On increasing wet-web strength with adhesive polymers

ROBERT PELTON, DONG YANG, AND EMIL GUSTAFSSON

ABSTRACT: Fiber-fiber adhesion, called "bonding" in the old paper physics literature, is a critical component of the overall strength of dry paper. With freshly formed very wet pulp fiber webs, all evidence suggests there are no fiber-fiber crossings with significant adhesive joint strength. With water removal, a point will be reached where fiber-fiber adhesion starts to contribute to the overall wet-web strength.

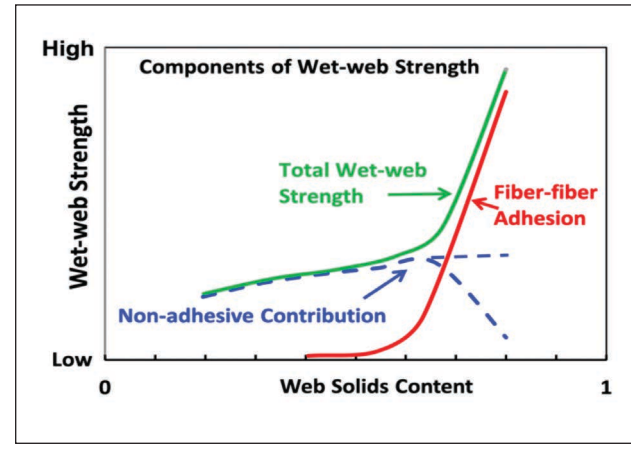
The literature reveals very few examples of polymers that increase fiber-fiber joint strength in freshly formed webs. Here, we summarize the literature and explain why it is so difficult to promote fiber-fiber wet adhesion with polymers. Nevertheless, ongoing research in areas as diverse as tissue engineering scaffolds and biomimetic adhesives gives clues to future developments. Advances in paper machine engineering have lessened the importance of wet-web strength. By contrast, a critical issue in many of the evolving nanocellulose technologies is the strength of objects first formed by aqueous processing, the green strength—the strength of wet bodies before drying. For example, 3-D printed nanocellulose objects and ultralow density cellulosic aerogels can be destroyed by capillary forces during drying. There is a need for adhesives that strengthen freshly formed, wet lignocellulosic joints.

Application: Can wet-end polymers improve wet-web strength during papermaking? Based on the literature and new work, this paper describes strategies where the answer may be yes.

This contribution addresses the potential for polymer additives to increase wet-web strength by increasing fiber-fiber wet adhesion. There is a substantial amount of literature that describes the influence of pulp types [1], fillers, and other papermaking variables on the wet-web strength. These factors are not addressed here because they were recently summarized in a thorough review [2]. The focus of this presentation is the role of adhesive, water-borne polymers as agents to increase wet-web strength. This contribution has extracted highlights from a much broader review article published this year [3].

There are no adhesive interactions between wood pulp fibers in water in the absence of added polymers because all fiber-fiber interactions (electrostatic and/or steric) are repulsive. In dilute aqueous suspension, flexible wood pulp fibers form flocs because of mechanical entanglement [4]. The classic explanation of wet-web strength invokes capillary forces pulling fibers into contact. Page modified his paper tensile strength model to account for capillary forces and was able to explain the influence of fiber length and coarseness on wet-web strength [5].

