

Polymer-Grafted Cellulose Fibers. I. Enhanced Water Absorbency and Tensile Strength

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Received 26 July 1996; accepted 17 January 1997

ABSTRACT: To enhance the water absorbency of wood fibers, various acrylic monomers were grafted to these fibers using cerium IV initiation followed by base hydrolysis. The absorbent capacity of hydrolyzed methyl acrylate- or acrylonitrile-grafted wood pulp fibers was an order of magnitude greater than ungrafted pulp fibers. A portion of this enhanced absorbency could be attributed to graft-induced osmotic forces. Enhanced absorbency was relatively independent of wood fiber type. Paper handsheets incorporating 20% grafted fibers had a fivefold increase in absorbent capacity, a twofold increase in dry tensile strength, a threefold or greater increase in wet tensile strength, and were more stretchable. In addition to enhanced absorbent capacity, the rate of absorbency was approximately 50% greater. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1463–1469, 1997

Key words: wood fiber; methyl acrylate; acrylonitrile; paper; absorbency; tensile strength

INTRODUCTION

Our objective in this investigation was to enhance the absorbency of paper, particularly paper towels. Given the limitations of capillarity and the void volume of a handsheet,¹ we endeavored to change not the handsheet structure but instead the absorbency of the wood cellulose fiber itself. Enhanced absorbency can be achieved by increasing the inherent capillarity of the absorbing structure as well as by building in osmotic forces within the fiber. We endeavored to incorporate both mechanisms by adding osmotic forces for water storage and by increasing the capillarity of the cellulose fiber wall by altering its internal composition and structure.

Due to the void structure created by wood fibers

in paper towels, capillarity provides a fast rate of absorbency, but the absorbent capacity (ability to hold the fluid tightly) is low. Conversely, charged hydrogels consisting of crosslinked sodium polyacrylates have a huge absorbent capacity due to their inherent high osmotic force, but their capillarity and rate of absorbency is low.^{2,3} Our approach to enhanced absorbency in paper towels was to combine the best characteristics of these two different absorbing structures by chemically creating a charged hydrogel within the cellulose wall of individual wood fibers. In this article we describe the production and physical properties of the grafted fibers and handsheets. In the accompanying two articles we describe the chemical and structural alterations of grafted fibers, demonstrating the successful incorporation of crosslinked sodium polyacrylate polymer grafts within the cellulose fiber wall that accounts for the enhanced absorbent rate and capacity,⁴ and then describe the structural alterations of handsheets incorporating grafted fibers that account for the increased tensile properties.⁵

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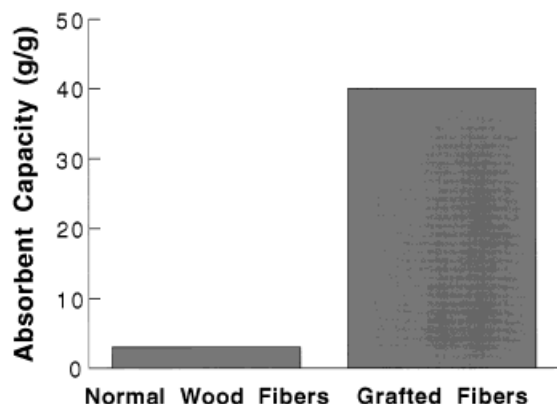


Figure 1 Water uptake capacity (TBGV in g/g) of normal ungrafted SSK wood fibers is an order of magnitude less than that of SSK fibers grafted with methyl acrylate at a 3 : 1 monomer/pulp weight ratio and hydrolyzed.

EXPERIMENTAL

Materials

Northern Softwood Kraft (NSK) and Southern Softwood Kraft (SSK) pulp fibers, aspen and eucalyptus pulp fibers, and cotton linter were obtained from Buckeye Cellulose, Inc., Memphis, TN. Acrylic monomers were purchased from Polyscience Inc. Ceric ammonium nitrate was obtained from Fisher Scientific Co.

Synthesis

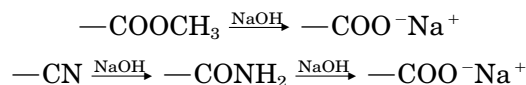
Grafting

Following the general procedure of Lepoutre and Hui,⁶ and as described in detail elsewhere,⁷ pulp in water was filtered to ~ 30% consistency and diluted approximately sixfold with water acidified with concentrated nitric acid to pH 2. Monomer at 0.5 to 4 times the weight of pulp was added and agitated for 10 min. Under a nitrogen or argon atmosphere, ceric ammonium nitrate, approximately 5 wt % of the pulp, was dissolved in water acidified with nitric acid to pH 2, added to the reaction mixture, and the contents agitated for 15 min. After allowing the reaction mixture to set for 4 h, it was filtered and washed with distilled water to remove any ungrafted material. This grafting procedure was done at room temperature.

