

# Fiber Surface Engineering to Improve Papermaking Raw Material Quality

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## ABSTRACT

We used polymers of alternating cationic and anionic nature to build up shells on fiber surfaces, strengthen the worn-out fibers and improve paper properties made from such fibers. OCC and ONP pulps were either dipped or salted out in the cationic polyallylamine, polyacrylamide and starch solutions. After centrifugal drying, these were followed by treatments in anionic polyacrylic acid, poly-acrylamide, and starch solutions, respectively. The shell-enhanced fibers were formed into handsheets and their physical properties evaluated. The results show that building multiple shells on worn-out fiber surfaces can strengthen the fibers and paper. The simpler and more practical impregnation-centrifuging treatment provided the desired effects, whereas salting out the polymers produced somewhat superior fibers. The latter process, were impractical, however. The first pair of polymeric shells imparted marked strength improvement, whereas later layers had diminishing efficacies. Overall, the methods can improve fiber quality, attaining paper strength requirements without resorting to expensive measures. Alternate cationic polymer and filler powders were also deposited on fiber surface based on the microparticle system in an anticipation of stiffness gains. Platy minerals, such as montmorillonite, bentonite, sericite, clay and talc were added following cationic PAM. After dewatering of polymer-pigment shelled fiber of one to 3 pairs of layers, handsheets either calendered or uncalendered were evaluated. The results indicate that regardless of calendaring, stiffness of the handsheets did not improve appreciably while certain other strength properties showed gains. We also attempted the novel starch gel filler addition method wherein tapioca starch and fillers (PCC, sericite or clay) were mixed at high solids content of 50% and cooked until gelatinized. The filled handsheets were dried under various conditions and then tested for their properties. Improvements in strengths of modified filled paper were observed.

**Key words:** Fiber surface engineering, polyelectrolytes, pigment, handsheets, paper properties.

## INTRODUCTION

The domestic paper industry in Taiwan is dominated by the production of industrial packaging paperboards, which is largely based on recycled old corrugated containerboard (OCC) for raw materials. Fibers from such sources tend to degrade and worn-out with each recycling. Replenishing the stock with fresh virgin fibers or less recycled secondary fibers would amend the situation. However, secondary fibers are under increasing demands and competition for the supply could be rather fierce. Surface hornification of the degraded fiber leads to lower bonding potential and poorer stiffness and strengths (Ackermann et al. 2000). Strengthening additives such as cationic starch and PEI are often needed to pick up fiber strengths (Moeller 1996, Wågberg and Björklund 1993, Lindström et al. 2005),

or using multiple headbox to form multiplied paper, or using surface sizing to impart strengths. The bonding potential of fiber surfaces is known to be affected by compatibility of the surface molecules. Pelton et al. (2000) found that forming paper with fibers whose surfaces were modified with both hydrophilic and hydrophobic dextrin had the poorest strengths at the 1:1 mixture, while the purely hydrophilic or hydrophobic fibers with self-compatibility all had good strengths. Barzyk et al (1997) used a specific oxidative reaction to alter the surface chemistry and swelling property of fibers. He found that charged functional groups on fiber surfaces could strengthen inter-fiber bonding more so than having the same amounts of the functional groups on the interior of the fibers. All these studies denoted the importance of the outer surfaces of fibers to the

bonding strengths. Ionic groups on the polyelectrolytes can be as effective as polymers that form covalent bonds with the surface molecules of fibers (Stratton and Colson, 1993). All these agents can cause the rupture zone of fiber walls to shift from the S1 layer to the stronger S2 layer. Valadez-Gonzalez et al. (1999) used alkaline treatment to wet fiber surface then treated natural fiber with silane to improve interfacial shear strength of the fibers with a thermoplastic matrix. Decher (1997) first proposed the potential of applying layered polymeric multi-components in fuzzy nano-assemblies. Inspired by the concept, Wågberg et al (2002) made a breakthrough when they built alternating cationic-anionic polyelectrolyte shells on fiber and found marked strength improvement, allowing unbeaten fibers to reach the strengths of beaten fiber, and the method was effective for beaten fibers as well. The construction of multiple electrolyte shells presents an advance in fiber modification in nano-technological arena. In the present study, we carried out study based on the Wågberg study and proceeded to use 3 sets of polyelectrolytes to build shells on domestic OCC and ONP pulp. Although originally we included MOW, but due to the uneven nature of the material and generally adequate strength properties of its recycled fibers, ONP was adopted instead. Furthermore, Wågberg et al. used a salting out procedure to make the polyelectrolytes bind tightly to fibers. In addition to follow their process, we deemed that a simpler dip-dry cycles of alternate cationic-anionic solutions could be a potentially more viable procedure.

