How polymers strengthen filled papers

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ABSTRACT: We compared two strategies for strengthening filled papers. One used polymers to increase cellulose-cellulose adhesion, the other used polymers to increase cellulose-calcium carbonate adhesion. We made two-ply laminates from wet, filler-free handsheets with a sparse coating of precipitated calcium carbonate (PCC) in the ply-ply interface. After those had dried, we measured the force required to delaminate them. Polymer treatment of one or both plies increased the strength of laminates with low PCC contents due to enhanced cellulose-cellulose adhesion. However, at intermediate filler contents this strategy failed. Treatment of PCC with polymer to strengthen cellulose-PCC adhesion gave modest strength improvements. By far the strongest laminates were obtained when cellulose fines were present in the PCC layer.

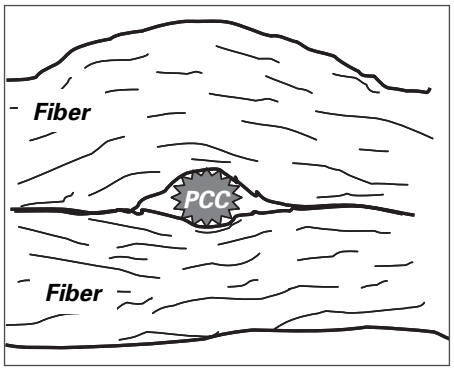
Application: This study evaluates the effectiveness of various combinations of polymers, fines, and PCC to strengthen paper.

The calcium carbonate filler content of paper products has increased over the years. Mills add the filler to reduce cost, increase bulk, and improve optical and printing properties [1,2]. However, fillers also weaken paper by disrupting fiber-fiber joints (**Figure 1**), so mills set limits on the filler contents of many paper and paperboard grades [3-5].

Past research on the effects of fillers on paper properties, reviewed in a previous paper [6], showed that:

- Fillers lower paper strength, and bulky filler shapes are more detrimental to paper strength than are laminar particles [3].
- For a given filler type, the smallest fillers have the most detrimental effects on paper strength.

Detailed mechanistic investigations of fillers on paper strength are complicated by the inability to control filler distribution and filler aggregation in conventional papermaking. For example, higher filler loadings require retention aids which, in turn, induce uncontrolled filler and fiber aggregation. Li et al. described a novel approach to filled paper investigations that circumvented these difficulties [6]. In their method, a sparse coating of precipitated calcium carbonate (PCC) is imprinted on the surface of a wet, filler-free handsheet and then a second wet, filler-free handsheet is placed on top to give a two-ply laminate with a sparse filler layer between the plies. The laminates are dried and then the 90° peel delamination force is measured.



1. A filler particle disrupting a fiber-fiber joint.

The fundamental assumption in Li's study was that the ply-ply delamination force models the fiber-fiber joint rupture in conventional paper. The authors showed that the delamination peel strength decreased exponentially with filler coverage (i.e. the mass of filler per area of joint). They also confirmed the findings of earlier reports that the smallest PCC particles had the most negative effect on delamination force [6]. In addition, spiky scalenohedral PCC was slightly more disruptive than blocky prismatic PCC [7].

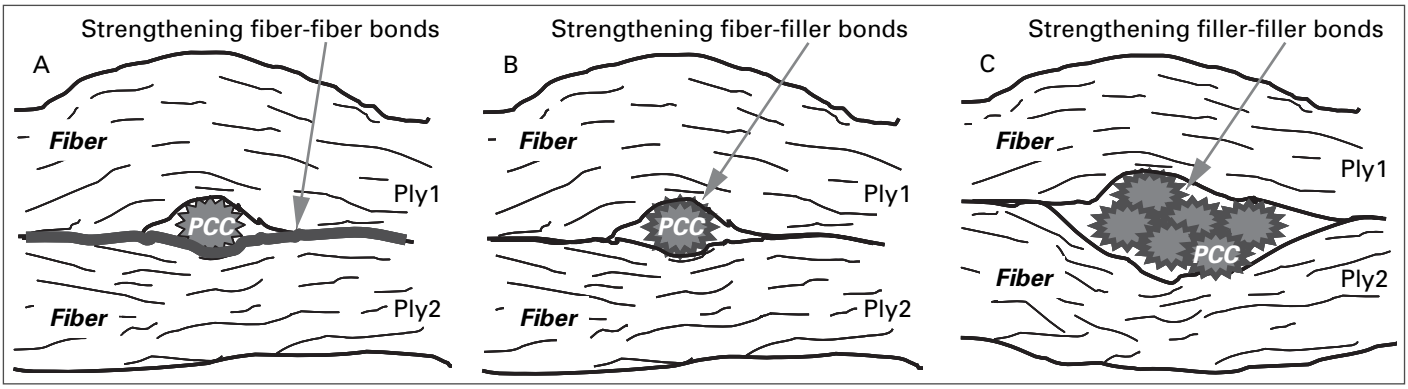
The papermaker has two tools to compensate for filler-induced strength loss: fines [8] and strength-enhancing polymers [9-12]. In our last paper we showed that softwood bleached kraft pulp fines were particularly effective at strengthening the laminates [8]. We proposed that the fines acted as micrometer-scale gaskets which increased fiber-fiber and fiber-PCC contact area. However, fines are not a perfect solution as they require refining energy, they are slow to drain, and filling in too many voids will lower filler light scattering efficiency.