Hydrolysis

As described in detail elsewhere,⁷ grafted fibers were added to a stirred 3% sodium hydroxide solu-

tion at approximately 90°C and allowed to react for 2 h. The reaction is shown below for methyl acrylate and acrylonitrile.



The fibers were removed and washed with distilled water.

Handsheet Preparation

Handsheets were prepared by the conventional TAPPI method. Briefly, pulp and acrylate-grafted fibers were properly mixed at 0.1% consistency in the Deckle box. They were drained on wire, exposed to vacuum to remove most of the water from the fibers, and dried by a drum drier.

Physical Measurements

Absorbent Capacity

Absorbent capacity was assessed by Tea Bag Gel Volume (TBGV), defined as the water retained after centrifugation for 10 min at 125 G (gravity) force.⁷

Absorbent Rate

Absorbent rate was determined as the initial slope of water sorption (g/g) vs. time over the first 10 s, as assessed in horizontal gravimetric wicking experiments (zero load); in these experiments, handsheets are placed on a balance and

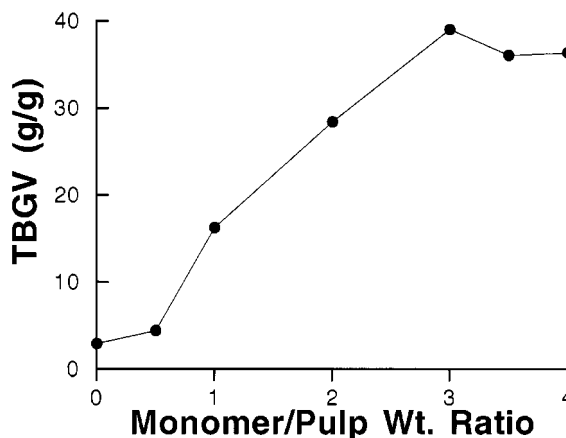


Figure 2 Effect of the ratio of monomer/pulp during synthesis on the absorbent capacity of hydrolyzed methyl-acrylate-grafted (HMAG) SSK fibers.

Table I Characterization of Hydrolyzed Methylacrylate-Grafted NSK Fibers: Water Absorbency and Carboxylate Number

Monomer/Pulp Weight Ratio	TBGV g/g	Carboxyl Number (mEq/100 g)	
		Titration	NMR
1 : 1	12.2	413 ± 7	270
2 : 1	24.5	552 ± 12	361
3 : 1	36.1	651 ± 9	552
4 : 1	31.2	768 ± 80	612

fluid delivered from below through a small-diameter (6 mm) tube under zero hydraulic pressure. Weight gain (fluid uptake) is monitored continuously until equilibrium is attained.

Grafting Level

The grafting level was measured gravimetrically and confirmed by carboxyl number as determined by ^{13}C -NMR⁸ and by direct titration as described in TAPPI Standard Methods T237 os-77: "Carboxyl Content of Pulp."

Tensile Strength

Dry tensile strain, dry tensile force, and wet tensile force were measured essentially as described in TAPPI Standard Methods T456-OM-82 and T494-OM-81 at the standard conditioning and testing atmosphere described in TAPPI T402-OM-83. Additional details are given elsewhere.⁷

Swollen Fiber Morphology

The morphology of swollen fibers was investigated at the light microscopy level using a Wild stereomicroscope and Polaroid film or a Zeiss Universal Research Microscope with image capture by videotape using a Hamamatsu newvicon camera and Photonic Microscope live video processor. Fiber swelling was characterized as "no swelling," "ballooned,"⁹ or "unrestrained swelling."

RESULTS AND DISCUSSION

Grafted Fibers

Fiber Absorbent Capacity

Figure 1 presents a typical comparison in absorbent capacity between normal ungrafted SSK fibers and hydrolyzed methyl-acrylate-grafted (HMAG) SSK fibers. The HMAG fibers exhibit an order of magnitude increase in absorbent capacity relative to ungrafted fibers. The absorbent capacity of grafted fibers is directly related to the monomer/pulp weight ratio used in synthesis, as shown in Figure 2. There is a nearly linear increase in absorbent capacity (TBGV) with monomer concentration, although absorbent capacity appears to saturate at a monomer/pulp ratio near 3.0. The saturation in absorbency is not due to saturation in grafting levels, as shown in Table I for HMAG NSK fibers. As indicated in this table, increasing monomer levels during synthesis directly leads to an increasing incorporation of acrylate (carboxyl) functionalities in grafted fibers. Although acrylate levels of grafted fibers continuously increase with the increasing monomer/pulp ratios, absor-