Regarding filled papers, we noted that the micro-particulate system of polyelectrolyte-pigment particle retention and deposition mechanism as explained by Asselman and Garner (2002) might equally applicable to fiber surface modification that might put stiff "armor-plating" on the limp secondary fiber and might potentially lead to improved paper stiffness from such fiber stock.

## MATERIALS AND METHODS

### 1. Multilayer polyelectrolyte shells on OCC and ONP fibers

The corrugating medium and liner pulps from OCC were obtained from a central Taiwan industrial

paper mill either as dry or wet laps. The dry pulps were store indoor at room temperature and the wet ones in a 4°C cold room. The polyelectrolytes used included cationic polyallylamide (PAA, Magnafloc Lt-31, Chemmax Ltd.), cationic polyacrylamide (cPAM, Percol 182, Chemmax Ltd.), and cationic starch (CS, Katax-Nta, Shieh Tai Chemicals & Starch Ltd.); and the anionic polyacrylic acid (PAH, VC-30, Chemmax Ltd. ), anionic-PAM (aPAM, Percol 155, Chemmax Ltd.) and anionic starch (Emcoat, Chemmex Ltd.).

Thirty-six o.d. lots of either OCC or ONP pulps were dispersed in 1200 ml each of deionized water to a consistency of 3.0%. Polyelectrolytes at 0.1% concentration of the cationic polyallylamine, (PAA), and polyacrylamide (c-PAM), and the anionic polyacrylic acid (PAH), and a-PAM were also prepared. To the dispersed pulp, 1080 ml of the cationic polyelectrolyte solutions were added, after mixing (5 min) and standing (30 min), the pulp was centrifuged with the spin-dry cycle of a washing machine to about 30% consistency. Anionic polymers were then added to the reslashed pulp and again spun to dryness. The procedure above built one shell-pair on fibers and we proceeded to make up to 4 more shells on the pulp.

For the salting-out treatment, the procedure of Wågberg et al. (2002) was followed. Afterward, the treated fibers were made into handsheets and various physical properties of the paper evaluated.

### 2. Multilayer polyelectrolyte-(platy) pigment on OCC and ONP fibers

In this set of study, filler pigments, particularly the platy type with strong surface anionic charges were selected. The minerals include a mica mineral, sericite (4.5 µm average particle diameter, Sunmica Co., Taiwan), talc (Chao-Hwa Co., Taiwan), bentonite (Sudchemie, Chemmax Co.), montmorillonite (Bai-Kang, KC 980-A, nano-preparation) etc,

The method entailed using cationic polyelectrolytes alternating with an anionic platy pigment to form micro-particulate dual system shell. To the OCC pulp dispersed at 3% consistency, cationic PAM (Percol 182) at 0.1% concentration was added at 3% dry fiber amount. After adsorption of the polymer, spun-drying, and the fiber was reslashed and individual pigments at 0.1% suspension was added at 3% dry fiber amounts to constitute a 'shell' layer. Certain pigments (PCC and montmorillonite) were

also added at 6% levels with respect to dry fiber as well. Additional layers of shells might be built on the first one, up to 3 shells. The treated fiber was formed into handsheets. Half of the handsheets was tested directly for their physical properties; the other half was calendered first then tested. Handsheets made of the OCC pulp with cationic polymer and OCC pulp only were prepared as control groups

