

Puzzling Aspects of the Hydrophobic Sizing of Paper and its Inter-Fiber Bonding Ability

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Internal sizing agents make it possible to prepare water-resistant paper from an aqueous suspension comprising water-loving fibers and an emulsified hydrophobic agent. Why doesn't the hydrophobic treatment get in the way of inter-fiber bonding? The answer appears to involve the order in which nano-scale events happen during the manufacture of paper. It appears that the inter-fiber bonded areas develop first. Molecular distribution of the hydrophobic agents appears to happen later, especially during the later stages of evaporative drying. The topic seems to be crying out for someone to carry out appropriate experiments to shed more light on the mechanism.

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Are we just lucky, or what?

It seems that papermakers are just plain lucky. Otherwise, how can one explain why it is possible to internally size paper – making it resistant to penetration by aqueous liquids – while at the same time avoiding any serious deterioration in inter-fiber bonding? Since sizing agents such as alkenylsuccinic anhydride (ASA) and alkylketene dimer (AKD) (and to some extent emulsified rosin products as well) coat the fiber surfaces with a molecularly-thin layer of hydrophobization, one might expect that such treatments would have a very negative effect on the ability of the fibers to form hydrogen bonds with each other. And yet one almost never hears complaints suggesting that internal sizing treatments seriously get in the way of development of paper strength. Furthermore, there does not seem to be any serious concern when such hydrophobized paper is recycled. Indeed, it is possible to redisperse sized paper and then use the recovered fibers to prepare quite satisfactory recycled paper sheets – with hardly any evidence being suggested about a penalty in bonding ability stemming from the hydrophobic nature of the size-treated fibers.

Various hypotheses come to mind:

- Papermaking technologists are just very lucky.
- Papermaking technologists are very persistent – trying lots and lots of different approaches until they stumble onto a combination that achieves their objectives without causing other problems.
- Papermaking technologists fully understand what they are doing and always have.
- Maybe such a penalty of reduced paper strength could be quantified, if someone actually took the time to carry out a careful study.

If We Understood What We Were Doing

Suppose we were to start from scratch and design a chemical system to make paper hydrophobic without interfering with the inter-fiber bonding. It would make sense to form the inter-fiber bonds first, and then, as a second step, to coat the remaining surfaces of the paper with a water-repellent layer. For instance, after forming the sheet, one could apply hydrophobic agents at a size press, or maybe even by vapor deposition. But that's not what most papermakers actually do. Hydrophobic sizing agents such as ASA, AKD, and rosin products are almost always added to the furnish – the aqueous suspension of fibers and other materials that will be formed into a sheet and dried on the paper machine. And somehow this approach works. The hydrophobic material does not seem to block the intended hydrogen bonding between the fibers.

Let's consider what happens, on a molecular level, during internal sizing of paper. The sizing agents ASA, AKD, and the dispersed forms of rosin size are distributed in the paper furnish as tiny droplets or particles having dimensions in the neighborhood of 1 μm . Because the molecules have long hydrophobic tails, they have very low vapor pressures until they are strongly heated. So it is reasonable to expect that vaporization of the particles will not cause their redistribution until the paper gets quite hot – especially towards the end of the drying process. Another likely mechanism of distribution of sizing agents over the solid surface of paper is surface diffusion. It is reasonable to expect that such two-dimensional spreading of thin films of sizing agent over the fiber surfaces will be suppressed as long as there is a film of water present covering those surfaces. So again, one expects most of the distribution to take place during the later stages of drying of the paper.

But when do the bonded areas within a paper sheet become established? The wet-pressing operation is clearly very important with respect to the formation of inter-fiber bonds in paper. In a conventional wet-pressing operation a damp sheet of paper is subjected to huge pressures, often over 10 MPa. The adjacent fibers are literally crushed together. Upon exiting from the press nip, the adjacent fibers are prevented from coming apart due to the action of capillary forces. Such capillary forces, per unit area, can be estimated by the equation $\Delta P = 4 \gamma / x$, where γ is the interfacial tension and x is the distance between the surfaces. The equation predicts that the forces drawing the adjacent surfaces together will become stronger as the surfaces become closer together – either as a result of wet-pressing or as a further consequence of the evaporation of water. Perhaps the adjacent fibers are drawn together into molecular contact fairly early in the process of pressing and drying the sheet. This could explain why sizing agents do not appear to spread out and coat the surfaces within the areas of contact between adjacent fibers.

But what about the recycling of paper? Wouldn't those hydrophobized parts of the fibers get in the way of their bonding in subsequent cycles of papermaking? Again, it does not appear that enough research has been carried out to provide a full explanation. A partial explanation can be based on the fact that a substantial proportion of the cellulosic surfaces will have been within the bonded areas – and thus sheltered from being covered with hydrophobic material. And it is likely that further refining of the fibers, in the course of recycling, will have tended to expose additional surface area that is not covered by material resistant to hydrogen bonding.

Yes, it seems that paper technologists are lucky. Not only do chemical and physical phenomena often work in our favor, but also we can have fun trying to figure out what is happening at a mechanistic level.