MECHANISM AND DYNAMICS OF THE ROUGHENING OF PAPER IN CONTACT WITH MOISTURE

Toshiharu Enomae and Pierre Lepoutre

Paper Surface Science Program, University of Maine, USA

ABSTRACT

When paper is contacted by water or simply exposed to high humidity, the fibers swell and bonds break. The paper structure is altered; it loses strength and it roughens, adversely affected the print quality. Several hypotheses have been proposed to explain this roughening. Among them: Fibers swell and this causes a shape reversion from ribbon to tube; fibers swell and this leads to bond breakage; drying stresses are relaxed by the water or high humidity, and the paper structure changes, reaching a new equilibrium structure; the calendering stresses, that keep mechanical fibers flattened, are relaxed by water and the fibers return to their tubular shape.

There is now experimental evidence to support the view that surface structural changes are the result of changes both at the surface and in the bulk. Kinetics of the roughening phenomenon have been measured using a special device that monitors simultaneously the change in gloss (a good measure of roughening) and in moisture content when paper is subjected to a step change in relative humidity. Results show that gloss lags behind moisture pickup, confirming that bulk structural changes contribute largely to the surface changes.

It has been shown that it is not the changes induced by water, *per se*, that are the problem, but their irreversibility in a cycle of wetting and drying. Indeed some papers exhibit strong roughening in the environmental microscope but return to their smooth original state after drying.

The phenomenon of shape recovery (from ribbon to tube) has been given particular attention. Forseth *et al*¹⁾ have examined the decollapse of mechanical fibers in calendered papers, using image analysis on cross-sections. Their work shows a systematic correlation between amount of fiber decollapse and roughening, the effect increasing with cell wall thickness. The work also shows the effect of decollapse in the bulk of the sheet. We have examined the shape recovery from ribbon to tube for the case of Kraft fibers. Kraft fibers in a handsheet were examined after soaking in water, after defibering, after beating and compared to fibers from a reslushed lap pulp and the never-dried pulp by examining cross-sections of freeze-dried specimens. In the handsheets, surface fibers showed more extensive swelling than those inside, presumably because they are constrained from one side only. The collapsed fibers in the handsheet returned to the tube-like shape of the never-dried pulp, but only after beating.

It is concluded that, only in the case of mechanical fibers, is shape recovery a significant contribution to the roughening process. In mixed furnishes, swelling of the Kraft fibers may assist in decollapsing mechanical fibers.

INTRODUCTION

Water is applied to paper during coating and during printing, such as offset, water-based gravure, flexo and inkjet. It interacts with fibers and fiber network. It causes dimensional changes in plane as exemplified by cockling that occurs because of non-uniform drying and shrinking and misregister because of shrinking and out-of-plane as exemplified by surface roughening and fiber rising that all affect print quality.

Now, practical experiences of surface roughening are taken into account. In coating, coating smoothens surface by filling up voids but water in a coating color roughens up surface. In printing, gloss drops and becomes non-uniform. Fibrous texture appears behind the coating. This is called "fiber-rising."

These three electron micrographs show how fiber

rising happens. A specimen of uncalendered Light-Weight-Coated paper was observed in Environmental Scanning Electron Microscope, which permits to observe samples in humid environment²⁾. When water condensed on the coated paper surface (see picture "Wet"), fibers appeared to rise and push up the coating layer. The surface was rough in the wet state. Then, when the sample is dried again (see picture

What's the Problem ?

- Water is applied during:
 coating
- printing (offset, water/based gravure, flexo, inkjet)
- It interacts with fibers and fiber network

 It causes dimensional changes in-plane (cockling, misregister) and out-of-plane (roughening, fiber-rising) that affect print quality

The effect

- Coating.
 - Coating smoothens surface by filling up voids but
 - Water roughens up surface
- Printing
 - Gloss drops and becomes non-uniform
 - Fibrous texture appears behind the coating: "fiber-rising"

Fiber rising in ESEM



"Redry"), the fibers returned to the original locations and the surface looked similar to the initial dry one (see picture "Dry").

To acquire a roughening phenomenon quantitatively, a novel apparatus was developed to measure gloss changes. The figure is a sketch of the GlossMachine³⁾. A paper sample is attached to a metal stage with two-sided adhesive tape. The

stage is directly supported on a top-loading balance so that sample weight can be converted into moisture content. The chamber ceiling is equipped with a light source and detector for gloss measurement set at equidistant angles of 75 degrees. A metal plate is used as a reference. The ratio of paper gloss to that of the reference plate provides a relative gloss value. This system is for compensating for electrical drift and for eliminating absorption of light in the near infrared



Kinetics

- GlossMachine measures simultaneously: – Gloss change
 - Moisture pickup
 - during step change in humidity

band by water vapor. Humid air or dry air is supplied through small openings.