**RESULTS AND DISCUSSION**

**1. Multilayer polyelectrolyte shells on OCC and ONP fiber**

Due to importance of OCC fibers in the local paper industry it is a prime subject for fiber surface engineering by the polyelectrolyte shells. The experimental results based on 2 pairs of polyelectrolytes and 2 methods of shell building indicate that the PAM series showed more marked strength improvement using both modes (dip-dry or salting out) of shell building. A single shell of salted-out polyelectrolytes caused a gain of 41.5%, 60% and almost tripling in tensile strength, bursting index, and folding endurance, respectively. The same single shell polyelectrolytes by the dip-dry method led to a gain of 45%, and 86% in tensile and bursting, respectively. Subsequent shell layers of PAMs generally showed incremental gains, and leveling out at 4th shell for the salted out treatment and lesser increments for the dip-dry method. Probably due to the tighter packaging of shell layers under the ionic strengths exerted by the ionic species of salt in the solutions, fibers with the salted out shells usually had better gains in strengths than the dip-dry ones did. Fibers treated with PAA and PAH pairs were generally not as strong as those with PAMs shells. The results differed from those obtained by Wågberg et al. (2002) despite using the same protocols. Reasons for the differences could be difference in fiber stock and the difference in the DP and DS of the PAA and PAH used for studies. Handsheet strength properties were dependent upon the intrinsic fiber strengths, and the tearing strength, influenced mainly by the fiber length, was largely not affected by the polymeric shells. Thus, fiber surface engineering basically modifies only the inter-fiber bonding capacity of the fibers. Figs 1 to 4 show the changes in some handsheet physical properties along with the number of shells wrought by either method. Adding cationic starch gave tensile strength gains comparable to those of the other polyelectrolytes, but it seemed to boost bursting strength to a lesser extent.

When the same polymeric enhancement protocols were applied to the recovered news prints, strengths mediated by inter-fiber bonding quality showed marked increases, mostly for the PAMs. On the other hand, the PAA-PAH polyelectrolytes shells on the ONP pulp were largely ineffectual, particularly

for the dip-dry treatment. Causes of the null effect might arise from the lignin-rich fiber surfaces having poor affinity with the polyelectrolytes. Bursting strengths of the salted-out PAM electrolyte shells endowed the fiber with 2.65 times increase, while the dip-dry treatment produced at best close to 2 times increase in bursting index. For the ONP pulp, multiple electrolyte shells seemed to have no notable benefit than merely a single shell, as there was no discernible incremental gain in most strength properties.

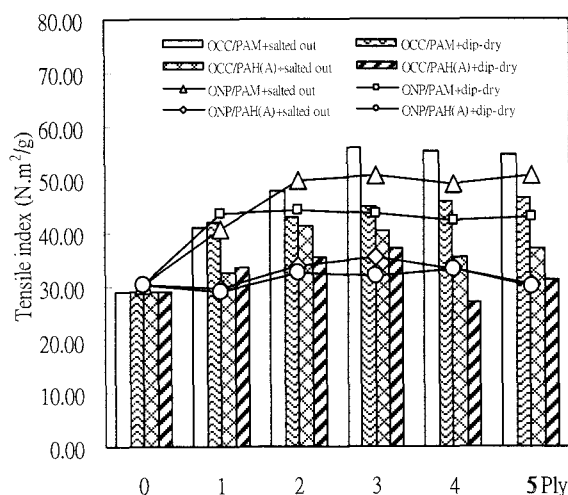


Fig. 1. Tensile strength modification by the polyelectrolyte shells for the OCC/ONP pulp.

