Polymer-Grafted Cellulose Fibers. III. Interactions of Grafted and Ungrafted Fibers in Handsheets

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ABSTRACT: In addition to enhanced absorbency, handsheets incorporating hydrolyzed methyl-acrylate-grafted (HMAG) Kraft fibers exhibit enhanced tensile strength and stretchability [E. Rezai and R. R. Warner, *J. Appl. Polym. Sci.,* **00,** 000 (19XX)]. These handsheets have a unique morphology. In a handsheet, grafted fibers form stretched planar sheets that appear to bond with neighboring ungrafted fibers. This meshwork of interwoven, stretched cellulose/polymer sheets bonding with normal ungrafted fibers likely accounts for the enhanced tensile strength and stretchability of HMAG-containing handsheets. Analytical electron microscopy is shown to be a useful technique for investigating polymer-grafted fibers in handsheets. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1487–1492, 1997

Key words: wood fiber; handsheets; grafted fibers; methyl acrylate; morphology; electron microscopy; AEM; EPA; SEM

INTRODUCTION

Compared to handsheets of normal Kraft fibers, handsheets incorporating 20% hydrolyzed methyl-acrylate-grafted (HMAG) fibers have a twofold increase in dry tensile strength, a threefold or greater increase in wet tensile strength, and a greater stretchability with a fivefold increase in tensile strain, as shown in an accompanying paper.[1] In an effort to understand the enhanced mechanical properties of handsheets containing grafted fibers, electron probe analysis (EPA) and analytical electron microscopy (AEM) were used to visualize the sodium counterion in HMAG fibers, as in the preceding paper,[2] and thereby determine the distribution of grafted fibers within handsheets. These techniques revealed an altered morphology of handsheets containing HMAG fibers that provided a clear understanding of their enhanced mechanical performance.

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EXPERIMENTAL

Handsheets were prepared as described previously.[1] A control handsheet was prepared from ungrafted Southern Softwood Kraft (SSK) fibers. A similar handsheet was prepared containing 10% HMAG SSK fibers (grafted with a 3 : 1 ratio of monomer/pulp). A third handsheet was prepared with 50% HMAG (3 : 1) fibers.

Scanning Electron Microscopy (SEM)

A 1-cm square was cut from a handsheet and secured to a specimen stub with double-sided Scotch tape. Analyses were performed with a Hitachi S-800 field emission SEM operated at 2 kV on gold-palladium coated specimens.

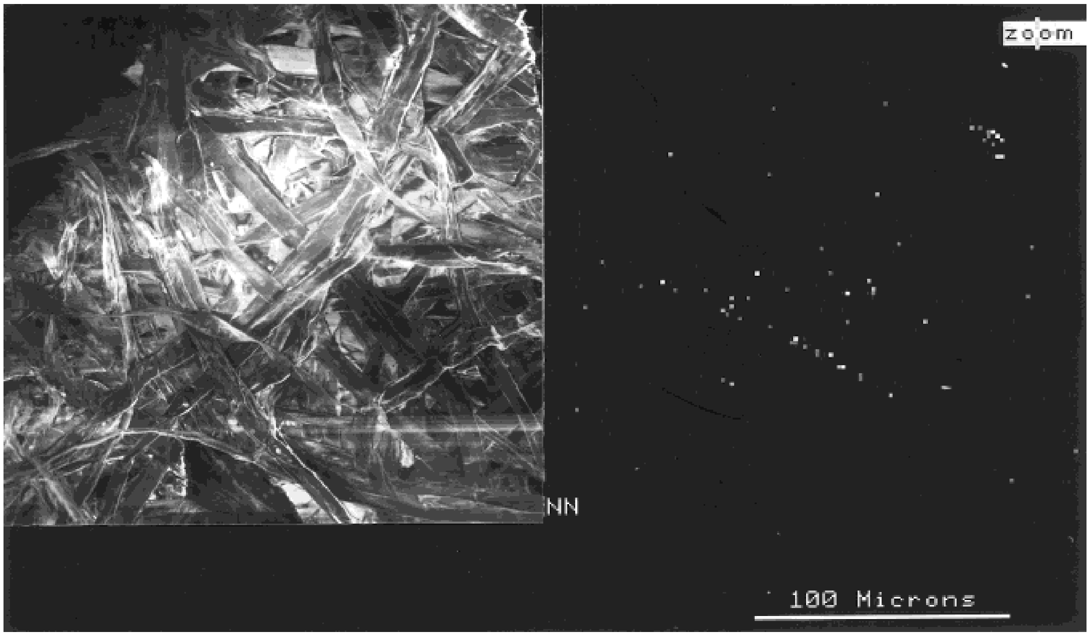

Figure 1 The left EPA image (equivalent to an SEM image) shows a control handsheet made of ungrafted SSK fibers. The right image is the corresponding X-ray map showing the distribution of sodium in this sample. White denotes high levels of sodium (there are few), and gray indicates lower values. The two images correspond point by point. Generally, sodium is absent from the fibers. 100×.

