cellulose Hate Water – “Change it, cover it, confuse it, or accept it as it is”

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In many of its current and potential applications, technologists treat the surface of cellulose to render it more hydrophobic. By use of a variety of hydrophobic sizing treatment strategies, the bulk cellulose phase becomes covered up with a layer having lower polarity and less inclination to interact with water. Often, the goal is to use a relatively low amount of additive to cover up or change just the surface of the cellulosic material, while still benefiting from the strength, recyclability, relatively low cost, and other favorable features of the bio-based material. But what often gets forgotten is that the hydrophilic nature of pure cellulose is not very high, and there are ways to manipulate such characteristics without reacting the material or covering it up. Sometimes reacting the cellulose with hydrophobic substituent groups appears to make it more water-loving. So, when thinking broadly of processing options for new applications, there are several contrasting approaches to consider.

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Why Cellulose Is Moderately Hydrophilic

The cellulose macromolecule has three hydrophilic –OH groups per anhydroglucose unit in its chains. But when cellulose forms a crystal, during the natural growth of plants, those –OH groups mainly become oriented in a planar manner. In addition, given the relatively high degree of crystallinity of natural cellulose, most of those groups become tied up in stable inter-chain and intra-chain bonding. Therefore, only a small proportion of the hydrophilic –OH groups remain available to interact with water.

The intermediate and changeable character of cellulosic material, with respect to wetting by water, is readily apparent in the behavior of cellulose-based sponges, as used in washing dishes in the sink. A damp sponge can be used effectively to wipe up wet spills. But a dry sponge is likely to feel stiff and, at least at first, it might have little ability to absorb aqueous liquids. Part of the difference is no-doubt related to the formation of inter-fiber hydrogen bonds in the course of drying of the sponge material. It appears that the numbers of those bonds, as well as their arrangement, are sufficient to enable the material to resist wetting, at least for several seconds.

“Confuse it” – How to Fool Pure Cellulose into Being Less Hydrophilic

In addition to the striking difference between a damp sponge and a dry sponge, it has been found that the wettability characteristics of cellulose can be markedly different depending on the details of regeneration of cellulose from different solvent systems. Yamane *et al.* (2006) attributed such differences to the orientation of different crystalline

faces of cellulose. In particular, they found that regeneration of a solution of cellulose initially in the ionic liquid N,N-dimethylacetamide/lithium chloride (DMAc/LiCl), by rinsing a spread film with acetone and then toluene, gave rise to an unusually hydrophobic film of pure cellulose. The researchers attributed these characteristics to the predominant outward orientation of a more hydrophobic crystalline face of cellulose towards the surface of the film.

“Change it” – How Bulk Cellulose Can Be Rendered Hydrophobic

Cellulose can be rendered hydrophobic by bulk chemical reactions, and there are certain applications for which such treatments may be preferred. For example, cellulose acetate and related esters have found usage as textile fibers, cigarette filters, and eyeglass frames, among other uses. However, to make such products, relatively high degrees of substitution are required, which is in contrast of a common goal of industrialists to use low amounts of treatment agents, especially when the agents are expensive. Zhou *et al.* (2016) showed evidence of more hydrophobic character with increasing acetylation.

Ehrnrooth *et al.* (1977) found something odd when they used low degrees of substitution in the treatment of cellulosic fibers. The water-retention value of the fibers went through a maximum at an acetyl content of about 4 or 5% when they were treated from a pyridine solvent system. The tensile strength and elastic modulus of paper made from the fibers went through similar maxima. Such results suggest that a relatively low proportion of substituent groups can disrupt the regularity of the macromolecules, thus decreasing the tendency of the cellulose to form tight crystalline or semi-crystalline structures.

“Cover it” – Hydrophobic Sizing Technologies

There are basically three categories of hydrophobic sizing that account for the major practices used within the paper industry. These can be called rosin sizing, reactive for “alkaline” sizing, and sizing with amphiphilic copolymers. All three approaches end up with a layer of hydrophobic molecular groups facing outwards from the cellulosic surface. The differences are related to how those groups become anchored and oriented.