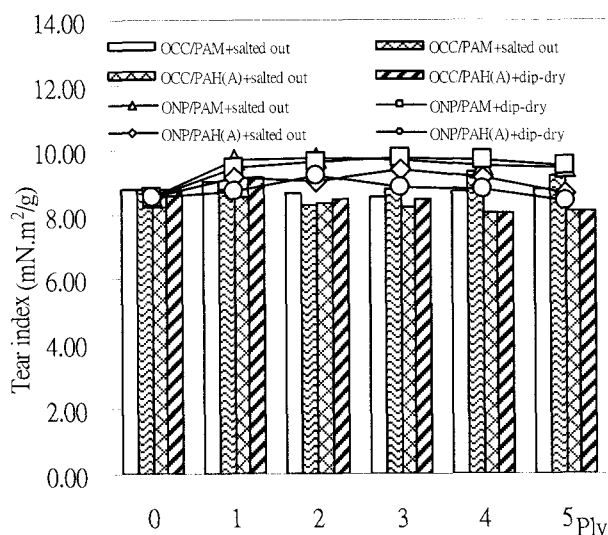


Fig. 2 Tear strengths of OCC/ONP pulps are generally unaffected

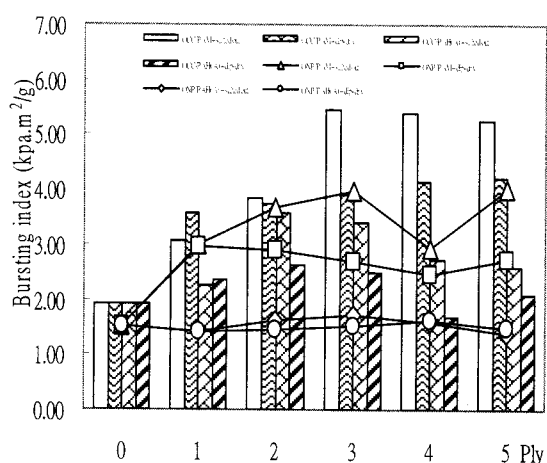


Fig. 3. Bursting indices of OCC/ONP pulps mostly improved with polyelectrolyte shells

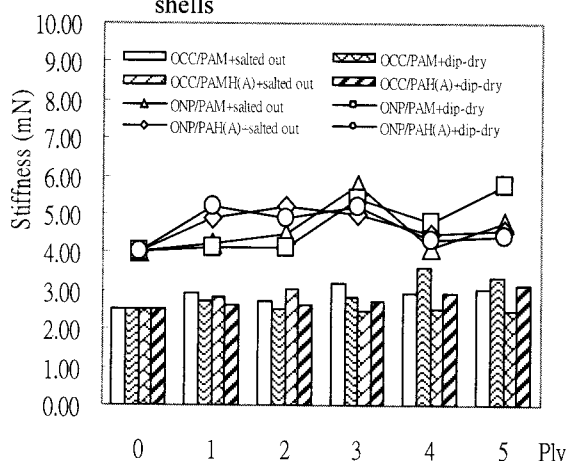


Fig. 4. Stiffness of OCC/ONP pulps showed slight modification.

We've noted that the polyelectrolyte solutions often tended to be viscose even at a concentration of 0.1%. The polymeric chains may be forced to shrink into spherical shapes under the same-charge ionic force exerted by other polymer molecules, reducing effective contacts with fiber surfaces, and could cause sloughing off with the multi-shells. Thus, it is probably warranted to test lower concentrations of the polyelectrolytes, as well as different dosages with regard to dry pulps. Higher charge densities on the polymer chains could exert potentially stronger ionic interaction with the fiber surfaces, allowing the avoidance of salting out, which is deemed impractical in on-line applications.

## 2. Multilayer polyelectrolyte-(platy) pigment on OCC and ONP fibers

Paperboard made from weak recycled pulp tends to be limp and lacking stiffness. Thus it is a prime subject for fiber engineering using polyelectrolyte shells. Instead of the anionic polyelectrolytes, we used mineral pigments to built micro-particulate dual retention systems on the fiber surfaces. The precept was that the stiff pigment-polymer shell might impart stiffness to the fibers despite a potential loss of

inter-fiber bonding strength. Results of the series of experiment are shown in Figs. 5 and 6.

In Fig. 5, handsheet properties of OCC pulps with 5 types of polymer-pigment shells up to 3 layer built onto fiber surfaces are shown. The handsheets were also split into calendered and uncalendered groups (A and B). Calendering made paper more compact, and denser. The A graphs on tensile, bursting, and folding strengths showed marked improvement when polymer-talc and polymer-sericite shells were built on the OCC fiber surfaces, while the corresponding montmorillonite and bentonite polymer shells didn't show much modification effects. The differences might have something to do with the specific charge densities of the pigments and the swelling characteristics of the layered inorganic (specifically bentonite and montmorillonite), might also reduce the effectiveness of the polymer-pigment shell. Tearing strength which largely dependent on intrinsic fiber length, was generally unaffected or slightly decreased by the modification procedures. Stiffness of the handsheet showed inconsistent modification through the procedures. Smoothness and air permeability of the handsheets decreased with montmorillonite or bentonite shells; and were comparable to the blank with the sericite or talc shells. Number of shell layers had minor or erratic effects on the general trends.