Electron Microprobe Analysis (EPA)

A 1-cm square was cut from a handsheet and secured to a specimen stub with double-sided Scotch tape. The sample was coated with carbon in a Denton 502 evaporator and analyzed at 10 kV and 5 or 8 nA sample current with a Cameca MBX microprobe equipped with a Tracor Northern 5500 energy dispersive X-ray spectrometer.

Analytical Electron Microscopy (AEM)

Squares or rectangles a few millimeters on a side were cut from a handsheet and submerged in nitrogen-free, pre-evacuated L. R. White resin (Ted Pella Co., Redding, CA) and polymerized overnight at 60°C. Sections 1 μm thick were cut dry using an ultramicrotome with glass knives. Sections were mounted on Formvar films stretched across nickel slot EM grids (Ted Pella Co.). Analyses were performed with a Hitachi H-500 operated in the scanning transmission electron microscopy (STEM) mode at 100 kV and 0.5 nA sample current. Digital STEM images and X-ray sodium maps were obtained with a Tracor Northern 5500 energy dispersive spectrometer equipped with a beryllium window (Noran Instruments, Madison, WI). X-ray maps were acquired for 4–8 h. Since the acrylate functionality exists predominantly as the sodium salt, the localization of sodium effectively localizes the polyacrylate grafts (see below).

RESULTS AND DISCUSSION

Control NSK Handsheet

The morphology of a control handsheet is shown in the left (EPA) image of Figure 1. Ignoring the sample charging (white glare) commonly observed in the SEM analysis of paper, wood fibers are plentiful and intertwined. At points of contact they interact with sufficient bonding to form a cohesive structure. The right image of Figure 1 is the corresponding X-ray map of the sodium distribution. As described previously,[2] the right and left images correspond point by point. From the X-ray map, sodium is generally not present in the handsheet, similar to results shown previously for normal fibers using AEM.[2] Occasionally, localized regions of some fibers do contain sodium at low levels, as indicated by the white dots sparsely distributed across the X-ray image.

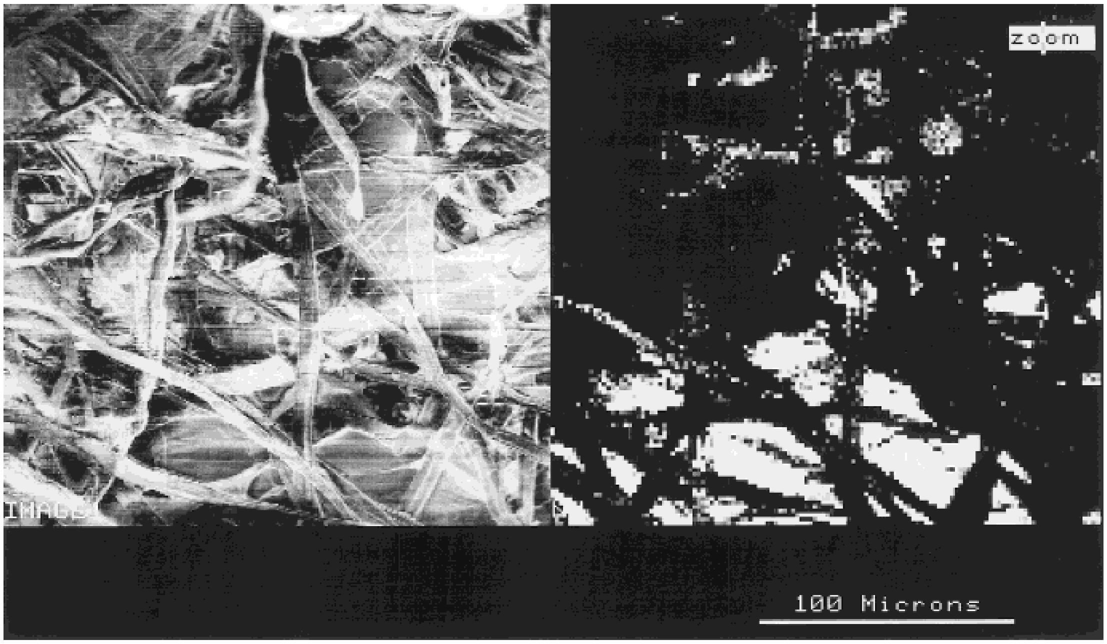

Figure 2 The left EPA image from the handsheet with 10% grafted fibers shows semitransparent planar "sheet-like" regions just beneath the surface. The corresponding X-ray map shows the sodium (acrylate) distribution. The two images correspond point by point. White in the X-ray map denotes high sodium levels, which largely correlate with the planar regions. 100×.

