Scanning Microscopy

Volume 8 | Number 1

Article 3

3-10-1994

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Päivi Forsberg
University of Maine

Pierre Lepoutre
University of Maine

Recommended Citation

Forsberg, Päivi and Lepoutre, Pierre (1994) "Environmental Scanning Electron Microscope Examination of Paper in High Moisture Environment: Surface Structural Changes and Electron Beam Damage," *Scanning Microscopy*: Vol. 8 : No. 1 , Article 3.
Available at: https://digitalcommons.usu.edu/microscopy/vol8/iss1/3

Scanning Microscopy, Vol. 8, No. 1, 1994 (Pages 31-34)
Scanning Microscopy International, Chicago (AMF O'Hare), IL 60666 USA

0891-7035/94$5.00+.25

ENVIRONMENTAL SCANNING ELECTRON MICROSCOPE EXAMINATION OF PAPER IN HIGH MOISTURE ENVIRONMENT: SURFACE STRUCTURAL CHANGES AND ELECTRON BEAM DAMAGE

Päivi Forsberg and Pierre Lepoutre*

Department of Chemical Engineering, University of Maine
Jenness Hall, Orono, ME 04469-5737

(Received for publication January 31, 1994, and in revised form March 10, 1994)

Abstract

Supercalendered and coated papers (SC and LWC) were examined using an environmental scanning electron microscope (ESEM). Moderate structural surface changes were observed as water condensed on the surface in a high moisture environment. The changes were fully or partially reversible depending on the sample origin. A wide range of contact angles could be observed when condensing water on uncoated wood fibers. While there was no visible indication of irradiation damage on the commercial paper samples examined nor on mechanical pulp fibers, attempts to look at chemical pulp fibers during wetting to examine fiber swelling were unsuccessful because of very rapid irradiation damage.

Key Words: Wood fibers, paper, fiber-rising, electron microscopy, surface properties, contact angle, supercalendered paper (SC), and light-weight coated paper (LWC).

*Address for correspondence:
Pierre Lepoutre,
University of Maine,
Jenness Hall,
Orono, Maine 04469-5737
Telephone number: (207) 581-2278
FAX number: (207) 581 2323

Introduction

Over the years, scanning electron microscopy (SEM) has found a wide range of applications in paper technology. In particular, SEM has been used successfully in the study of paper surfaces and of coating and printing defects. Until recently, water-fiber interactions could not be observed directly in SEM because of the high vacuum in the microscope chamber. The advent of the Environmental SEM (ESEM), which can be operated at low vacuum, allows the observation of paper structure when contacted with water.

We have recently used an ESEM to examine the roughening of paper surfaces when exposed to moisture. Cellulosic fibers are sensitive to moisture and during printing with offset or water-based gravure inks, interactions between water and paper can lead to undesirable changes in the paper structure. The most important effects are a reduction in gloss and a roughening of the paper surface. The fibrous texture of paper may also become apparent. This is often called "fiber-rising". The processes that cause roughening and fiber-rising are believed to be due to stress relaxation, swelling, and debonding. The fiber rising phenomenon has received much attention recently [4, 8-10].

The objective of our work was to study the roughening phenomenon "*in-situ*". The course of the work led us to examine the effect of electron beam on wet and uncoated cellulosic fibers.

Experimental

The ESEM (ElectroScan, Wilmington, MA) can observe specimens at relatively high pressures up to 20 Torr. Different parts of the microscope are maintained at different pressures. The electron gun still requires high vacuum and the vacuum is gradually lowered towards the specimen chamber using a series of pressure limiting apertures [2, 11].

Two different types of detectors can be used in the ESEM. The environmental secondary electron detector (ESD) collects ions and secondary electrons and the imaging is possible in the presence of almost any gas such as water vapor, oxygen, nitrogen, argon and methane. The back scattered electron detector (BSE) is a standard light probe which is operated at low pressure (< 1 Torr).

Our instrument is equipped with a thermoelectric stage (Peltier), which can be heated up to 100°C and cooled to 0°C, when connected to a constant temperature bath. In this work, water was made to condense on the paper surface by cooling the stage until the vapor pressure of water was above saturation.

Two commercial printing papers, supercalendered and light-weight coated papers (SC and LWC) were selected for this study. These competing paper grades are both supercalendered papers containing a mixture of mechanical and chemical pulps. The main difference between these grades is that SC paper is uncoated and LWC paper is coated. The LWC coatings are typically clay coatings with small amounts of adhesive binder.