The B graphs show the uncalendered handsheet properties of the same sets plus polymer-PCC encrusted fibers. The observed trends and value ranges were largely the same as the calendered ones.

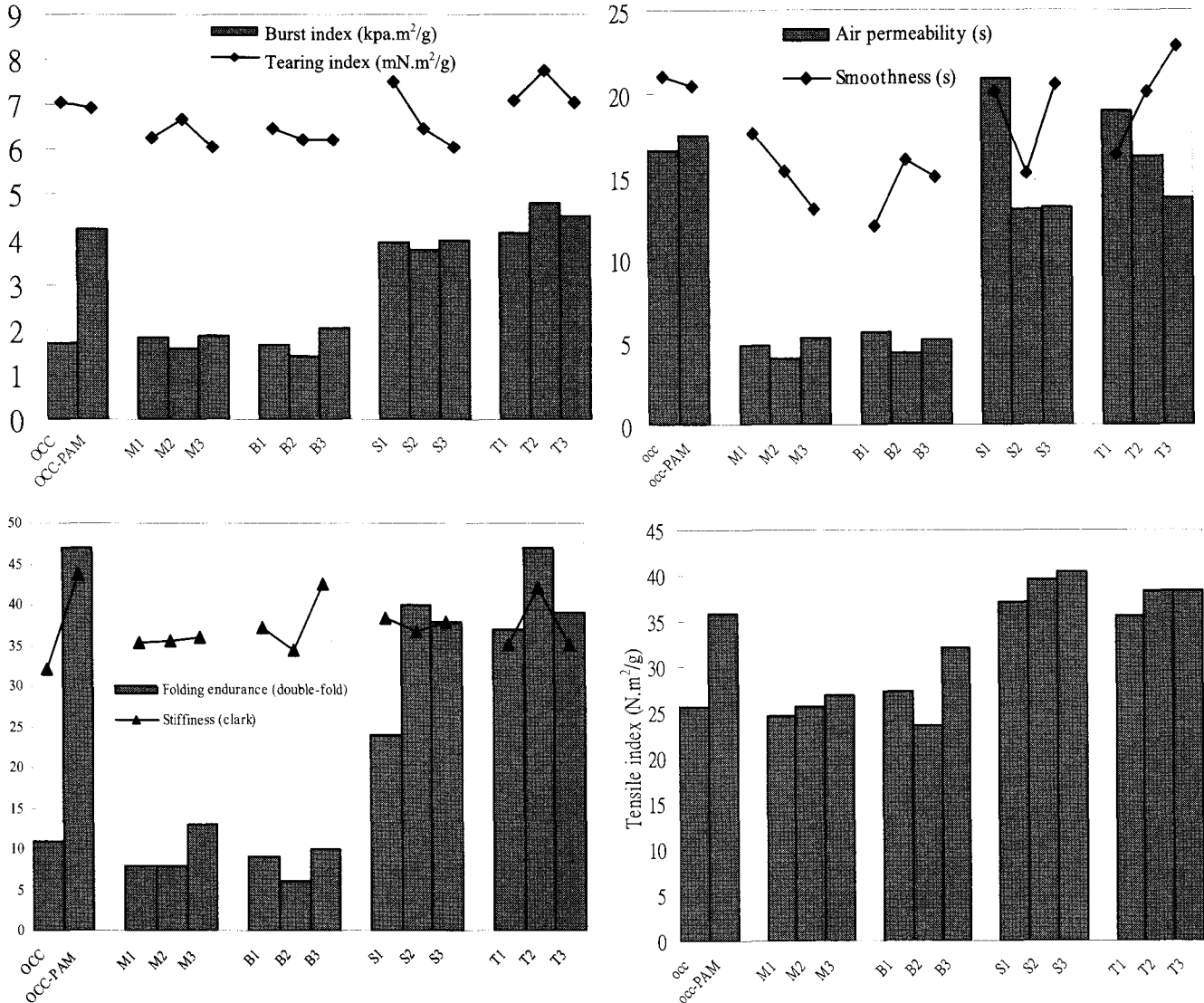
In Fig. 6, the uncalendered handsheets with 3% PAM and 6% PCC or montmorillonite were tested. The gain in stiffness was spotty, with PAM-PCC shells providing small increases, particularly at the double-shell level. The PAM-montmorillonite shells, however, had lower stiffness at the first shell, while the double-shell was stiffer than the original OCC pulp. In general, the PAM-PCC shell strengthened handsheet properties, provided notable increases in tensile, folding, and bursting in particular. Air permeability and smoothness of the PAM-PCC shells were also superior to the plain OCC handsheets. The PAM-montmorillonite shells gave lower performance than the blank, with folding endurance, air permeability was particularly poorer. The divergence of the 2 polymer-pigment shells was intriguing. Adding filler pigment to paper interferes with inter-fiber bonding and lowers paper strengths. In our modification scheme, the PAM-montmorillonite behaved as expected, but the PAM-PCC complex exhibited different characteristics, and provided a strengthening effect. In some cases, the enhancing or detracting characteristics of the polymer-pigment shells were proportionally to the shell numbers, suggesting that the shells may be fairly stable. The platy nature of montmorillonite and the spheroid PCC apparently