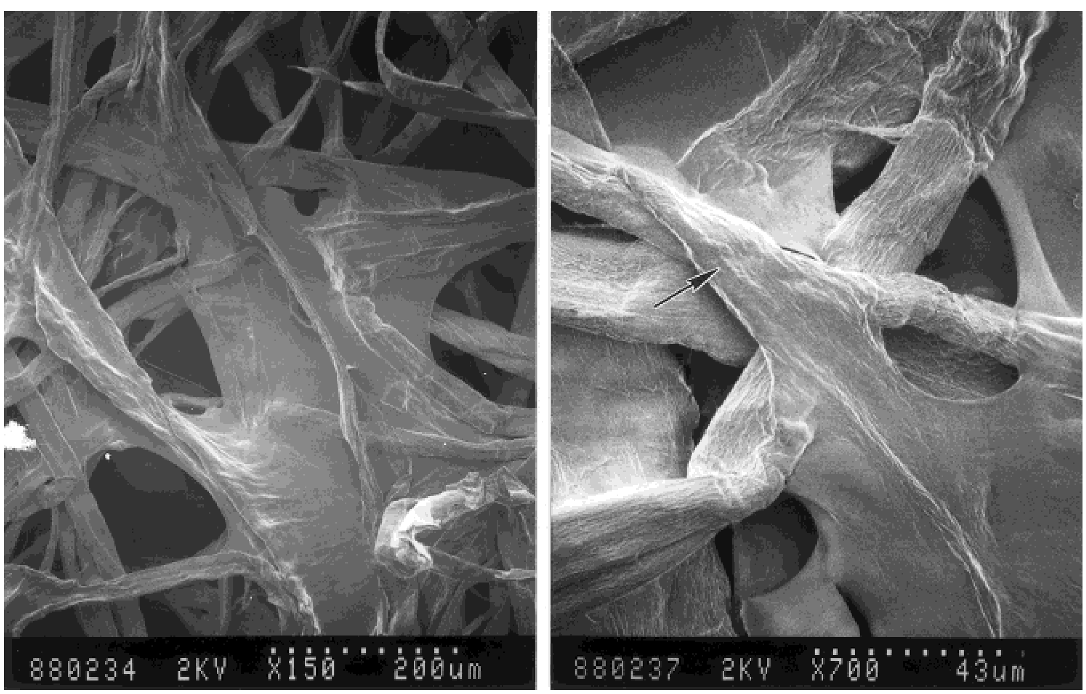

Figure 3 SEM images of a handsheet composed of 50% ungrafted SSK fibers and 50% hydrolyzed methyl-acrylate-grafted (HMAG) SSK fibers. Planar regions enmesh ungrafted fibers. Left image 150×; right image 700×.

