

The Preparation and Properties of Acrylic and Methacrylic Acid Grafted Cellulose Prepared by Ceric Ion Initiation. III. Some Physical, Mechanical, and Ion Exchange Properties

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Synopsis

The first two articles were concerned, (1) with the preparation and, (2) with the water retention properties of the grafted cellulose. This article presents some physical, mechanical, and ion exchange properties. Bleached sulfite softwood pulp filter paper was the substrate and polyacrylic acid the grafted side chains. The thickness of the paper increased with grafting accompanied by a decrease in area, particularly in the machine direction. The air permeabilities of the grafted papers were essentially unchanged even at high degrees of grafting. The dry tensile strength increased somewhat with grafting but the zero span strength decreased. Wet tensiles increased considerably up to about 50% graft, but then decreased. The wet elongations, however, steadily increased but began to level off at 120% graft. Strength properties were also measured with melamine wet strengthened paper. The ion exchange capacities of the dispersed paper pulp indicated that all the grafted polyacid groups were rapidly utilized.

INTRODUCTION

A convenient and practical all-aqueous system of ceric ion grafting to cellulose was described in Part I of this series.¹ In particular, the method was found to work well, with little homopolymer formation, using acrylic and methacrylic acids as monomers. The pure and saline water retention properties were described and discussed in some detail in Part II.² The graft copolymers have a number of important applications in addition to those associated with their water-sorbing and supersorbing properties. These are mainly concerned with the acid groups themselves, in particular their ion exchange capacity for various separations and other end uses. The removal of color and toxic materials from effluent streams and the recovery and removal of the ions of precious and other metals are among the applications which have been explored in detail. Other uses suggested are for the sterile filtration of gases and for hemostatic gauzes. The acid groups can also be reacted with suitable compounds to confer bactericidal, hemostatic, and other useful properties.

EXPERIMENTAL

The grafting itself was carried out on filter paper made from bleached sulfite softwood. The property studies were conducted on the grafted paper

per se or after transforming to pulp form using a Waring blender at low speeds. In all cases the grafted samples were extracted to remove homopolymers. Details of all the procedures have been published^{1,2} and will not be repeated here.

The ion exchange capacities of the grafted cellulose samples were determined according to the method described by Helfferich.³ About 0.1 g of the grafted cellulose sample was completely converted into its H⁺ form by equilibrating the sample with 0.1*N* HCl for 2 h and washing it thoroughly with deionized water until the washings were free of acid. This sample was vacuum oven dried, and the exact weight of the sample was recorded. The sample was then transferred into a dry 50-mL Erlenmeyer flask. Exactly 40 mL of a 0.1*N* sodium hydroxide solution was pipetted and added to the flask. The contents of the flask were stirred for about 2 h and then 1 mL of supernatant solution was withdrawn and backtitrated to the phenolphthalein end point with standard 0.01*N* hydrochloric acid. By knowing the amount of alkali consumed, the ion exchange capacity was calculated. Although potentiometric methods can be used, this method was found to be convenient and reproducible.

The rates of cation exchange of the polyacrylic-acid-grafted cellulose samples were determined according to the batch technique.³ The procedure adopted here was essentially the same as was used for determining the ion exchange capacity except that 1 mL of the supernatant liquor was withdrawn at various times and back titrated with 0.01*N* hydrochloric acid. The percent equilibrium capacity attached was calculated on the basis of total ion exchange capacity.

Before carrying out the physical tests on the papers themselves, they were conditioned according to TAPPI Standard T-402. Wet tensile tests were carried out after immersing the samples in water at 23°C for 24 h; the samples were placed between pieces of blotting paper to remove the excess water immediately prior to testing.

Wet tensile strength, dry tensile strength, and elongation were measured according to TAPPI Standards T-456 and T-494, respectively. All tensile tests were carried out along the machine direction of the paper. The tensile tests were carried out on an Instron testing machine (Table Model Tm-M) using 15 mm wide strips of a grafted paper. The tests were performed with 1-in. span and with a crosshead speed of 0.5 in./min (i.e., 50%/min strain rate). The zero span breaking lengths of grafted papers were determined using the Clark attachment, according to TAPPI Standard T-231.

The air permeability of grafted and ungrafted filter papers was determined according to ASTM Standard D-737, on a permeability testing machine, used for determining air permeability of textile fabrics.