In this paper, we describe the results of a mechanistic study of polymers in filled papers. In principle, a polymer could strengthen fiber-fiber joints, fiber-filler joints, and filler-filler joints. Furthermore the optimum polymer for one type of joint is unlikely to be the optimum for another. Thus the specific objective of this work was to compare the relative benefits of strengthening fiber-fiber versus fiber-filler versus filler-filler joints. **Figure 2** shows these three possibilities.

EXPERIMENTAL

This study used dry-lap softwood bleached kraft pulp (SBK) from Bowater (Thunder Bay, Ontario, Canada). Specialty Minerals Inc. (Bethlehem, Pennsylvania, USA) provided the scalenohedral PCC (ALBACARR 5970) filler, with an average size of 1.7 mm and a specific surface area of 6.58m^2/g, as a dry powder.

Table I summarizes the properties of the polymers used in this research. Two poly(N-vinylformamide-co-vinylamine)s (BASF, Ludwigshafen, Germany) with different molecular weights were further hydrolyzed to give polyvinylamine (PVAm). For this, about 75 g poly(N-vinylformamide-co-vinylamine) (20%) was dissolved in 225 g sodium hydroxide (NaOH) solution (6.7%). The hydrolysis was carried out at 75°C under the protection of nitrogen (N_2) for 5 days. The products were purified by 12 days of dialysis and were freeze-dried to give a dry white powder. Complete hydrolysis was



2. Schematic illustration of a polymer strengthening: (A) a fiber-fiber bond; (B) a PCC-fiber bond; and, (C) PCC-PCC bonds.

confirmed by hydrogen nuclear magnetic resonance (^{1}H NMR).

We bought carboxymethyl cellulose sodium salt (CMC), with a degree of substitution of 0.9, from Aldrich, Oakville, ON. SMI, Allentown, PA provided the cationic polyacrylamide (Percol 175), which was manufactured by Ciba Specialty Chemicals Ltd., Bradford, U.K.

Name, type	Composition mol %	MW Da	Charge Density, meq/g
PVAm 105 (Polyvinylamine)	100% hydrolyzed	150,000	23
PVAm106 (Polyvinylamine)	100% hydrolyzed	950,000	23
PVAm/CMC	-NH_2:-COOH 19:1 (PVAm 105 and CMC)	—	—
Percol 175 Cationic polyacrylamide	9% cationic monomer	5,000,000	1.1 [13]
CMC sodium carboxymethyl cellulose	Degree of substitution 0.9	250,000	3.8
PAMVP-3 Poly(acrylamide-co-vinyl phosphonic acid)	Vinyl phosphonic acid 8.7%	79,000	2.0
PVAP poly(vinyl alcohol) phosphate	Phosphoric acid, 50%	~ 240,000	4.7

I. Cationic polymers used to treat fiber surfaces and the anionic polymers for PCC treatment.

Phosphate-containing polymers—poly(acrylamide-co-vinyl phosphonic acid) (PAMVP-3) and poly(vinyl alcohol) phosphate (PVAP)—were synthesized at McMaster through procedures described in a previous publication [18].

PVAm/CMC polyelectrolyte complexes were prepared by mixing 500 mL of 1 g/L PVAm 105 in deionized water and 20 mL of 5g/L aqueous CMC together for about 10 min in a 1 L beaker with a magnetic stirring bar.

We measured the PVAm/CMC particle size distributions with a Malvern Mastersizer 2000 (Malvern Instruments Ltd., Malvern, Worcestershire, UK). The nonspherical particle and general purpose analysis model for volume percent distribution measurement was applied using a refractive index of 1.40.