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formed polymer-pigment shells on fiber with different behaviors. The former probably formed a scale like covering on the fiber surfaces that reduced air permeability appreciably, while the random scaly structure might lower the smoothness. Furthermore, the swelling nature of montmorillonite might cause it

to adsorb fines particles and lowered effective bonding with fiber. On the other hand, the PAM-PCC shells were probably pliable and capable of good bonding with each others and provided strengths to the handsheets.

**A) Calendered**



B) Uncalendered

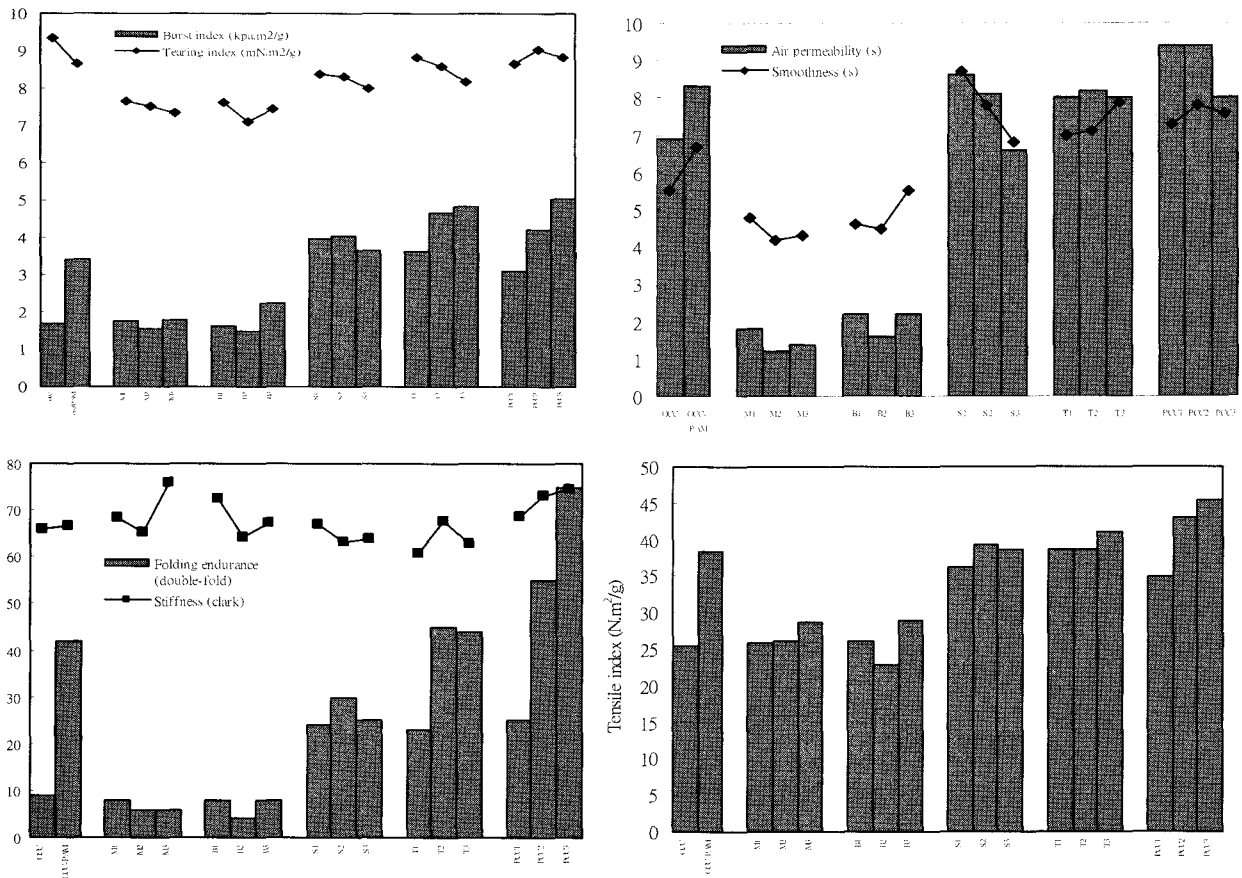
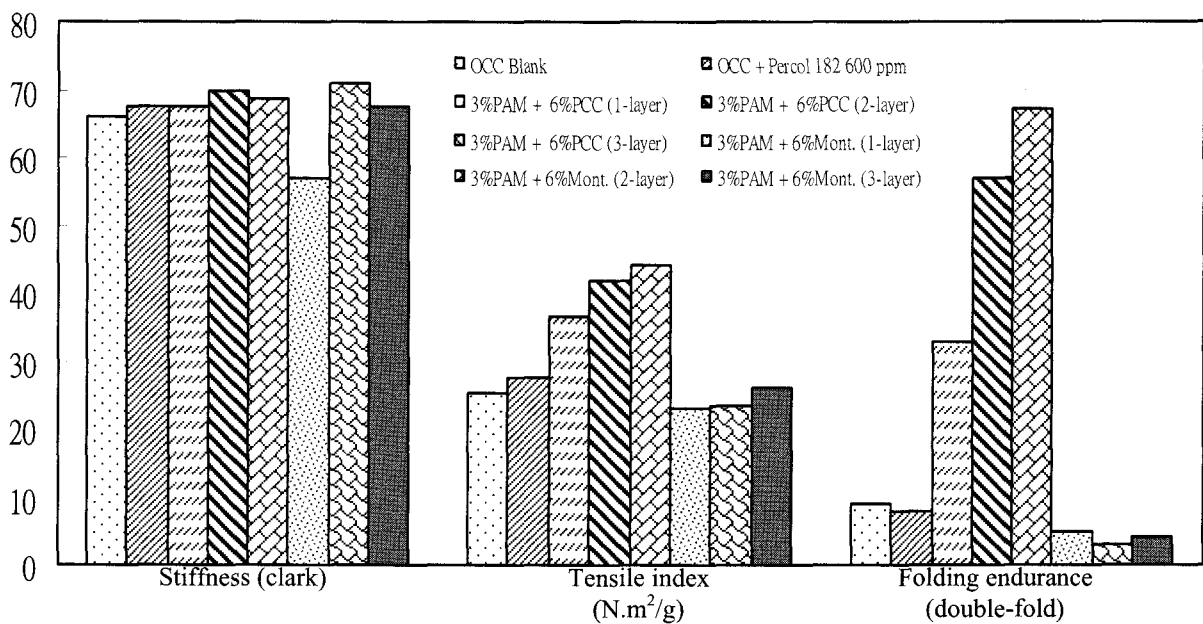


Fig. 5. A: Calendered handsheet properties prepared from OCC pulp modified with 3% PAM and 3% pigment shells of montmorillonite (M), bentonite (B), sericite (S), and talc (T), the number denote the shell layers. B: Uncalendered hand-sheet properties of the same modified pulp with precipitated calcium carbonate (PCC) included.