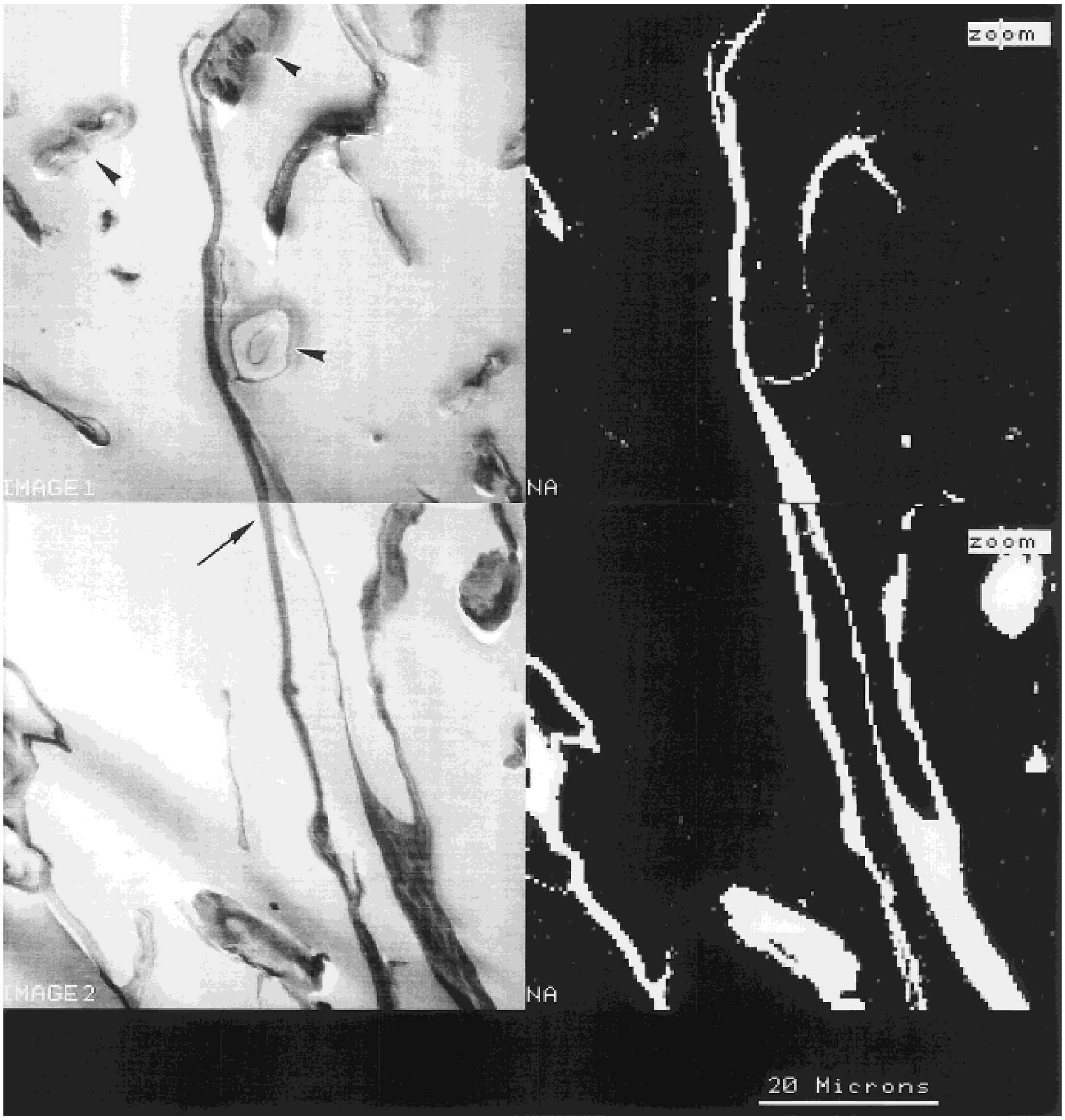

Figure 4 A composite (montage) of two STEM images and their corresponding sodium X-ray maps from a cross section of a plastic-embedded handsheet containing 50% HMAG fibers. Comparing the STEM images and X-ray maps, the planar regions are seen to contain polyacrylate. 1500×.

Handsheet Incorporating 10% HMAG Fibers

As shown in the left (EPA) image of Figure 2, this handsheet differs from the control in that an additional component is present; slightly below the surface fibers are semitransparent sheetlike regions. As shown in the corresponding X-ray map of the sodium distribution, these sheetlike regions are high in sodium (white denotes high sodium levels) and therefore polyacrylate. The sheetlike structures were formed from HMAG fibers during handsheet formation; from the previous paper, sheetlike structures were not associated with HMAG fibers dried from ethanol.[2]

Handsheet Incorporating 50% HMAG Fibers

Sheetlike regions are also observed in the 50% HMAG fiber-containing handsheet shown in the SEM images of Figure 3. As shown in the left image, planar sheetlike material appears to be