Polymer treatment of PCC particles

About 0.5 g of scalenohedral PCC was dispersed in 0.01M sodium chloride (NaCl) solution at 20% and sonicated for 5 min. This suspension was further diluted to about 10 g with 0.01M NaCl and mixed well. The pH of the suspension was adjusted to 8.5 and 2 mL of 5 g/L CMC or phosphate-containing polymers were added. The suspension was tumble mixed for 48 h at about 40 rpm. The PCC suspension was centrifuged (Beckman Coulter, Inc., Model Allegra 25R centrifuge, Fullerton, California, USA) at 7000 rpm for 1 h. The supernatant was decanted and the PCC particles were redispersed in 10 g deionized water. The procedure was repeated to ensure that any polymer present was adsorbed on the PCC particles.

We used a Brookhaven ZetaPlus zeta potential analyzer (Brookhaven Instruments Corporation, Holtsville, New York, USA) to measure the electrophoretic mobility of PCC particles after polymer treatment at a phase analysis light scattering (PLAS) mode. The PCC particles were dispersed in a 0.001M potassium chloride (KCl) solution. We adjusted the pH of suspension with 0.1N hydrogen chloride (HCl) or NaOH solution. The PCC particle size distributions were measured with a Malvern Mastersizer 2000. (nonspherical particles and general purpose analysis model using a refractive index of 1.57).

Polymer treatment of wet handsheets

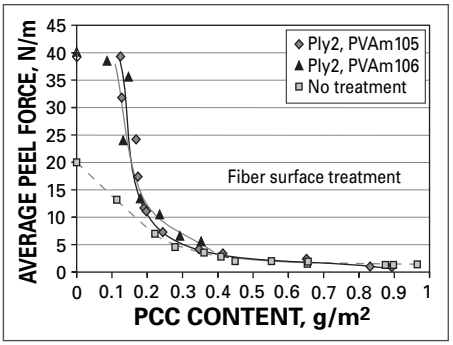
Softwood bleached kraft pulp was beaten mildly (1000 PFI revolutions) and used to prepare 30 g/m^2 handsheet plies in a LABTECH semi-automatic sheet former (LABTECH Instruments Inc., Laval, Quebec, Canada) according to TAPPI handsheet forming procedures (T205 sp-95). The handsheet ply with the blotting paper was then placed blotter side down on a perforated plastic plate fitted to a vacuum flask (for more details see [14]). To protect the fragile, wet handsheet, we gently placed a 10 mm, 142 mm diameter Isopore™ polycarbonate membrane (Millipore, Billerica, Massachusetts, USA) on the surface. In the final step, we fixed a 132 mm diameter PMMA cylinder on top and added about 20 g of 0.1% PVAm or PVAm/CMC to the cylinder. The vacuum was controlled so that the 20 g of polymer drained through the fiber pad in about 35 s. After this, 200 mL of deionized water was passed through the ply to remove unadsorbed polymer.

Laminated handsheets fabrication

PCC was dispersed in deionized water at 20% and sonicated for 5 min. We further diluted an aliquot of PCC in 100 mL of deionized water and filtered that on a 0.4 mm Isopore™ polycarbonate membrane (142 mm). This membrane was carefully placed on the top wet handsheet ply 1 and was pressed for 2 min at 345 kPa. The membrane was carefully removed after pressing.

The second wet handsheet, ply 2, was placed on top of ply 1 and the two handsheets were laminated following TAPPI T205 sp-95. The laminate was slowly dried under restraint in a constant temperature and humidity room.

The force required to delaminate the dry laminated handsheets was measured by a 90° peel test. Details of the sample

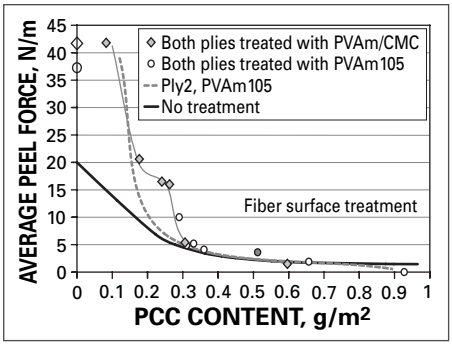


3. The influence of polyvinylamine (PVAm) on the delamination strength versus filler coverage curves.

Treatment Method	Polymers	a_2	R^2
None	—	0.370	0.9856
Fiber	PVAm105[a]	0.385	0.9783
	PVAm106[a]	0.455	0.9192
	PVAm105[b]	0.237	0.9602
	PVAm/CMC[b]	0.334	0.9538
Filler	CMC[c]	0.255	0.8278
	PAMVP-3[c]	0.378	0.9671
	PVAP[c]	0.440	0.9642
	Percol175	0.409	0.5623

[a] Only ply 2 treated with polymer.
[b] Both plies treated with polymer.
[c] PCC particles treated with polymer.

