Nanocellulose Addition to Paper and the 'Cai Lun Principle' – Maybe Not Such a Good Idea After All

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Family groups in the ancient cultures of China, Korea, and Japan have toiled for generations in an effort to out-compete their neighbors in the pursuit of handmade paper products having better strength performance, in addition to flatness, uniform appearance, and other desirable attributes. Study of the history of the papermaking craft reveals a remarkable ability of ancient peoples to discover advantageous ways to prepare the cellulosic pulp, to improve its brightness, and to form uniform and strong paper sheets. But though the ancients knew how to "beat" the pulp to improve its bonding ability, there is no evidence of any of them having attempted to greatly "over-beat" some of the fiber, thus making nanocellulose, for potential addition to the fiber mixture. Why not? In this editorial, it is proposed that the ancients may have discovered that adding very highly fibrillated cellulose material to paper was not a good idea.

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A Cottage Industry and the Evolution of Papermaking

The craft of papermaking appears to have originated as a cottage industry somewhat more than two centuries ago in China. The invention of papermaking often has been attributed to Cai Lun, an official in the Han dynasty, who was first (in the year 105) to record improvements in the nascent technology. While its endorsement by the emperor certainly would have bolstered the status of the craft, archeological finds along the Great Wall of China have revealed that paper already had been in use as a writing medium long before the time of Cai Lun (Hunter 1947).

Think about how a cottage industry works: Let's suppose that then Chen family has a business of making paper – maybe as a seasonal money-making scheme. They are competing against some other families up or down their valley, and also some families working in other valleys – always in places where they have a source of fresh water, with which to prepare the pulp. Over the years, from time to time, they scheme about ways in which they might make a product that exceeds the quality of what their neighbors are making. An obvious thing to try would be to tell one of your sons or daughters working in the shop to attempt a very high level of beating of the pulp material. One can imagine the head of the operation saying to members of the clan: "We know that the beating of pulp increases the bonding strength within the paper sheet. So let's overtake the quality of the Zhang family down the valley by beating some of our pulp ten times as much as they do." The result, beyond the sore muscles of the unfortunate family or clan members faced with that assignment, was undoubtedly a pulp material that drained exceedingly slowing, stuck to the forming screen, and which made dense, brittle, and cockled sheets that were clearly less attractive than the paper the Zhang family was selling in the marketplace each year.

Confirmation Bias

The term confirmation bias refers to a tendency of people to pay excessive attention to evidence that agrees with what they already think (Mynatt *et al.* 1977). For example, for many years researchers assumed that tropical forests would show greater susceptibility to insect herbivores; however, such effects are not reported in studies where the researchers were unaware of the tropical *vs.* non-tropical origins of data (Kozlov *et al.* 2015).

Nanocellulose has achieved the status as a "hot topic" (Mahmood *et al.* 2024). Already in 2024 there have been 87 review articles published on this topic in journals included in the Web of Science database. There even have been review articles about using nanocellulose, a material that is notoriously expensive to produce and difficult to filter and dewater, for the treatment of polluted water (Sahari *et al.* 2023; Abelhamid 2024; Nordin *et al.* 2024; Othman *et al.* 2024), for which better and cheaper technologies already exist.

Suppose that you are a newly hired assistant professor, and you hear about "nanocellulose" as a topic that has been receiving a lot of attention, including opportunities to compete for funding. You write a successful research proposal in which you include a bunch of highly optimistic terms, such as "game-changing" and "superior properties". Likewise, when you rush to submit your first research article, featuring the results or experiments carried out by a student or students under your supervision, you use words such as "successful" and "best". Now, multiply the effects of that publication by the hundreds of articles with similar themes being published each month all over the world. Trust me, you will have to look very hard in the literature to find an article describing anything to do with nanocellulose as "disappointing" or "unfavorable". To the extent that some of your results were disappointing, you probably would not publish those items.