Table II Characterization of Hydrolyzed Methylacrylate-Grafted SSK Fibers: Water Absorbency and Swelling Behavior^a

Monomer/Pulp Weight Ratio	TBGV g/g	Swelling Degree (% of Fibers)		
		No Swelling	Ballooned	Unrestrained Swelling
0	3.0	100	0	0
0.5 : 1	4.5	50	50	0
1 : 1	16.3	6	63	31
2 : 1	28.5	0	22	78
3 : 1	39.1	0	0	100
4 : 1	36.4	0	0	100

^a Swelling assessment based on observations of 11–16 fibers per sample.

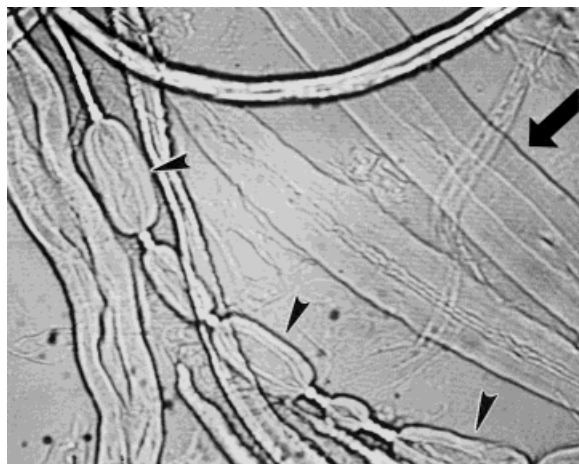


Figure 3 Light micrograph of HMAG fibers in water following grafting at a 3 : 1 monomer/pulp level (60 \times).

bent capacity (TBGV) nevertheless saturates. The saturation in absorbent capacity is likely due to a limitation of the fiber itself, as shown in Table II. As monomer/pulp ratios increase from 0 to 1 : 1, more fibers balloon when subsequently exposed to water. Ballooning has been described previously⁹ and is illustrated in Figure 3 (arrowheads). As grafted monomer levels increase further from 1 : 1 to 4 : 1, ballooning decreases and unrestrained fiber swelling occurs [a fiber that has undergone unrestrained swelling is shown in Fig. 3 (arrow); as described in the following article,⁴ an unrestrained fiber has lost the integrity of its S1 layer and swells to its natural limit]. From Table II, absorbent capacity (TBGV) is seen to follow unrestrained fiber swelling; when

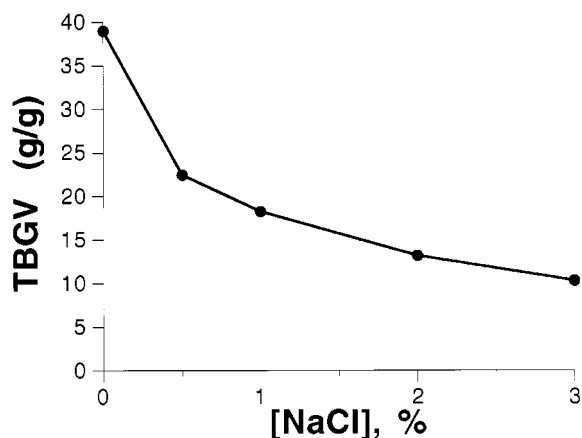


Figure 4 With increasing electrolyte levels, the absorbent capacity of grafted fibers decreases. Study conducted with HMAG (3 : 1) SSK fibers.

Table III Absorbent Capacity and Yield for NSK Fibers Treated with Various Monomers

Monomer	TBGV (g/g)	Yield (%) ^b
None (ungrafted)	3	—
Acrylic acid	10	20–25
Acrylonitrile	34	80–90
AMPS ^a	3	very low
Dimethyl itaconate	6	30
Ethyl acrylate	10	50
Methyl acrylate	41	70–80

^a 2-Acrylamido-2-methylpropanesulfonic acid.

^b Yield = weight of treated fibers/(weight of fibers + monomer).

all fibers achieve unrestrained swelling (100%), TBGV no longer consistently increases with increasing acrylate levels. The correlation between fiber morphology and absorbent capacity is explored in greater detail in the following article.⁴

Effect of Monomer Type

The effect of monomer type on absorbent capacity and yield [weight of treated fibers/(weight of fibers + monomer)] is shown in Table III. Only two monomers, acrylonitrile and methyl acrylate, result in grafted fibers with a high absorbent capacity. Use of those two monomers also results in high yield. The lower yield of the other monomers appears to be due to homopolymerization rather than fiber grafting; the homopolymers are then washed away after grafting and prior to hydrolysis.