II. The slope and R^2 values for plots of ply 2 PCC content versus total PCC content.



4. Ply treatment with PVAm105 and with PVAm/CMC complex.

preparation and peeling have been described previously [6]. The quantity of PCC on each ply after the peel test was determined by dissolving the calcium carbonate and measuring the calcium ion concentration with ethylenediaminetetraacetic acid (EDTA) titration.

RESULTS

The main goal of this work was to compare the three types of polymer-enhanced joints in filled paper (see Figure 2). For polymer strengthened fiber-fiber bonds (Figure 2A), handsheet ply 2 (or in some cases, both plies) was treated with polymer solution before the lamination with ply 1, which was coated with PCC particles. Note that ply 2 was exposed to a great excess of polymer and then was rinsed with water. This treatment will give a saturated layer of adsorbed polymer on the exposed fiber surfaces.

Figure 3 compares the delamination force versus PCC coverage for laminates made without and with pre-treatment of ply 2 with PVAm 105 and 106 cationic wet and dry strength enhancing polymers (see Table) [15]. For PCC coverages less than 0.2 g/m^2 (i.e. the amount of PCC per area of the joint), the PVAm reinforced laminates were much stronger than the polymer-free control. Indeed, without PCC the polymer-treated laminates did not delaminate at the ply-ply interface, but instead failed within ply 1, which was not impregnated with PVAm. The delamination forces for the 150,000 Da PVAm 105 were similar to the 950,000 Da PVAm 106; the insensitivity of adhesion strength to molecular weight has been reported for PVAm wet strength [16] and for other polymers [12, 17].

The maximum PCC content of the laminates in this work was less than 1 g/m^2 because laminates with higher PCC contents were too weak to accurately measure the delamination force. If we assume that PCC particles are spheres with a diameter of 1.7 μm and a density of 1600 kg/m^3, the coverage corresponding to cubic close packing on a smooth surface is 2.79 g/m^2. In our experiments, PCC is applied to ply 1 in a contact printing process from a PCC decorated membrane. Our previous results [7,8] suggested that only about half of the ply 1 surface comes in contact with the membrane during the PCC transfer process. Presumably some interfiber voids on the handsheet surface are too deep to give PCC particle transfer. Therefore the coverage corresponding to a saturated monolayer of PCC particles is approximately 0.5•2.8=1.4 g/m^2. Consequently, all of the PCC contents in this work were less than a monolayer coverage which, in turn, means there should be very few instances of PCC particles lying on top of other PCC particles. Thus, filler-filler adhesion (Figure 2C) is not significant in our experiments.

Reinforcing fiber-fiber bonds with polymer more than compensated for the presence of some PCC. However, the results in Figure 3 also show that for PCC coverages above 0.35 g/m^2 there was no advantage in treating ply 2 with polymer. We propose that there are essentially no filler-free ply-ply contacts at these high PCC contents. Furthermore, the low delamination force (< 5 N/m) shows that the strength of unreinforced PCC/fiber bonds is low.

The PCC content of each ply was determined after the delamination experiments. Previously we have shown that for polymer-free laminates the ply 2 PCC content was a linear function of the total PCC content with a slope of about 0.4. In other words, about 40% of the total PCC originally added to ply 1, ended up on ply 2 after peeling. If every PCC particle were in contact with both plies with same the adhesion, we would expect the slope to be 0.5.

The PVAm 105 slope (**Table II**) was approximately equal to the untreated slope. Thus, treating only ply 2 with PVAm 105 did not increase the quantity of PCC on ply 2 after peeling. This means that the PVAm 105 did not increase PCC/fiber adhesion, whereas the higher molecular weight PVAm 106 did slightly increase PCC/ply 2 adhesion.

Figure 4 summarizes the results of experiments in which both plies were treated with two types of polymer. PVAm/CMC is a cationic complex formed by adding a small amount of CMC to PVAm, resulting in hydrogel particles with an approximate diameter of 200 nm (measured with Mastersizer). The advantage of using a colloidal polymer complex is that much higher amounts of polymer will deposit on the fiber surfaces [18].