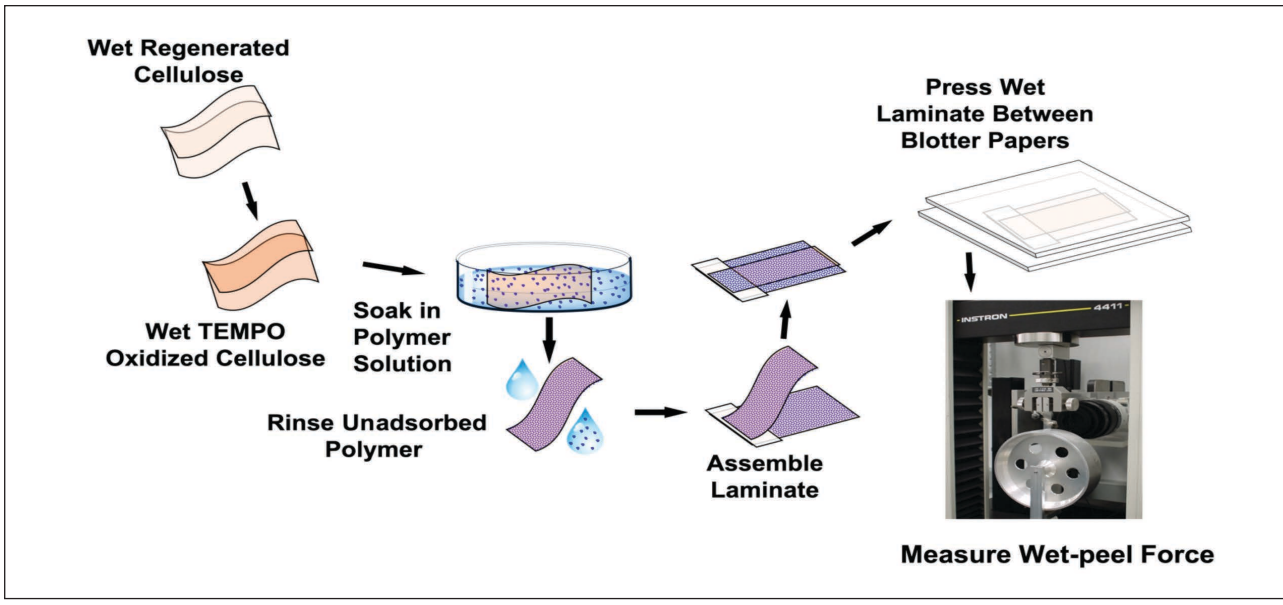
Tejado and van de Ven critically evaluated the classical theories of paper wet-web strength and proposed that wet-web strength is a combination of entanglement friction plus a fiber-fiber adhesion component at higher solids contents [6]. Entanglement involves the work required to pull apart mechanically entwined, long thin fibers. Thus, it depends upon fiber length, flexibility, and friction coefficient, whereas the entanglement contribution is not particularly sensitive to the solids content.



1. Contributions to the wet-web strength [3].

Figure 1 shows a more generic version of a figure by Tejado and van de Ven in which wet-web strength is divided into adhesive plus non-adhesive contributions. Capillary forces, a non-adhesive contribution, will disappear when the free water is gone, whereas entanglement forces may increase with solids content. The detailed nature of the non-adhesive contributions (entanglement vs. capillary forces vs. something else) remains an open issue. The focus of this review is the potential to increase the adhesive contribution with polymers, shifting the fiber-fiber adhesion curve towards the upper left of Fig. 1.

The interpretation of wet-web mechanical properties in the presence of polymeric adhesives is complicated by the



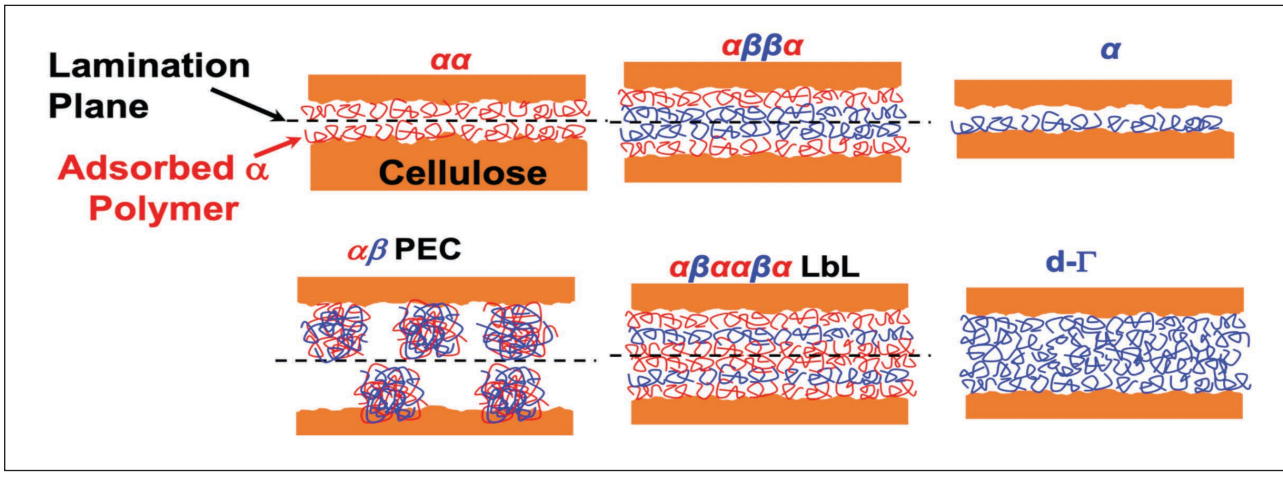
2. The wet-peel method measuring never-dried adhesion between polymer-treated regenerated cellulose membrane surfaces. The membranes are usually TEMPO oxidized to introduce surface charge (carboxyl) groups and reactive aldehydes.

fact that polyelectrolytes can enhance drainage—drier webs are always stronger. Polymers can also change the sheet structure by increasing fines deposition and fiber flocculation. Therefore, polymers that improve the wet-web strength do not necessarily influence fiber-fiber adhesion or friction. Trout emphasized the need to compare wet-web properties as a function of the solids content [7].