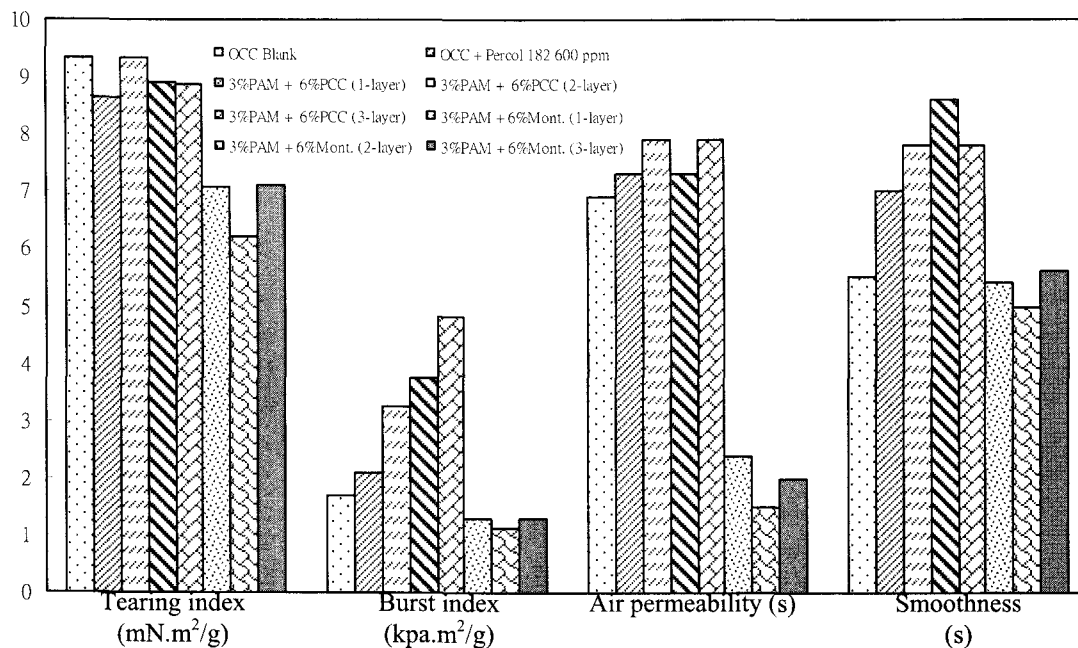


Fig. 6. Uncalendered handsheet properties prepared from OCC pulp modified with 3% PAM and 6% pigment shells of montmorillonite (Mont.) and precipitated calcium carbonate (PCC).

## CONCLUSIONS

We investigated some novel approaches to chemically modify weak secondary fibers. Alternating cationic and anionic polyelectrolytes shells built on fiber surfaces strengthened the fibers and improved paper properties made from such fibers. OCC and ONP pulps were either dipped-spun dried or salted out in the cationic polyallylamine, polyacrylamide and starch solutions. Subsequently treatments in anionic polyacrylic acid, polyacrylamide, and starch solutions were carried out, respectively. The results show that building multiple shells on worn-out fiber surfaces can strengthen the fibers and paper. The simpler and more practical impregnation-centrifuging treatment provided the desired effects, whereas the impractical salting out method produced somewhat superior fibers. The first pair of polymeric shells imparted marked strength improvement, whereas later layers had diminishing efficacies. Overall, the methods can improve fiber quality, attaining paper strength requirements. Alternate cationic polymer and pigment powders were also deposited on fiber surface based on the microparticulate system in anticipation of a stiffness gains. Platy minerals, such as montmorillonite, bentonite, sericite, clay and talc were added following cationic PAM. The results indicate that regardless of calendaring, stiffness of the handsheets did not improve appreciably while certain other strength properties showed gains.

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