Treatment of both plies with either PVAm 105 or with PVAm/CMC complex gave slight improvements over single ply treatment from 0.2 g/m^2 to 0.3 g/m^2 PCC (Figure 4). Polymer treatment of one or both plies offered no advantage at high PCC contents.

The results in Figure 3 and 4 show that the polymer can increase cellulose-to-cellulose adhesion (see Figure 2A). The alternative approach is to adsorb polymer onto PCC to increase filler-cellulose adhesion (Figure 2B) and filler-filler adhesion (Figure 2C). Because aqueous PCC is positively charged, polymer treatment is easiest with negatively charged polyelectrolytes.

PCC suspensions were exposed to concentrated (5 g/L) polymer solutions followed by washing to give particles saturated with adsorbed polymers. Because flocculation is always a possibility, the PCC particle size distributions were measured before and after treatment. **Table III** summarizes the results. Only the flocculant Percol 175 caused a significant PCC flocculation.

Figure 5 shows PCC electrophoretic mobility as a function of pH for three anionic polymers (see Table I). Two of the polymers, PVAM-VP3 and PVAP, bear phosphate or phosphonate groups, which have a high affinity to soluble calcium and calcium carbonate [18]. As expected, the anionic polymers reversed the charge of PCC particles.

Laminated handsheets were prepared with anionic polymer-treated PCC. **Figure 6** shows the delamination forces as functions of PCC coverage. The three anionic polymers increased the delamination strength; however, filler treatment seems much less effective than fiber-fiber bond treatment (compare with Fig. 4). The anionic polymers gave a slight strength increase at very high PCC coverages, perhaps indicating a strengthening of PCC-PCC adhesion. However, the improvements were modest.

Finally, a number of papers and patents have claimed that flocculated fillers are less detrimental to paper strength [19-21]. Explanations include the following:

- Large flocs are retained by filtration in the papermaking process and thus are less likely to be located within the fiber-fiber joints.
- Polymer induced flocs are conformable.
- Polymeric flocculant increases fiber-filler adhesion.

PCC suspensions were flocculated with high molecular weight cationic polyacrylamide, giving 16 µm flocs (Table III). The flocs were incorporated into laminated handsheets. The delamination results in **Figure 7** compare filler flocculation with fiber-fiber bond enhancement with PVAm 105 and with CMC filler-filler bond enhancement. At filler coverage (0.2 g/m^2 to 0.6 g/m^2) the laminates made with flocculated fillers were a little stronger than the laminates with polymer treated fibers or fillers.

The inset in Figure 7 shows the effect of mixing softwood fines with the PCC on the laminate strength. These results were extracted from our previous publication [8]. Note the x-axis span (i.e. the maximum filler content) of the inset is 10 times greater than that achieved with the polymer enhanced laminates prepared for this work. Clearly, softwood fines are much more effective at strengthening the laminates than were any of the polymer strategies used in this work, including phosphorous containing polymers designed to adhere to calcium carbonate.

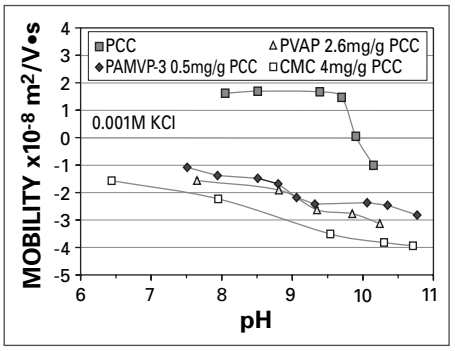
DISCUSSION

The original objective of this work was to compare polymer approaches to strengthening fiber-fiber, fiber-filler, and filler-filler bonds—the three cases in Figure 2. However, we were unable to measure PCC-PCC bonds. Laminates with multiple PCC layers were too weak to characterize because fiber-PCC adhesion was so low. For example, Figure 3 shows that adhesion was very low at PCC contents above 0.5 g/m^2. In this regime the PCC-fiber contacts are the dominant interaction in the ply-ply joint. We would not expect a significant number of PCC-PCC contacts until the PCC coverage was near 1.4 g/m^2. The arrow on Figure 2 shows where the polymer-free curve converges with the polymer-enhanced cellulose-cellulose bonds in the interply joint. In other words, for PCC contents above the arrow (0.4 g.m^2) there were few cellulose-to-cellulose contacts in the ply-ply joint.