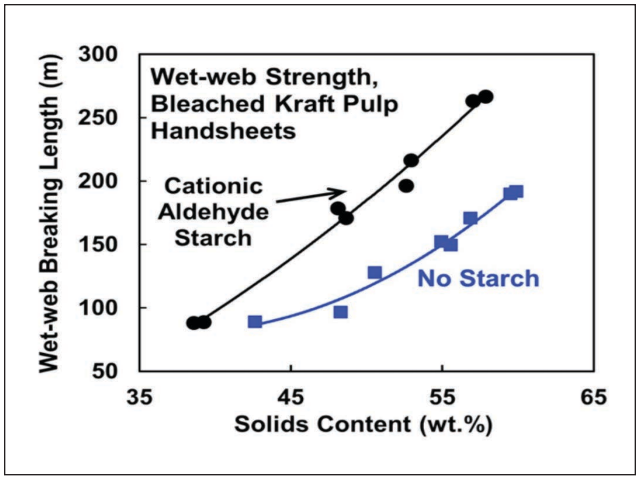
METHODOLOGY

In an effort to measure the fiber-fiber adhesion contribution, decoupled from the non-adhesive contributions (entanglement friction, capillary forces) to wet-web strength, we have developed a physical model to simulate once-dried and never-dried fiber-fiber wet adhesion. **Figure 2** illustrates a procedure we call wet-peeling. More details are available in a recently published review [8]. Regenerated cellulose membranes are cut from dialysis tubing, TEMPO oxidized, and pairs of membranes are laminated after adsorbing the polymer of interest. The method is rapid, reproducible, and is particularly effective at ranking candidate polymeric adhesives.

The wet-peel methodology offers the ability to evaluate a variety of adhesive configurations in the cellulose/cellulose joint. **Figure 3** shows idealized illustrations of ways to organize one or two polymers in an adhesive joint. In papermaking, strength enhancing polymer is adsorbed onto fibers in the wet-end. In the forming section, pairs of polymer coated fibers come together forming wet fiber-fiber joints. This situation is depicted as an αα joint in Fig. 3. The αββα joint type involves two polymer types sequen-



3. Idealized configurations for one or two adhesives in a cellulose/cellulose joint. With a d-Γ joint, Γ is the coverage of adhesive in mg/m².



4. Influence of the cationic aldehyde starch (CAS) on the tensile strength of never-dried laboratory sheets made from a mixed bleached kraft pulp. Data replotted from Laleg and Pikulik [9].

tially adsorbed on fibers. PEC refers to polyelectrolyte complexes that are colloidal hydrogel particles formed when oppositely charged polymers are premixed in water. LbL refers to layer-by-layer sequential adsorption of oppositely charged polymers in the wet-end. The final two joint types, α and d-Γ, cannot be formed by a conventional papermaking process. The α joint is formed by bringing together one fiber coated with polymer with a bare fiber. A d-Γ joint has a thick polymer layer between the cellulose surfaces, where Γ is the polymer coverage in the joint expressed as mg/m^2. These non-conventional joints can be prepared and tested in the wet-peel assay, giving mechanistic information.

The literature contains very few examples of a polymer increasing wet-wet strength by promoting fiber-fiber adhesion. Perhaps the best example is the work of Laleg and Pikulik [9]. An example of their results with cationic aldehyde starch (CAS) is shown in **Fig. 4**, which plots wet tensile strength as a function of sheet solids, with and without treatment with CAS. Treatment with CAS improved the wet strength over the whole range of sheet solids contents. The authors observed the same type of improvements in paper machine trials [10,11]. A much more recent study by Retulainen showed similar results [12]. Note that conventional cationic starches do not improve wet-web strength.