Wetting and drying of paper in ESEM

A sample of the paper to be examined was attached to an aluminum specimen mount using double-faced tape. The sample mount was tilted 45° (in vertical direction) to enhance the changes in topography of the paper surface. The specimen mount was then brought into the microscope chamber and a picture was taken at room temperature. The microscope settings were 15 kV voltage, 50-70% condenser lens setting, 5-7 Torr vapor pressure, and 150-175x magnification. The sample was then wetted by cooling the stage to a temperature close to 0°C by circulating ice water through the stage until water was seen condensing on the paper surface. A picture of the wet paper was taken using the same microscope settings. After complete wetting, the sample was dried by letting the temperature of the thermoelectric stage warm back to room temperature. A picture of the dried sample was taken.

Results and Discussion

Roughening of the surface

Figures 1a, b, and c are micrographs of a commercial LWC paper before, during and after exposure to water. Before exposure to water, the surface looks relatively smooth. The features seen are fairly representative of LWC papers. Fibers are discernible, partially covered with coating, but they mostly lay flat. Small cracks in the coating can sometimes be seen, usually along the side of the fibers. When water is introduced, the fibers appear to swell. After drying, the structural changes may be almost totally reversible and the surface returns to its original state, or they may be only partially reversible, and the surface returns to an intermediate state as on Figure 1c. By comparing Figures 1a and c slight increase in cracking is evident along the edges of the fibers. The extent to which fine surface detail has been preserved is remarkable. On the other hand some increase in the amplitude of the undulation about the two underlying fibers is noted between Figures 1a and c, that is consistent with the even greater swelling of the same fibers apparent in the wet state (Figure 1b). We submit that such increase in irregularity may be responsible for the roughening and reduction of gloss. The changes seen with this particular LWC paper are typical for all six commercial LWC papers examined.

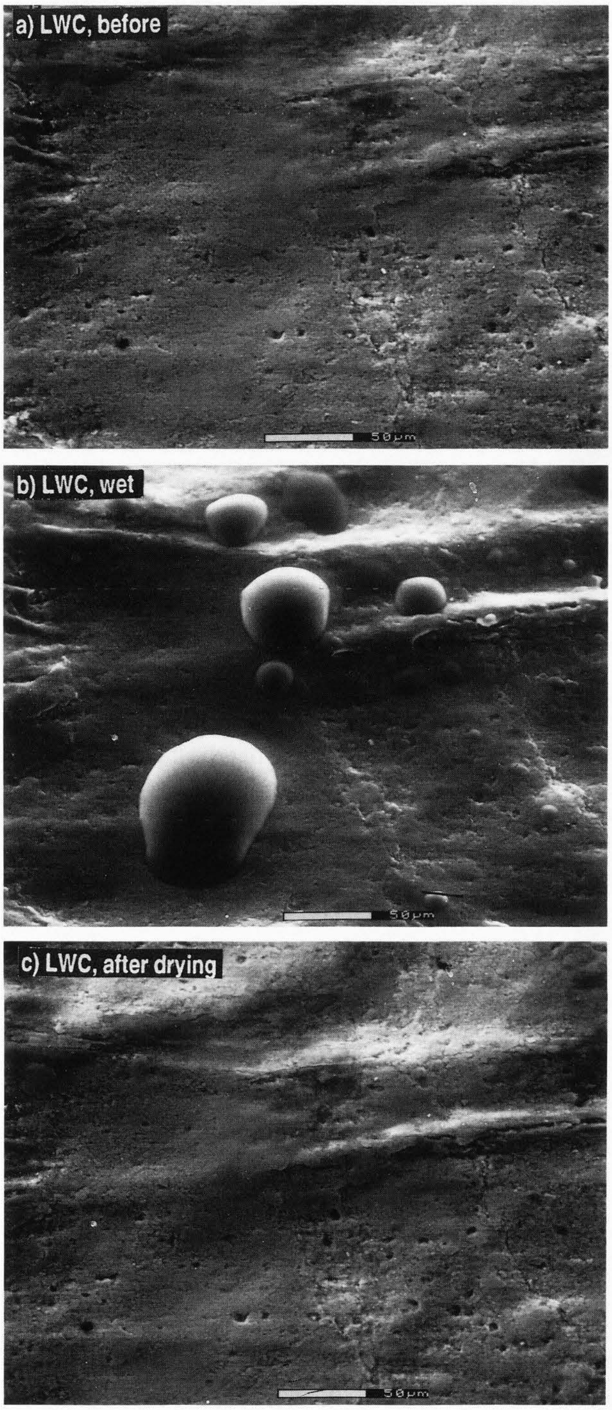

Figure 1. Light-weight coated (LWC) paper before wetting (a), wet (b), and after drying (c).