There are two main ways in which rosin products are applied to paper, *i.e.* rosin soap sizing and rosin emulsion sizing (Hubbe 2007; Ehrhardt and Lecky 2020). Rosin soap sizing starts with saponified rosin dispersed in the fiber suspension. As in the case of a typical household soap, the rosin soap will be present as a sudsy mixture, with micelles of surface-active monomeric material. The anchoring mechanism typically involves the addition of papermaker’s alum (aluminum sulfate) or sometimes a related product such as polyaluminum chloride (PAC). The acidic nature of alum ideally causes the pH of the fiber furnish to be in a range of about 4 to 4.5, which favors the formation of aluminum abietate and related compounds. Particles of these compounds either form on the fiber surfaces or become precipitated onto them within a few seconds in an agitated pulp suspension. The essential steps of the hydrophobic sizing of the paper, including anchoring and orienting of the hydrophobic parts of the rosin, are thus already completed at the wet-end of the paper machine.

Rosin also can be applied as a protonated “free acid” in emulsified form, *i.e.* rosin emulsion sizing. The protonated form of rosin is insoluble in water, so it needs to be heated above its melting point and then agitated in an aqueous solution that contains a suitable stabilizer. Cationic polymers, *e.g.* polyamidoamine-epichlorohydrin or cationic starch,

adsorb onto the emulsion droplets as they are being formed. The droplets are thus prevented from immediately sticking together again and coalescing into larger droplets or agglomerates of rosin particles. The cationic polymer coating the rosin particles allows them to be retained efficiently onto the negatively charged surfaces of typical papermaking fibers. The spreading of the rosin at a molecular level over the fibers surfaces does not take place until the paper is being dried and the temperature once again exceeds the melting point of the rosin. A dehydration reaction allows the rosin to associate itself to alum byproducts already present at the fiber surfaces. Depending on how efficiently the rosin molecules spread during drying of the paper, rosin emulsion sizing has the potential of requiring less rosin material to impart water resistance to the paper, compared to rosin soap sizing, for which the deposited rosin can have the form of nano-sized or larger particles.

When papermakers are adding calcium carbonate as a filler, they no longer have the option of employing acidic pH conditions, which would be needed for the effective usage of alum and related products. For it to be effective in the setting of rosin size products, the alum needs to be either in the form of trivalent aluminum (especially for soap size) or in the form of oligomers, which are very effective coagulants (Strazdins 1984). However, when the pH is about 7 or higher, the alum will have been converted mainly to neutral $\text{Al}(\text{OH})_3$ and related species.

The major alkaline size products being used are alkenylsuccinic anhydride (ASA) and alkylketene dimer (AKD) (Dumas 1981; Ehrhardt and Lecky 2020). As in the case of rosin emulsion products, these sizing chemicals are formulated by dispersing the droplets in aqueous media that contains a suitable stabilizer, such as cationic starch. The particles of sizing agent are later retained at fiber surfaces by a charge mechanism, and the spreading at a molecular level does not take place until the paper is being dried. Evidence suggests that the spreading of the sizing agent mainly does not take place until after the bonded areas between fibers already have become established (Hubbe 2014; Korpela *et al.* 2021). Because of the efficient coverage of the fiber surfaces, usually involving a monolayer or less, covering mainly the non-bonded areas, these ASA and AKD systems require relatively low dosages to achieve the needed hydrophobicity.

Papermakers have yet another option, which might be useful for various specialty products or when higher and more permanent levels of water resistance are needed. That is, hydrophobic agents can be added at a size press. In fact, AKD can be added at a size press too, but such a strategy can lead to slippery paper, especially at high levels of treatment. Agents such as styrene maleic anhydride (SMA) or styrene acrylate can be formulated so that they can be dispersed in aqueous media and added to starch solutions that will be applied at a size press (Bildik Dal and Hubbe 2021). As the starch films are being dried, it appears that the hydrophobic copolymers migrate to the surface and become oriented with hydrophobic groups facing outwards from the paper.

Summing Up

Papermakers have multiple tools by which to render the paper surfaces more hydrophobic, and these tools allow them to achieve product goals over a wide range of conditions, including acidic or alkaline pH during papermaking. But there are additional strategies that often escape attention. These may involve orientation of the cellulose molecules themselves, the tying up of $-\text{OH}$ groups with inter-fiber hydrogen bonding, and the bulk chemical conversion of cellulose to cellulose acetate or other compounds.

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