GlossMachine measures simultaneously gloss change and moisture pickup during step changes in humidity.

RESULTS AND DISCUSSION

These figures show changes in gloss and moisture content for supercalendered uncoated wood-containing paper. After drying, the sample was moistened at 90% relative humidity. On switching to 90% RH, the moisture content quickly increased and continued to increase even after 12 hours. Gloss decreased correspondingly, but its



initial rate of decrease was lower than the rate of moisture pickup as shown by the top right blow-up. The fact that gloss lags behind moisture pickup and is still decreasing well after the equilibrium at surface suggests that the surface continues to reflect the reconfiguration of fibers across the bulk even after a long time. In this sense, gloss relaxation can be considered, paradoxically, as a "bulk" process.

The figure shows the gloss relaxation and moisture content change as relative humidity was varied cyclically. Moisture content changed the same way every cycle. However, the gloss dropped step-by step during the humidity cycles. This way, gloss reduction was accompanied by irreversible changes as if mechanical stress relaxation had occurred.



- Gloss-change lags behind moisture pickup in the bulk.
- Thickness and roughness changes go hand in hand.

> Conclusion:

• Roughening is not only a "surface effect". But the reflection of irreversible structural changes in the bulk.

Possible mechanisms of roughening



This (above left) summarizes findings regarding gloss kinetics. Gloss-change lags behind moisture pickup in the bulk. Thickness and roughness changes go hand in hand. So, the conclusion here is: Roughening is not only a "surface effect", but the reflection of irreversible structural changes in the bulk.

This schematic diagram (above right) illustrates what kind of structural changes happens with a surface and a bulk of paper in contact with moisture or water. Possible mechanisms of surface roughening are fiber swelling, stress relaxation, fiber-fiber debonding and recovery to uncollapsed original shape. In addition, irreversibility is combined.

Details of the possible mechanisms indicated by the diagram will be discussed. The first one is relaxation of internal stresses. Internal stresses can be created during drying or during calendering. Internal stresses

are relaxed by the plasticization effect of water. Elements under stress, whether microfibrils or fiber segments, are now free to move to relax stresses. The relaxation is evidenced by: In-plane and out-of-plane movements of surface fibers in the ESEM, and shape recovery: Fibers which were not collapsed before calendering tend to recover their uncollapsed shape. Both are observed mostly with stiff, thick-walled mechanical pulp fibers.

The second possible mechanism is debonding. Cross-sectional changes due to swelling or shape recovery push apart bonded fibers when the bonds are weak and further weakened by water. If bonds break, fiber elements under stress may move irreversibly. This is evidenced by that in-plane drop in tensile strength is about 10% after wetting and redrying, but the effect is larger at surface since one-side bonded.

Mechanisms (cont'd)

• Fiber swelling

- BK fibers have the highest swelling potential (WRV increases by 100% as a result of beating)
- Swelling stresses are significant (Skowronski, 1988)
- Swelling is quite "visible" in the ESEM
- One would expect swelling stresses to cause collapsed kraft fibers to go from ribbon to tube ?

Mechanisms

Relaxation of internal stresses
 Internal stresses can be created during drying or during calendering.
 Internal stresses are relaxed by the plasticization effect of water. Elements under stress (whether microfibrils or fiber segments) are now free to move to relax stresses.
 Evidence:

 In-plane and out-of-plane movements of surface fibers in the ESEM.
 Shape recovery: Fibers which were not collapsed before calendering tend to recover their uncollapsed shape

 Observed mostly with *stiff, thick-walled* mechanical pulp fibers

Mechanisms (cont'd)

Debonding

- cross-sectional changes due to swelling or shape recovery push apart bonded fibers when the bonds are weak and further weakened by water
- If bonds break, fiber elements under stress may move irreversibly
- Evidence ?
 - In-plane drop in tensile strength is about 10% after wetting and redrying(Forseth, 1996)
 - But effect is larger at surface since one-side bonded

Mechanisms (cont'd)

• Fiber swelling

 Measurements on BK beech fiber cross-sections (round, thick-walled) reveal expansion about 7-10% between 10 and 90% RH (Nanko & Tada, 1995)

Presumably much larger with liquid water.

