

The Sometimes Antisocial Nature of Nanofibrillated Cellulose and Some Other Papermaking Fiber Surfaces

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The word “antisocial” appears to well describe some aspects that have been observed when nanofibrillated cellulose (NFC) has been added to papermaking fiber suspensions, in combination with some chemical additives that are commonly used in that process. The analogies of folded hands or a clenched fist can be used to convey a hypothesis of an inability of certain cellulosic fibrils to become engaged in a microscopic three-dimensional structure, which appears to be essential for the development of paper strength. Though this editorial points to some important drawbacks of NFC as an additive for conventional papermaking, it also sheds more light on the wisdom of conventional pulp refining technology. One can envision refining partly as a way to activate cellulosic nanofibrils at the fiber surfaces such that they are ready to intertwine with each other efficiently at a nano scale during the formation of the sheet. In this way they can achieve a favorable combination of dewatering rate, efficient of retention of the fibrillated matter, and notable increases in strength properties.

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Open Hand vs. Crossed Arms or a Clenched Fist

Suppose that you walk into a room occupied by some people whom you have not yet met. Someone near to the door extends a hand, with fingers slightly spread. A feeling of welcome washes over you. Now, suppose instead that as you looked into the room, your host had stood with crossed arms? How would that make you feel?

This editorial follows up on some points that were introduced, but not fully considered, in an earlier editorial titled “Nanocellulose addition to paper and the ‘Cai Lun principle’ – Maybe not such a good idea after all” (*BioResources* 20(1), 21-24). Since the release of that editorial, some pertinent articles have been published. In particular, an article in *TAPPI Journal* by Kozel *et al.* (2025) documented the failure of cationic starch-treated nanofibrillated cellulose (NFC) to increase the strength of recycled copy paper in a system that also included the usage of cationic polyacrylamide (cPAM) retention aid and colloidal silica. Surprisingly, the strength of the paper was not improved by the NFC addition, even with the imposition of high levels of hydrodynamic shear just before sheet forming. The high level of agitation not only made the sheets more uniform, but it also decreased the content of mineral filler. Both of those effects ordinarily would be expected to result in paper with a higher mechanical strength – but no such effect was observed.

In a “coffee break” webinar that I shared with members of the TAPPI Nano Student Committee (June 12, 2025), I introduced the term “antisocial” to characterize this

behavior of the nanocellulose in our recent experiments. I told the audience that the effect is analogous to what happened routinely in traditional hand-made paper manufacturing shops in Europe before the emergence of mechanized paper machines. As explained in a review article of traditional papermaking (Hubbe and Bowden 2009), as each fresh sheet was removed from the forming screen, by means of pressing against a felt, it was then placed on a “post” of similarly damp sheets. Later, after having accumulated dozens of such sheets, the whole post was placed in a screw press, which was tightened to compress the paper. The pressing not only caused a lot of the water to be expelled, but it also increased the apparent density of the paper sheets. The next step, in many papermaking shops, involved peeling groups of about ten sheets each and carrying them up to the attic to dry while draped over ropes. After drying, the papermakers were able to peel the sheets apart.

So here’s the question: How did the fibers on the surface of one paper sheet “know” that they were part of that sheet and not the adjacent one, that had been pressed and dried in contact with it? How did the sheets ‘know’ that they were sheets of paper, rather than just a big block of paper material that had been dried in contact with each other after the pressing?

McKenzie (1984) proposed that one of the requirements for establishing effective strength within a paper structure is something called “diffusion-controlled adhesion”. The idea is that the polymer-sized cellulosic fibrils at the fiber surfaces need to be able to intertwine with each other in a three-dimensional manner, and that this would happen as a result of a diffusion process happening over nanometer distances. If one draws the analogy to an open hand of welcome, one can envision the fibrils achieving interdigitation with each other, as when one folds one’s hand together in that way. But hands individually folded as fists are unable to do that. Figure 1 contrasts these different conceptual models involving people’s hands.