RESULTS

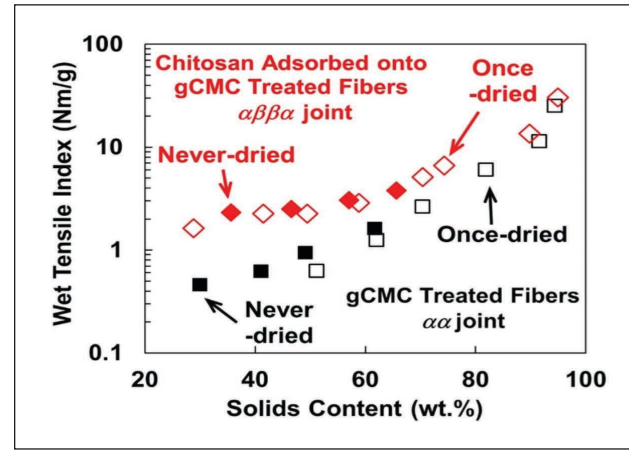
We employed our wet-peel procedure to screen a number of polymers for their potential to increase fiber-fiber adhesion in wet webs. **Table I** shows results obtained using two types of cellulose surface treatments, TO-RC and gCMC. TO-RC refers to TEMPO-oxidized regenerated cellulose, whereas gCMC denotes carboxymethyl cellulose (CMC) irreversibly deposited onto regenerated cellulose membranes. The CMC deposition technology was developed by Laine and Lindström [13]. For each case summarized in Table I, a series of wet-peel experiments was conducted as

Adhesive	TO-RC		gCMC	
	Joint	WP55	Joint	WP55
None		2		5
CGuar	αα	3	αββα	8
PEI	d-15	13		-
CS	d-15	6		-
PDADMAC	d-15	3	αββα	4
PAE	α	14	αβα	4
PAE	αα	6	αββα	4
PVAm	α	24	αβα	6
PVAm	αα	3	αββα	16
GCPAM	α	11	αββα	39

TO-RC =TEMPO-oxidized regenerated cellulose membranes; gCMC = membranes coated with a grafted layer of CMC; WP55 = peel force interpolated to a laminate water content of 55%.

Polymers: CGuar = cationic guar; PEI = polyethyleneimine; CS = cationic starch; PDADMAC = poly(diallyldimethyl ammonium chloride); PAE = polyamideamine epichlorohydrin wet-strength resin; PVAm = polyvinylamine; GCPAM = glyoxalated cationic polyacrylamide. See [3] for more details.

I. The influence of adhesive polymer type, cellulose pretreatment, and joint type on the never-dried wet-peel strength.



5. Strength of the gCMC fiber webs prepared with and without treatment with chitosan after the web was formed. The once-dried measurements were made on rewetted sheets after room temperature drying, whereas the never-dried measurements were made with wet sheets without drying. Replotted data from Wu and Farnood [14].

a function of laminate water content. For comparison purposes, Table I reports the WP55 values, which are the interpolated wet-peel forces for laminates with a 55% solids content. For interpretation of the WP55 values, a value greater than 40 N/m is very high, 20 N/m is high, 10 N/m is weak, and less than 10 N/m is very weak.

Table I shows that both the polymer types and the joint architecture (Fig. 3) are important. For an individual poly-

mer, α joints were stronger than αα joints. However, the strongest joint was an αββα joint with GCPAM (the β layer) adsorbed onto CMC-treated cellulose (the α layer). GCPAM can form a polyelectrolyte complex with the surface CMC layer. The aldehyde groups also can form crosslink groups with other GCPAM molecules or with CMC molecules. Wu and Farnood reported similar results for αββα in wet webs, where the β polymer was chitosan instead of GCPAM [14]. **Figure 5** shows that CMC-treated fibers gave low wet-web strength (i.e., αα joints), whereas the sequential treatment with CMC followed by chitosan (i.e., αββα joints) gave high wet-web strength. With water removal approaching dry paper, the two types of fiber treatments gave similar tensile strengths. Finally, once-dried versus never-dried results were similar. This is very unusual. For example, PAE, a popular wet-strength resin, gives very high wet tensile if the sheet is dried, promoting grafting and crosslinking. By contrast, PAE does not promote adhesion in wet-webs or in our wet-peel model (Table I).