The third possible mechanism is fiber swelling (above left): There are a few evidences reported. Bleached kraft fibers have the highest swelling potential considering that Water Retention Value increases by 100% as a result of beating. Swelling stresses are significant. Swelling is quite visible in the ESEM. One would expect swelling stresses to cause collapsed kraft fibers to go from ribbon to tube?

And (above right), measurements on bleached kraft beech fiber cross-sections that are round and thick-walled reveal expansion about 7-10% between 10 and 90% relative humidity. Presumably, it would be much larger with liquid water.

The last possible mechanism for surface roughening is fiber shape changes. Mechanical pulp fibers are collapsed during calendering in the papermaking processes. The fibers recover a tube-like shape on re-wetting. In contrast, chemical fibers are easily collapsed during wet-pressing and drying and even more during calendering. After re-wetting and re-drying, fibers are collapsed. But,

what shape do chemical fibers take on re-wetting? This was the objective of our next experiment.

Before explaining the experiment, here is shape recovery behavior of mechanical fibers already reported. Mechanical fibers collapsed during supercalendering recovers a tube-like shape greatly after soaking in water and fairly after exposure to high humidity.







So, the objective (above left) of our next experiment is to determine to what extent kraft fibers, isolated, or in paper, recover a tube-like shape once wetted with water⁴⁾.

Samples were prepared following this flow-sheet (above right). Sample 1 is freeze-dried fibers prepared from never-dried kraft pulp. Sample 2 is a handsheet made from dry lap pulp after defibering and beating

without any additives. After ESEM observation of Sample 2, the specimen was soaked in water and freeze-dried. This is Sample 3. Sample 4 is freeze-dried fibers prepared from soaked and defibrated handsheets.



The micrograph (above left) shows fibers of never-dried wet pulp directly freeze-dried. Never-dried fibers appear to be tube-like and not to be collapsed.

The micrograph (above right) shows freeze-dried fibers prepared from soaked and defibrated handsheets. Fibers look all collapsed. Defibering should give a modest but certain effect on fiber swelling, so some swelling effect should be included in the shape. However, apparently the effect was not great enough to give rise to recovery to tube-like shape.

To examine fiber shape recovery more precisely, the same fibers on a handhseet surface were followed. The two micrographs show a surface of a dry handsheet and the same surface after soaking and

Handsheet Surface

Surface of handsheet made from beaten softwood kraft pulp





After soaking and freeze-drying (Wet sheet)



freeze-drying, which reproduces the wet state. They are very similar. However, it was found that some fibers shrank laterally very slightly by wetting.

If fiber edges are emphasized by image analysis, fiber width change is easily measured. The fiber width reduction was measured along indicated lines of the three fibers A, B and C.

The table shows the data of measured width shrinkage, which are 4.0, 9.0 and 11.5 %, respectively. If the fiber wall is assumed not to swell, the fiber shape can be predicted as shown by the sketches in the last column. Fibers A and B had a potential to recover some degree of tube-like shape. Probably, it is because those fibers are bonded on only one side and recover tube-like shape more easily. Fiber C underneath those two

Estimated Shape Change					
Shape of cross section	Thickness increase, %	<i>b</i> ,μm	<i>a</i> , μm	<i>r</i> ,μm	Width shrinkage, %
	0	0	11	3	0
	20	0.55	10.45	3	4.0 (Fiber C)
	40	1.25	9.75	3	9.0 (Fiber B)
	50	1.60	9.40	3	11.5 (Fiber A)

fibers recovered low degree of tube-like shape. The soaking time was 3 days. So, in conclusion, kraft fibers recover only a modest degree of tube-like shape even in the wet state.

CONCLUSIONS

Roughening by moisture is not a surface effect. It is mainly the surface reflection of bulk changes. Bulk structural changes occur as a result of water molecules diffusing into the fiber wall leading to: volumetric expansion in cross-section (swelling stresses), plasticization of the hemicelluloses thereby relaxing "dried-in" shrinkage stresses as well as the calendering-induced stresses that keep

Conclusions Poughening by moisture is not a surface effect. It is mainly the surface reflection of bulk changes Bulk structural changes occur as a result of water molecules diffusing into the fiber wall leading to: volumetric expansion in cross-section (swelling stresses) plasticization of the hemicelluloses thereby relaxing "dried-in" shrinkage stresses as well as the calendering-induced stresses that kee the fiber cross-section collapsed. Debonding of fibers at cross-over points, as a result of swelling and shape recovery.

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