Similar observations were made on SC paper with clear evidence of roughening. The roughening of the SC paper could be explained by changes due to stress relaxation in the fibers bringing the network structure to a new equilibrium. This structure is rougher [4].

One side aspect of this work was the observation of water contact angle. When wetting the base paper (not coated)

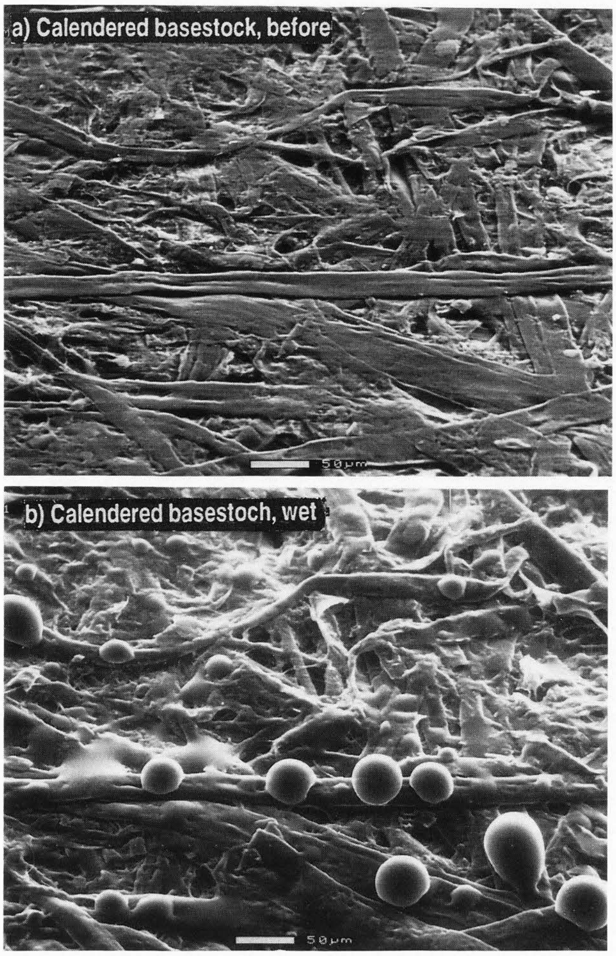

Figure 2. Calendered basestock before wetting (a) and wet (b).

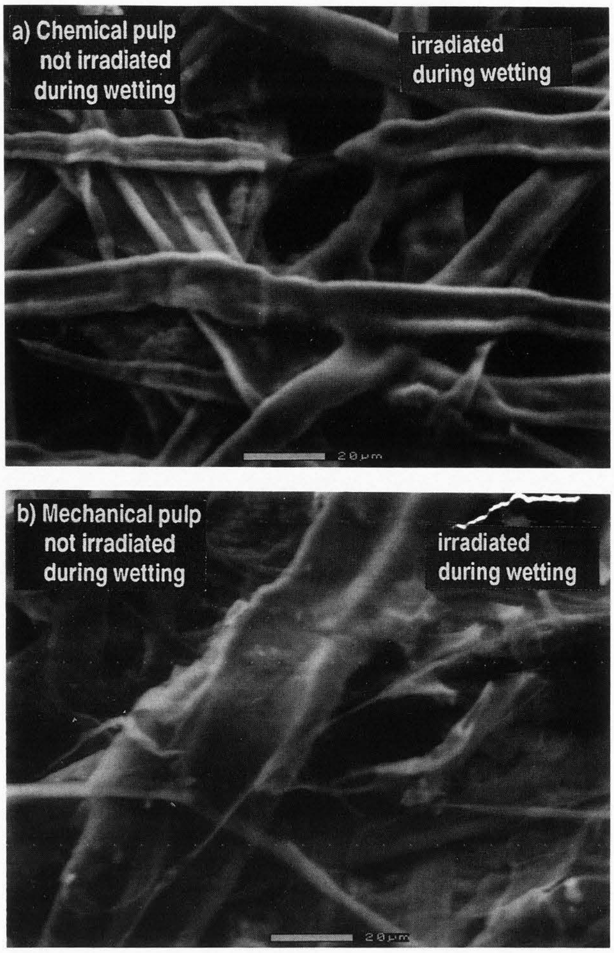

Figure 3. Handsheets of chemical (a) and mechanical (b) pulp after wet irradiation.

drops of water could be seen condensing on the surface of the fibers. One could follow the drops growing and observe a wide range of contact angles (Figures 2a and b). This gives an indication of the non-uniformity in surface energy of the basestock.