Effect of Pulp Fiber Type

The effect of pulp fiber type on absorbent capacity and yield is shown in Table IV. The various

Table IV Absorbent Capacity and Yield for Various Fibers Treated with Methylacrylate in a 2 : 1 Monomer/Pulp Ratio

Fiber Type	TBGV (g/g)	Yield (%)
Aspen	32.0	76
Eucalyptus	26.3	70
NSK	24.5	69
SSK	28.5	78
Cotton linter	10.2	46
Rayon	7.3	85

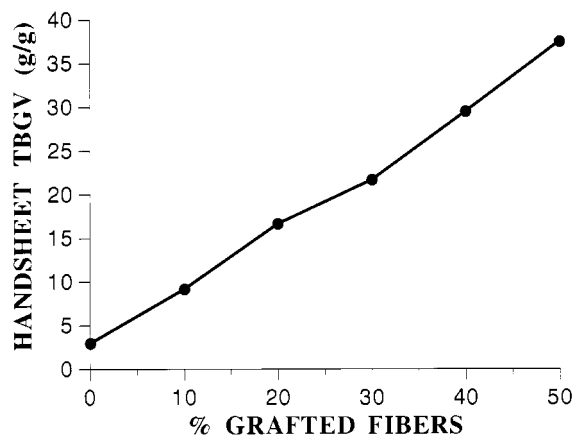


Figure 5 The absorbent capacity of a handsheet varies directly with the proportion of incorporated grafted fibers. Study conducted with handsheets made from normal NSK fibers and HMAG (3 : 1) SSK fibers (TBGV of 40 g/g).

HMAG wood pulp fibers have similar absorbent capacities, with aspen being the most absorbent, and the various grafted fibers could be produced with similar yields. Cotton and rayon did not produce very absorbent fibers.

Effect of Ionic Strength

Figure 4 suggests that a large portion of the enhanced absorbent capacity of HMAG fibers is due to the presence of osmotic forces. As the ionic strength of the absorbate increases, absorbent capacity decreases, as would be expected if osmotic forces contribute to absorbency. It would thus appear that HMAG fibers have achieved an osmotic force-dependent absorbent capacity similar to that of sodium polyacrylate hydrogels.²

Handsheets Incorporating Grafted Fibers

Handsheets Absorbent Capacity

As shown in Figure 5, the absorbent capacity of handsheets incorporating grafted fibers increases linearly with the concentration of HMAG fibers. The TBGV of the grafted fibers themselves was 40 g/g, a value essentially achieved by handsheets prepared with equal parts normal NSK fibers and HMAG fibers. We attribute some of this enhanced absorbency of handsheets to planar sheet formation described in an accompanying article.⁵

Handsheets Absorbency Rate

The rate of water sorption in normal handsheets and handsheets prepared with HMAG fibers (20%) is shown in Figure 6. The enhanced absorbent capacity that is ultimately achieved in the HMAG fiber-containing handsheet is apparent. Note, however, that the rate of water sorption is also greater in the HMAG fiber-containing handsheet, as seen by the higher slope at early time points. The ratio between water uptake rates at 10 s for handsheets containing 20% HMAG fibers and for normal handsheets is 1.7.

Handsheets Mechanical Properties

Table V shows the mechanical properties of four different handsheets: a control NSK handsheet and NSK handsheets incorporating 20% of either HMAG (3 : 1) SSK fibers, HMAG (3 : 1) NSK fibers, or acrylonitrile-grafted (3 : 1) NSK fibers. Along with an approximate fivefold increase in absorbent capacity in handsheets containing grafted fibers, there is an approximate doubling of dry tensile strength, a threefold or greater increase in wet tensile strength, and a fivefold increase in tensile strain (stretchability). In the presence of Kymene (a poly(aminoamide)epichlorohydrin wet strength paper additive^{10,11}; Hercules Inc., Wilmington, Delaware), wet strengths of control and grafted-fiber handsheets are approximately equivalent. The correlation between

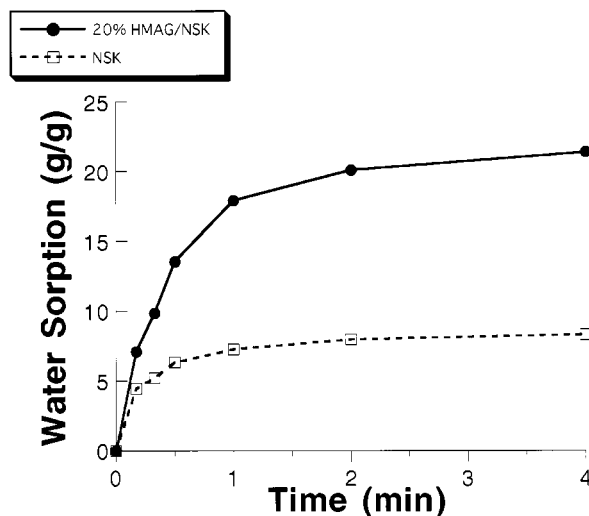


Figure 6 Time course of water uptake in normal (NSK) handsheets and handsheets containing 20% HMAG (2 : 1) SSK fibers (TBGV of 24 g/g).