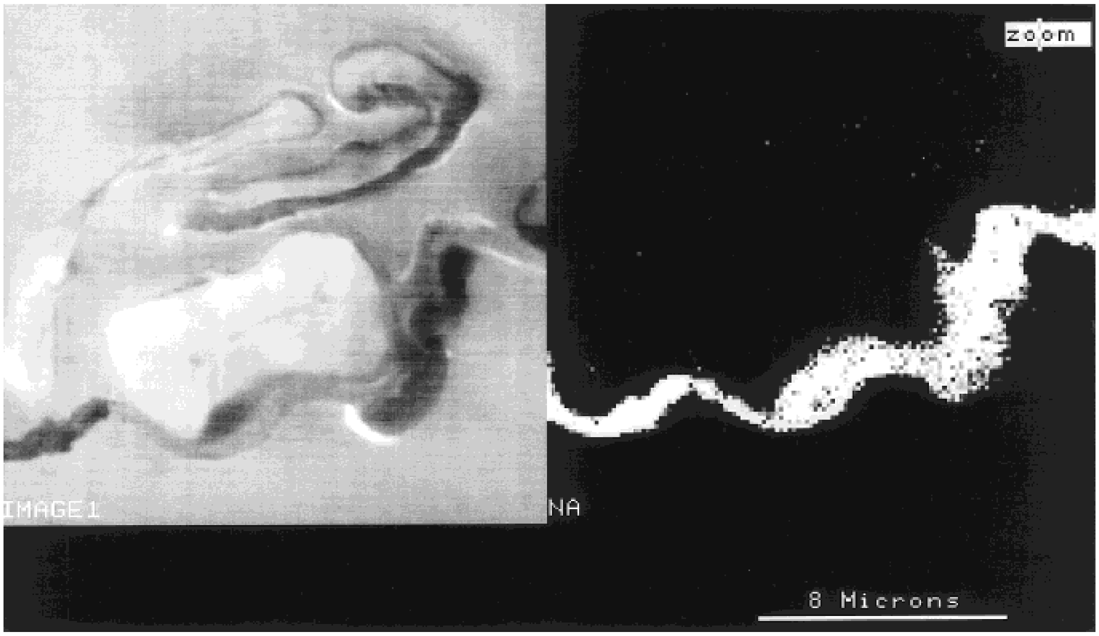

Figure 5 A STEM image and its corresponding sodium X-ray map from a cross section of a plastic-embedded handsheet containing 50% HMAG fibers. An ungrafted SSK fiber is in intimate contact with a ribbon of polyacrylate-containing material. 5000×.

acting like a "region weld," enmeshing and holding a number of fibers together. At a higher magnification in the right SEM image, what initially appears to be a fiber in the upper left region of this micrograph (arrow) becomes progressively stretched along its length until it forms an extensive planar sheet that completely fills the right side of this image.

A STEM image (composite) of a handsheet in cross section is shown in Figure 4. The two contiguous STEM images on the left show normal-appearing SSK fibers in cross section (arrowheads) along with irregularly shaped, often planar forms that are extensive in length, shown here vertically bisecting the two STEM images for nearly 150 μm (arrow). The corresponding sodium X-ray maps on the right of the STEM images reveal the distribution of the grafted fibers, marked by their sodium (polyacrylate) content. Two apparently intact HMAG fibers can be seen in the lower X-ray map; one in the upper right corner, the other in the lower middle of the image. The planar structures also contain polyacrylate. By comparing the STEM and X-ray images, some of these planar structures can be seen coating or adhering to ungrafted fibers, as shown along the extended planar cross section that bisects the upper X-ray map. An example of this interaction between ungrafted fibers and HMAG fiber "sheets" is shown more clearly at higher magnification in Figure 5. Near the bottom of the STEM image is a continuous ribbon shown by the corresponding X-ray map to contain (sodium) polyacrylate. This ribbon snakes across the field of view and contacts an ungrafted fiber, conforming very closely with its shape along nearly half of its circumference.

CONCLUSIONS

Handsheets containing HMAG fibers exhibit an unusual structure consisting of sheetlike planar regions that interconnect with ungrafted fibers. These planar regions contain high levels of sodium and therefore contain polyacrylate; that is, they were once fibers. It therefore appears likely that these planar regions are formed during the drying process as grafted fibers are stretched into sheets. That fibers do give rise to the planar regions was demonstrated in Figure 3, right image, which showed continuity between a fiberlike and planar region. One scenario explaining "sheet" formation envisions a highly swollen grafted fiber attaching itself to two adjacent ungrafted fibers. During drying, the swollen fiber would shrink but could not retract from its attachment to ungrafted fibers, which themselves might additionally separate due to the forces of drying. Consequently, the grafted cellulose would deform into a stretched sheet, as observed. The resulting handsheet structure is more cohesive, with grafted fiber "region welds" connecting multiple ungrafted fibers. This property is likely responsible for the increased tensile strength of handsheets containing grafted fibers, and connecting acrylate planes would explain the enhanced strain of these handsheets.

This study highlights the usefulness of electron probe analysis and analytical electron microscopy in elucidating the distribution of grafted fibers within a handsheet. These techniques were crucial for confirming the identity of the planar regions.

Handsheets formed from acrylate-grafted fibers have substantial enhancements in absorbent capacity, absorbent rate, wet and dry strength, and strain. We believe this remarkable feat is due to our chemically changing the morphology, absorbing mechanisms, and physical properties of wood fibers to produce paper that consists of a more absorbent material with simultaneously enhanced elasticity and inter-fiber bonding.

REFERENCES

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2. R. R. Warner and E. Rezai, *J. Appl. Polym. Sci.,* **65,** 1471 (1997).