Electron beam irradiation damage

In this work, there was no evidence of electron beam damage of the commercial papers examined even though severe irradiation damage of uncoated cellulosic fibers in an ESEM had been reported earlier by Sheehan [7]. However, examination of laboratory handsheets in the ESEM in the presence of condensing water (15 kV, 50% condenser lens setting, 40 µm condenser aperture, 10 minutes exposure under 5-7 Torr water vapor pressure at 1-4°C) confirmed that serious beam damage occurred with chemical pulp but not at all with mechanical pulp fibers.

The seriousness of the irradiation damage depended on the accelerating voltage, current intensity, scanning rate and magnification. It also depended on the environment (pressure and temperature of the gas) and on the specimen [3]. The beam damage of wood in a transmission electron microscope (TEM) has been reported earlier by Mary et al. [5].

Figures 3a and b show the border between the irradiated area and unirradiated areas after wetting and drying of handsheets of chemical fibers and mechanical fibers respectively. Both softwood and hardwood fibers (chemical pulp) lost all surface details and the images looked very fuzzy (Figure 3a). Some fibers or fiber fragments could be seen to fall apart or even disappear. Even the dry fibers were damaged if the same area was imaged long enough. However, the degradation of kraft fibers was accelerated significantly by elevated humidity (presence of water). The fibers either "melted" and disappeared or small bubbles were formed on the surface of the fibers. Mechanical pulp fibers did not show any evidence of irradiation damage even after prolonged wetting (Figure 3b).

The presence of lignin in the mechanical pulp fibers seems to protect them against irradiation damage. It has been long known that high energy irradiation reduces the degree of polymerization and crystallinity and increases the solubility of a cellulosic material [1]. Recently, Revol has shown that the most important effect of this damage in a TEM is a rapid loss of mass. About 30% of mass was lost for lignin, while the loss was close to 70% for cellulose. This would indicate that cellulose is more susceptible to beam damage than lignin [6].

Printing papers such as SC and LWC papers are made from a mixture of mechanical and chemical pulp fibers. In chemical pulping, lignin, the "glue" that holds fibers together is dissolved by treating wood chips with an alkaline solution under pressure. Further bleaching removes the residual lignin, leaving fibers consisting mainly of cellulose and hemicelluloses. In contrast, in mechanical pulping, fibers are separated by mechanical action so that they still contain lignin on their surfaces and also other components of wood, such as resin (abietic acid) and fatty acids. The presence of lignin, a complex aromatic compound and of these other chemicals seems to protect the mechanical pulp fibers but also the chemical pulp fibers in these commercial papers. We are currently examining this aspect further.

Conclusions

ESEM observations of LWC and SC papers as water condenses at the surface demonstrate that extensive roughening takes place even on papers for which the changes are almost completely reversible upon drying.

While extensive irradiation damage by the electron beam occurred rapidly upon wetting of chemical pulp fibers, no damage could be observed on mechanical pulp fibers, nor on any of the commercial paper samples examined even though they contained a large fraction of chemical fibers.

Acknowledgment

The authors wish to thank the industrial sponsors of the University of Maine Paper Surface Science Program.

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Discussion with Reviewers

T.A. Kuster: It appears that only certain fibers swell during wetting in Figure 1b. Could these be the same fibers that are subject to beam damage?

Authors: Interactions between water and paper can lead to undesirable changes in the paper structure. The most important effects are a reduction of gloss and roughening of paper surface, also called fiber-rising. This phenomena affects especially wood-containing papers like LWC and SC papers. The processes that cause fiber-rising are believed to be due to stress relaxation, swelling, and debonding. The fiber-rising phenomenon has traditionally been linked to mechanical fibers, as chemical pulp fibers (kraft) collapse when dried, and don't swell without mechanical action. In our experiments, chemical pulp fibers are damaged by the electron beam, while mechanical pulp fibers are not.

T.A. Kuster: You mention that perhaps the presence of lignin and other remaining chemicals seem to protect the mechanical pulp fibers from beam damage. Could it be just the opposite? The removal of lignin and other chemicals during chemical pulping could make the chemical pulped fibers susceptible to beam damage.

D. Caufield: Can you suggest possible mechanism by which the presence of lignin or lignified fibers prevents beam damage?

Authors: We hypothesize that the irradiation damage is the result of attack of the cellulosic polymer by free radicals whose production is accelerated by high humidity. Because the ESEM chamber is filled with water vapor, radiolysis products of water are always present and thus can degrade beam-sensitive specimens even in "dry" conditions. The presence of lignin in mechanical pulp fibers seems to prevent degradation. This could be due to the presence of aromatic groups in lignin that can absorb and stabilize free radicals that otherwise cause degradation. Indeed, lignin's ability to capture free radicals has already been utilized in the rubber industry where it is used as an antioxidant.