Inherent Problems with Nanocellulose Usage in Papermaking

It is well known that the inclusion of highly fibrillated cellulosic material in the suspension used to prepare paper will have a large negative effect on the rate of water release, making it necessary to slow down the production rate (Taipale *et al.* 2010; He *et al.* 2017). An attempt was made in the author's laboratory to overcome the poor drainage rates resulting from the addition of nanocellulose to the furnish (Leib *et al.* 2022). In that work, nanofibrillated cellulose was first treated with cationic starch; then, after addition of the treated nanocellulose to the fiber suspension, cationic acrylamide copolymer and colloidal silica were added in an effort to overcome the adverse effect on dewatering. The good news was that high rates of dewatering were restored by the colloidal silica treatment, in combination with the other additives. The bad news was that the treatment also eliminated any significant beneficial effect of the nanocellulose on paper strength, which was the main point of adding it in the first place. It had been proposed at the time that the situation might be overcome by applying higher levels of hydrodynamic shear, as would be expected in modern paper machine systems (Barrios *et al.* 2023). More recent work, involving application of a very wide range of hydrodynamic shear in the laboratory, has failed to confirm that optimistic statement. Rather, it has been shown that the treatment of the nanocellulose can lead to a hard-to-reverse "balling up" of the nanocellulose (Jones *et al.* 2023). This mechanism can explain why the nanocellulose can lose its ability to increase inter-fiber bonding within paper following the implementation of chemical strategies to increase the dewatering rate.

Dimensional stability is a critical aspect of the performance of typical grades of paper. It has been shown that adding highly fibrillated cellulose during papermaking makes the sheet more susceptible to dimensional changes when the relative humidity is changed (Manninen *et al.* 2011). Such effects can be expected to become severe in cases where the retention of small-size cellulosic material has a biased distribution in the thickness direction of paper. As shown by Tanaka *et al.* (1982) and by Zeilinger and Klein (1995), such non-uniform distributions of fine matter can result from filtering effects during sheet formation on certain kinds of paper machines. A particular challenge in the case of nanocellulose is the fact that the particles are too small to "stay in place" as the sheet is being dewatered. Rather, the flow of water being sucked and squeezed from the paper due to the actions of hydrofoils, forming blades, suction boxes, and wet-press nips can be expected to force much of the nanocellulose towards one side of the paper. Such effects may result in strong curling tendencies when the paper is subjected to changes in relative humidity.

In addition to the difficulty in removing water from nanocellulose suspensions, they also can contribute to a high viscosity (Hubbe *et al.* 2017). The effect is consistent with the very high ratio of length to thickness of the highly fibrillated material. Such effects become important when considering some other potential applications of nanocellulose in papermaking. For instance, it would make logical sense to add some nanocellulose to the size press starch formulation, with the goal of increasing the Young's modulus of the resulting starch film and thereby increasing the paper's stiffness. The problem with that way of thinking is that size press starch application technologies already depend on measures to decrease the viscosity of starch formulations (Hubbe 2024). Adding nanocellulose to such formulations would only add to the problem.

Ancient Wisdom

Back when the hypothetical Chen family of papermakers were attempting to out-compete their neighbors, the Zhang family, they learned that excessively over-refining (or "beating") some or all of the cellulose pulp was a bad idea. It made the sheets very slow to drain. Moreover, the "soupy" nature of the wet paper made it too weak to remove from the forming screen. They were never sure whether their highly fibrillated pulp was being retained in the paper, or whether a lot of it just passed through the wet sheet and got drained with the water leaving the sheet. When they dried the sheets in the sun, the paper with the highly fibrillated fibers tended to curl aggressively. "Maybe this wasn't such a good idea after all," they might have said to themselves. Indeed, the strategy of adding nanocellulose has not yet been widely adopted for conventional papermaking. As laid out in this editorial, hundreds of years of intense competition within a cottage industry failed to find an advantage of massively over-refining a portion of the papermaking pulp before making the paper. Therefore, maybe it should be no surprise that modern industrial papermakers are not adopting that strategy either. We don't know the names of the actual inventors of papermaking in China, so let's just call this phenomenon the 'Cai Lun principle'. It is wise to rely on many years of experimentation when considering "new" papermaking strategies.

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