CONCLUSIONS

It is possible to treat fibers with polymers that will give adhesive contributions to wet-web strength. However, most papermaking polymers employed in the usual manner are not effective. More specific conclusions are:

1. Adsorbing a highly charged, non-reactive water-soluble polymer onto fibers in the wet-end will not produce an adhesive contribution to wet-web strength. The resulting αα joints are weak because: a) thin adhesive layers must be grafted to the fiber surface; and b) electrosteric repulsion inhibits polymer-polymer contact and thus inhibits cohesion when two polymer layers come into wet contact. Weakly charged adhesives that are reactive, thus having the potential to crosslink with themselves and graft to cellulose, can give adhesive contributions to wet-web strength. Cationic aldehyde starch is a good example of this.
2. Pulp suspensions consecutively treated with oppositely charged polymers can give adhesive contributions to wet-web strength if the first (i.e., the α) layer is irreversibly bound to the fiber surface. Examples include gCMC + GCPAM or gCMC + polyvinylamine (PVAm).
3. With thin adhesive layers obtained by adsorbing one or two (consecutively) polymers on pulp fibers, wet-web adhesion requires the covalent grafting of the α polymer to the fiber surface. With thick adsorbed multilayers, grafting is less critical. **TJ**

ABOUT THIS PAPER

Cite this article as:
Pelton, R., Yang, D., and Gustafsson, E., *TAPPI J.* 19(2): 63(2020). https://doi.org/10.32964/TJ19.2.63

DOI: https://doi.org/10.32964/TJ19.2.63

ISSN: 0734-1415

Publisher: TAPPI Press

About this journal

ACKNOWLEDGMENTS

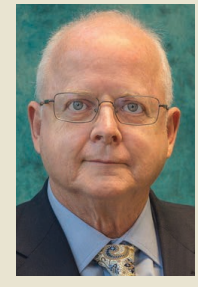
The authors thank the Canadian Natural Sciences and Engineer Research Council and the Canada Foundation for Innovation for funding, as well as BASF and Proctor & Gamble, who acted as industrial partners.

LITERATURE CITED

1. Seth, R.S., *Tappi J.* 78(3): 99(1995).
2. Belle, J. and Odermatt, J., *Cellulose* 23(4): 2249(2016). https://doi.org/10.1007/s10570-016-0961-7.
3. Pelton, R., Yang, D., and Gustafsson, E., *BioResources* 14(1): 2389(2019).

ABOUT THE AUTHORS

We found this topic of interest for research, as we have a long history of working with paper strength enhancing polymers. The most difficult aspect of the work was understanding the results, and it was interesting to see the complexity involved in strengthening webs. This work should help chemical suppliers develop more effective polymers for mills.



Pelton

Yang

Gustafsson

Pelton is professor and Yang is a post-doctoral researcher in the Department of Chemical Engineering at McMaster University, Hamilton, ON, Canada. Gustafsson is senior research project manager—BioProducts Institute at The University of British Columbia, Vancouver, BC, Canada. Email Pelton at peltonrh@mcmaster.ca.

4. Celzard, A., Fierro, V., and Kerekes, R., *Cellullose* 16(6): 983(2009). https://doi.org/10.1007/s10570-009-9314-0.
5. Page, D.H., *J. Pulp Pap. Sci.* 19(4): J175(1993).
6. Tejado, A. and Van De Ven, T.G.M., *Mater. Today* 13(9): 42(2010). https://doi.org/10.1016/S1369-7021(10)70164-4.
7. Trout, P.E., *Tappi* 34(12): 539(1951).
8. Yang, D., Diflavio, J.-L., Gustafsson, E., et al., *Nord. Pulp Pap. Res. J.* 33(4): 632(2018). https://doi.org/10.1515/npprj-2018-0013.
9. Laleg, M. and Pikulik, I.I., *J. Pulp Pap. Sci.* 19(6): J248(1993).
10. Laleg, M. and Pikulik, I.I., *Nord. Pulp Pap. Res. J.* 8(1): 41(1993). https://doi.org/10.3183/npprj-1993-08-01-p041-047.
11. Laleg, M. and Pikulik, I.I., *J. Pulp Pap. Sci.* 17(6): J206(1991).
12. Retulainen, E. and Salminen, K., "Effects of furnish-related factors on tension and relaxation of wet webs," in *Advances in Pulp and Paper Research, Trans. of the XIVth Fund. Res. Symp., Oxford, 2009* (S.J. I'Anson, Ed.), FRC, Manchester, 2018, pp. 1019–1037.
13. Laine, J., Lindstrom, T., Nordmark, G.G., et al., *Nord. Pulp Pap. Res. J.* 15(5): 520(2000). https://doi.org/10.3183/npprj-2000-15-05-p520-526.
14. Wu, T. and Farnood, R., *Carbohydr. Polym.* 114: 500(2014). https://doi.org/10.1016/j.carbpol.2014.08.053.