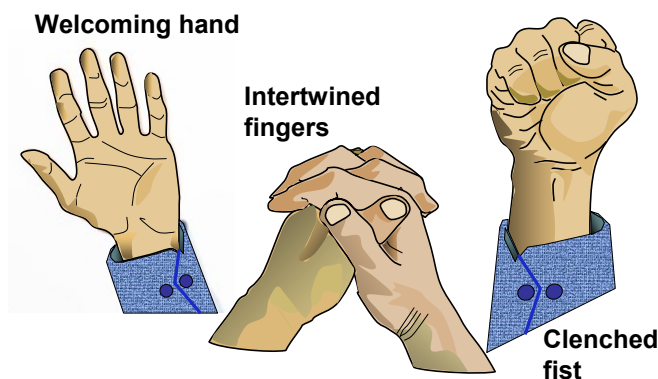


Fig. 1. Three ways of arranging fingers, with different implications regarding involvement

In the case of the cationic starch-treated nanocellulose, clues to the explanation were provided by Jones *et al.* (2024), who showed optical micrographs of clustered NFC particles. NFC clustering was also found by Atree *et al.* (2025) in cases where the cationic starch-treated NFC had been added to papermaking furnish and then treated sequentially by cPAM and colloidal silica. In none of these cases was application of intense hydrodynamic shear (in a mini-blender or in a WEPS sheet-forming device) able to fully redisperse the clusters. To continue the analogy of the hands, it is as if the interaction of the NFC with the chemical additives somehow converted them from being

like welcoming hands to being more like fists, or maybe like a set of bent elbows, as presented by a set of crossed arms. Thus, it is proposed that the chemical treatments caused the NFC to “know” that it is part of a cluster and not free to become fully engaged with the project of building strength in the paper sheet that includes the NFC clusters. These findings prompt some questions, as follows:

Can “Clenched” NFCs Be Opened into Engageable Fibrils?

The answer to this question appears to be “no.” Even with the imposition of high levels of hydrodynamic shear, such as in a blender, not all of the clustering could be reversed, even in systems where the NFC was treated only with cationic starch (Jones *et al.* 2024). Pre-shearing of the cationic starch-pretreated NFC in a blender did not yield any benefit with respect to the paper’s tensile strength (Hamm *et al.* 2024). As already mentioned, the same disappointing effects, with respect to strength, were shown in systems treated also with cationic retention aid and colloidal silica (Kozel *et al.* 2025). The general finding is that even hydrodynamic shear levels higher than what is experienced by fibers in high-speed paper machine systems did not restore treated NFC such that it was effective in the generation of bonding within the paper.

Can the “Clenching” of NFCs Be Avoided?

In principle, chemical-induced clustering of NFC might be avoided by not using any coagulants or flocculants. In that case, several problems can be expected:

1. In the absence of a retention aid, much of the nanocellulose will fail to be retained in the paper. Because nanocellulose is very small and has the same composition as the fibers themselves, it can be challenging even to keep track of how much is retained and how much is continually running around for multiple passes through the paper machine system.
2. In the absence of retention aid, the filtration mechanism can be expected to have a dominant effect on nanocellulose retention. An expected consequence is that the NFC will be unequally distributed across the thickness direction of the sheet (Tanaka *et al.* 1982), which is expected to result in curl problems, especially when the paper is subsequently exposed to different relative humidity conditions (Anderson 1991).
3. It is well known that NFC, by itself, has a markedly negative effect on the rate of drainage of paper from the paper during its formation. It has been shown that the drainage problem can be dramatically overcome by the use of a sequential combination of cPAM colloidal silica, at least in the case that the NFC has previously been treated with cationic starch (Leib *et al.* 2022; Kozel *et al.* 2025).

Cai Lun to the Rescue!

As was suggested in an earlier editorial (Hubbe 2025), the first papermakers, working in family units more than 2000 years ago in China, likely tried many alternative procedures. They were continually trying to make their paper sheets stronger than those of their neighbors, further down or up the stream. Though their systems of “beating” the pulp fibers were laborious and crude relative to a modern double-disk refiner, the results were much the same. If one had been able to have look through a microscopy (a much later invention), then one might have noticed “microfibrils,” *i.e.* something like nanocellulose, except that it was mainly still conveniently attached to the fibers. The

efficiency of retaining such fibrils, since they are attached to the fibers, is 100%. Because those fibrils are unable to move away from the fibers and into positions where they would block drainage channels (Cole *et al.* 2008), the papermaking families were able to maintain a suitable speed of production. Thus, it seems that papermakers may be coming full circle. Research related to nanocellulose is now revealing fresh insights about traditional papermaking. That process can be regarded as involving fibrillated surfaces of the fibers themselves. Such fibrillation, some of it on a nano scale, appears to be essential for achieving the needed “diffusion” of polymer segments as a means to achieving high bonding strength (McKenzie 1984). The rubbing action between adjacent fibers, as well as with refiner surfaces, appears to play an essential role in activating cellulose fibrils at the fiber surfaces such that when they are part of the paper, they can be acting like the intertwined fingers of your folded hands, as was shown in the figure.

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