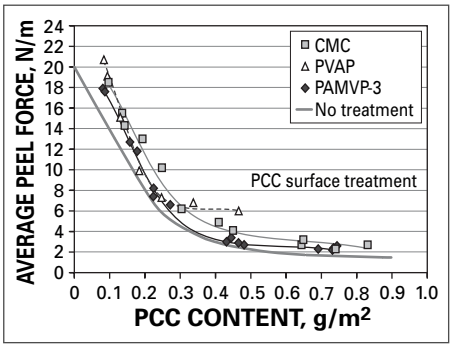
This work involved six different polymers plus one combination of two polymers (Table). These polymers were chosen because they would spontaneously adsorb onto the wet handsheets or onto suspended PCC particles. Also, all of them previously have been shown to have some efficacy at strengthening paper. However, in this work we did not measure or control the amount of polymer that ended up in the laminates. Thus, we do not recommend using these results as a comparison of polymer efficiencies.

Name	D, 0.1	D, 0.5	D, 0.9
PCC	1.4	3.0	5.2
CMC-treated PCC	1.4	3.2	6.2
PAMVP-treated PCC	1.5	3.1	5.5
PVAP-treated PCC	2.0	3.1	4.9
Percol 175 flocculated PCC	5.4	16.0	38.8

III. The size distribution of different polymer treated scalenohedral PCC particles measured with a Mastersizer. D(x) is the diameter in nanometers corresponding to probability x in the accumulative particle size distribution.

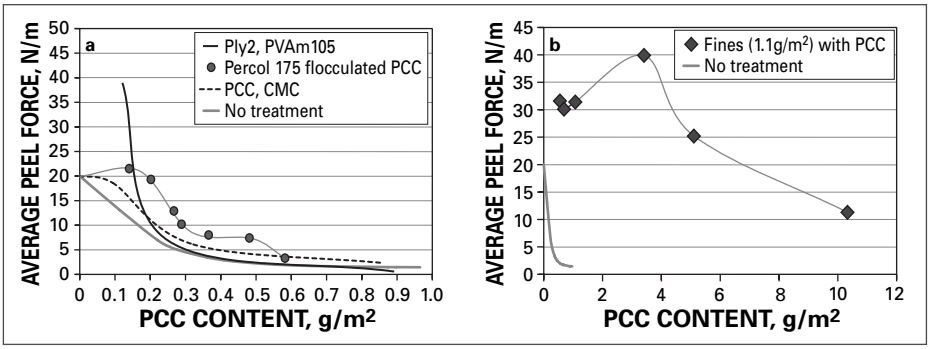


5. Electrophoretic mobility of PCC as functions of pH.



6. The influence of PCC surface treatment with different polymers on the delamination strength.

The most dramatic result in this work comes from the comparison of polymer treatment versus fines as a strategy for strengthening filled papers (see Figure 7). We propose that the fines are much more effective than adsorbed polymer because the fines are large enough to span the voids the PCC particles induce in the fiber-fiber joint (Figure 1). Thus fines act as a gasket. Although the contour length of a 1 million Da polymer is hundreds of nanometers, when adsorbed onto a surface the polymer layer thickness is typically a few nanometers [22]. Such a layer is too thin to fill the voids between rough fiber surfaces and spiky filler particles.



7. (a) The effects of flocculated filler on the delamination strength. (b) Shows previously published data [8] for laminated handsheets reinforced with softwood bleached kraft pulp fines.

Finally, paper companies do not sell laminated handsheets, they sell machine-made paper. The laminated handsheets are an experimental model. In our previous work we discussed methods to equate the filler contents of laminated handsheets to an equivalent filler content in conventionally filled paper [6-8]. By comparing laminated handsheet properties to the properties of sheets made on a dynamic sheet former, we showed that the laminated handsheet experiments exaggerate the detrimental effects of fillers. Nevertheless, the following conclusions can be made from this work and we believe that they apply to machine-made paper.

CONCLUSIONS

1. Water soluble polymers can strengthen cellulose-cellulose adhesion (Figure 2A) and cellulose-PCC adhesion (Figure 2B) in filled papers. Of the two, fiber-fiber joint enhancement with polymers gave the strongest laminates at low PCC contents.
2. Polymer preflocculated filler gave stronger laminates than untreated PCC.
3. None of the polymer treatments were as effective as adding softwood fines to the PCC layer, particularly at high PCC contents. We believe that fines are large enough to function as a gasket, enhancing fiber-filler bonds, whereas adsorbed polymer layers are simply too thin to provide this function. **TJ**

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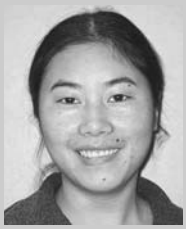
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