Table V Comparison between Mechanical Properties of NSK Handsheets and Handsheets with 20% Grafted Fibers

Mechanical Property	NSK Handsheet (TBGV = 3)	Methyl Acrylate/NSK Fibers ^a (TBGV = 36)	Methyl Acrylate/SSK Fibers ^a (TBGV = 39)	Acrylonitrile/NSK Fibers ^a (TBGV = 34)
Handsheet TBGV (g/g)	3.0	13.8	15.0	8.5
Dry tensile (g/in)	700	1470	1230	1300
Wet tensile (g/in)	5–10	28	30	82
Strain (%)	1.1	5.9	5.2	5.1
Wet tensile with 1% Kymene (g/in)	200	230	180	290

^a Grafted 3 : 1 monomer/pulp ratio.

the morphology of handsheets incorporating grafted fibers (planar sheet formation) and enhanced handsheet mechanical properties is explored in an accompanying article.⁵

CONCLUSIONS

Our approach to enhancing the absorbency of paper fibers in general and paper towels in particular was to essentially chemically incorporate the absorbent (osmotic) force of sodium polyacrylate hydrogels within the cellulose wall of individual paper fibers. This approach would be predicted to increase the absorbent capacity of grafted fibers and handsheets prepared with these fibers while maintaining or perhaps increasing the absorbent rate. We have shown that this approach was successful in increasing both absorbent capacity and rate. In addition, we observed an increase in mechanical strength of wet and dry handsheets incorporating these grafted fibers.

The enhanced absorbency of grafted fibers is due to the attachment of hydrolyzed polyacrylate to—or within—pulp fibers (Fig. 2 and Table I). In the following article we show that grafting occurs both on and within the fiber wall.⁴ An order of magnitude increase in absorbency is obtained with hydrolyzed methyl acrylate or acrylonitrile monomers (Table III). This increase in absorbency is due in large measure to the incorporation of an osmotic force for fluid uptake. This central role of an osmotic force is supported by the decrease in absorbent capacity of these fibers with increasing concentration of electrolytes, as shown in Figure 4. However, as seen in this figure, at very high concentrations of electrolytes (3%

NaCl) the absorbency of fibers is still significantly higher than that of untreated fibers by approximately threefold. We attribute this difference to an increase in capillarity of the grafted fibers (chemical beating).

The increased absorbency of grafted fibers is ultimately limited not by total amount of monomer (osmotic force) that can be incorporated within fibers but by an intrinsic limitation in the fibers themselves. As shown in Figure 2 and Tables I and II, for HMAG fibers the absorbent capacity peaks at a 3 : 1 monomer/pulp ratio; the incorporation of additional monomer does not lead to additional absorption. We believe that the addition of monomer beyond the 3 : 1 limit results in fiber fragmentation and loss with a resulting decrease in measured absorbency. Some fragmented fibers are observed at the higher grafting levels.

If enhanced absorbency is ultimately limited not by monomer levels but by the pulp fiber, then absorbency might be further increased by appropriate choice of fiber type. This idea is supported by the data in Table IV, where HMAG aspen pulp had a 30% higher absorbent capacity than similarly grafted NSK pulp (although all wood pulps had a relatively high absorbent capacity). We do not know the basis for this different behavior in pulp types; we found no correlation between absorbent capacity and fiber density, length, width, or wall thickness.

Handsheets incorporating HMAG fibers have both an enhanced absorbent capacity and an enhanced absorbent rate (Fig. 6). The increase in rate is relatively small, approximately 50%. We believe this measured increase in rate is due not only to changes in osmotic force but also in fiber

internal structure and handsheet organization (planar sheet formation) as discussed in the following articles.^{4,5} Handsheets containing grafted fibers also have increased dry tensile strength, wet tensile strength, and stretchability (Table V). We believe we have uniquely altered the morphology and absorbing mechanism of wood fibers and thereby uniquely produced paper with a concurrent enhancement in the absorbent capacity, absorbent rate, and mechanical properties.

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