

Hydrogen bonding between paper fibers: What do we learn from solvent exchange?

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Abstract

In this paper a discussion of the importance of hydrogen bonds in the bonding mechanism between paper fibers is presented. Based on a recent publication [1] it is shown that the interpretation of results obtained by solvent exchange during paper making has to be analyzed with great care. The results published in [1] are discussed in the light of both established and current data available in the literature. It is shown that the decrease in sheet strength is due to a reduction in the area in molecular contact and a decrease in sheet density and not due to a reduction in hydrogen bonding energy.

Keywords: Hydrogen bonds, Solvent exchange, Paper strength, Bonding Mechanism

Introduction

We would like to comment on a recent paper by Przybysz et al. [1] reporting that the strength properties of paper are progressively deteriorating when it is formed with increasingly apolar liquids (methanol, ethanol, n-propanol and n-butanol) instead of water. The authors conclude that the reduction in paper strength is due to a decrease in the energy of hydrogen bonds between the fibers due to the decreasing polarity of the solvents and claim that their results reflect the prevalent importance of hydrogen bonding for the adhesion of pulp fibers in paper. We would like to point out that their empirical findings are not novel and that the conclusions of the authors drawn from their findings are incorrect.

Discussion

Exchanging the solvent in paper sheet formation from water to less polar solvents is a well-known method to reduce bonding between pulp fibers. It has been used to make so called unbonded sheets for decades [e.g. 2 - 4]. Therefore, the fact that solvent exchange leads to a decrease in paper strength, even to zero paper strength in the case of a fully apolar solvent (benzene) [2 - 4] has long been known in the paper community.

The authors in [1] conclude that the decreasing dipole moment of the solvent leads to a decrease in the energy of hydrogen bonds between fibers. This interpretation follows the classic, yet outdated, belief that fiber-fiber adhesion is caused by hydrogen bonding. Przybysz et al. here entirely ignore current knowledge on bond formation and bonding mechanisms in paper. The mechanisms driving adhesion in paper fibers are not only hydrogen bonding but also Van der Waals bonding, Coulomb bonding, mechanical interlocking, interdiffusion, and the area in molecular contact between two bonded paper fibers [5, 6]. Recently, it was shown that the extremely low surface hardness of swollen pulp fibers is creating a large contact area on the molecular scale, which facilitates the strong adhesion between the fibers [7, 8]. The influence of both, relative humidity and submersion in water on the surface hardness of pulp fibers was demonstrated in [9]. The fact that different solvents influence both surface hardness and bond strength was clearly shown in [10]. The strong dependence of fiber bond strength on the surface hardness of regenerated fibers was shown in [11]. In addition, all these recently published findings were put together in the first quantitative bonding mechanism of pulp fiber bonds in paper [6], where DFT calculations for cellulosic surfaces show, that the major part of the bonding energy in fact descends from Van der Waals bonding between the surfaces.

If it is not the hydrogen bonds, what is causing the reduction in paper strength due to solvent exchange? The answer is the reduced swelling of the fibers and reduced sheet density. A correlation between swelling and sheet strength is well known in paper science [12, 13]. Fully swollen pulp fibers have a very soft surface that resembles a hydrogel-like structure [14] which enables adhesion. Exchanging the solvent leads to a massive reduction in fiber swelling as it is demonstrated in Table 2 of [1], which documents a reduction in swelling by 51% indicated by a drop in water retention value WRV from 201.45% to 99.90% [1]. Indeed, the data of Przybysz et al. [1] perfectly reflects the well-known relation between fiber swelling (WRV) and paper strength (breaking length, tear resistance), compare Figure 1, which has also been reported for

mechanical and chemical modifications of pulp like refining [15] or the exchange of counter ions on the fibers [12].

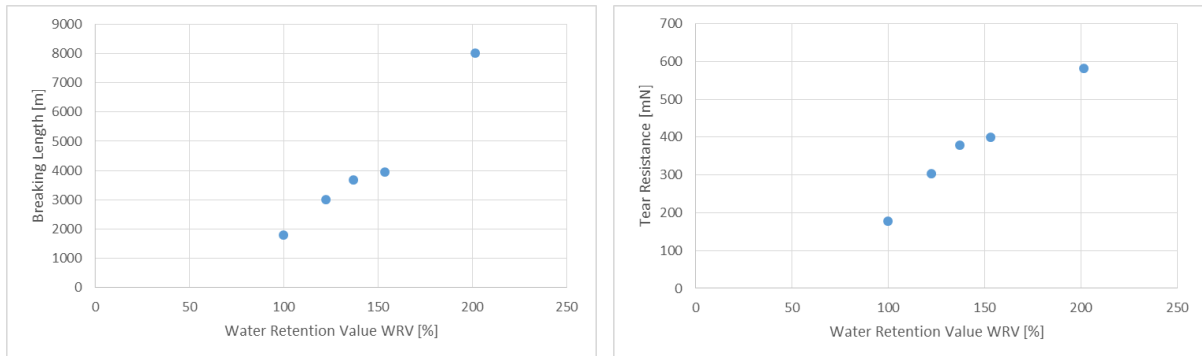


Figure 1: The relation between fiber swelling (WRV) and breaking length (left) and tear resistance (right), respectively. Data taken from [1].

Also the relation between sheet density and strength properties has been well known for a long time [16]. The solvent exchange from water to more apolar liquids leads to stiffer fibers (less swelling) and also lower capillary forces between the fibers and the solvent which reduces the sheet bulk. This is demonstrated in Table 2 of the paper by P. Przybysz et al. which documents a decrease in bulk by 13% from 0.6653 g/cm^3 to 0.57798 g/cm^3 [1]. Considering the textbook data for the effect of density on paper strength [17] only this decrease in density should already lead to a drop in breaking length of about 1500 m.

Conclusions

So, in conclusion, we find that the decrease in sheet strength found by exchanging the solvent for sheet forming to increasingly apolar liquids does not reflect the relevance of hydrogen bonding between pulp fibers. Instead it descends from a reduction in molecular contact area due to reduced fiber swelling and a decreased sheet density.

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