Wet strength resin filter papers were prepared as follows: A melamine-formaldehyde resin (PAREZ RESIN 607, American Cyanamid Co.) solution was prepared according to the method described in Technical Bulletin No. 9-D of the American Cyanamid Co. Various levels of weight increase of melamine resin were obtained by soaking the paper in solutions of different concentrations of resin until saturated; the papers were then pressed between blotting papers to remove the excess followed by curing in an oven at 105°C for 30 min. These were further washed with water and extracted with methanol before

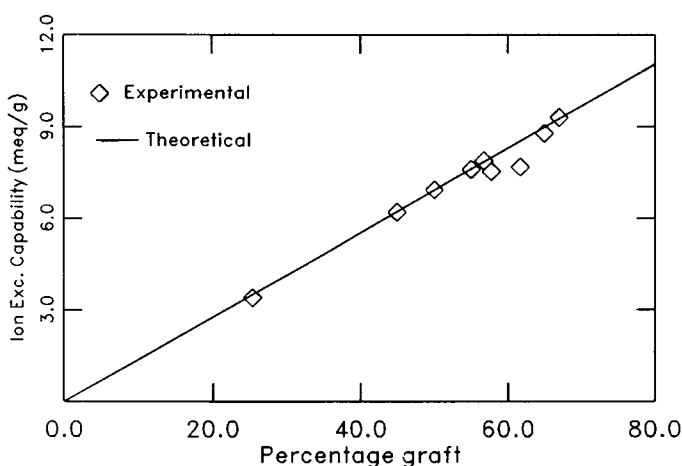


Fig. 1. Relationship between ion exchange capacity and percent graft expressed as composition.

the grafting experiments. The percent weight increases of melamine-formaldehyde resin was calculated by both increase in weight and by nitrogen determination by the Kjeldahl method (TAPPI Standard T-418). Calculations based on both methods were in close agreement.

RESULTS AND DISCUSSION

The ion exchange capacities, determined as described in the Experimental section, are plotted vs. the percent graft in Figure 1. The theoretical capacities are given by the dotted line. Excellent agreement between the two values are shown, the largest deviation being less than 10%. This value was, however, measured after 3 min. All the acid groups were therefore available for ion exchange purposes. A few rates were also determined and are presented in Table I. With one exception, essentially full exchange was achieved in 3 min.

The capacities are well within the range of commercial cation exchange resins and are reached with fast rates. For example, Battaerd and Sudak⁴ grafted acrylic acid to 22–36 mesh polyethylene powders and achieved 90% of capacity in 5 min, much faster than most commercial exchange polymers but slower than the grafted pulps studied in this work.

TABLE I
Rate of Ion Exchange of Acrylic Acid Grafted Cellulose Pulps

Ion exchange capacity (meq/g)	Percent equilibrium capacity attained (time in min)			
	1.5	3.0	6.0	20.0
6.2	93.7	100	—	—
7.1	85.0	98.5	—	—
7.6	58.8	73.6	78.6	100
8.6	77.2	96.8	100	—

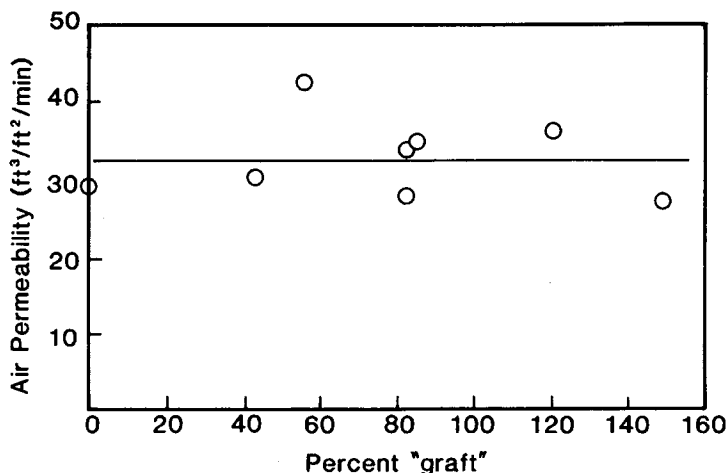


Fig. 2. Effect of percent "graft" on the air permeability. "Graft" is expressed as per 100 parts of cellulose.

The air permeabilities of the grafted papers are illustrated in Figure 2. Even substantial amounts, up to 150% add-on, did not diminish the porosity. This is of considerable importance when considering such papers as filters. It is interesting that this is not true with other grafts, as shown, for example, in Table II. Presumably acrylic acid penetrates more into the fibrous structure itself than the more hydrophobic monomers. These lead to more surface grafting, which tends to close up the pores. Interestingly, the paper texture and appearance was maintained with acrylic acid grafts rather than the "glassy" state sometimes found with very high add-ons of polymer.

A number of other physical properties were measured. The effect of grafting on the paper thickness is shown in Figure 3. The increase with percent grafting is roughly linear; a similar increase has been reported for a number of other monomers.⁵ Comparing the present system with other monomers,⁵ the

TABLE II
Air Permeability of Polymer Grafted Papers

Percent "graft"	Graft copolymer(s)	Percent acrylic acid in graft copolymer	Air permeability ^a (ft ³ /ft ² min)
0.0	—	—	30.8
3.3	AN	0	30.5
4.0	AN	0	27.1
28.3	AN	0	25.7
56.8	AN	0	20.8
12.8	MA	0	29.8
71.0	MA/AA	—	27.7
144.4	MA/AA	71.0	10.8
261.4	MA/AA	58.3	6.1
106.4	AN/AA	84.2	5.2

^a Permeability values reported are at 65% RH and 70°F.

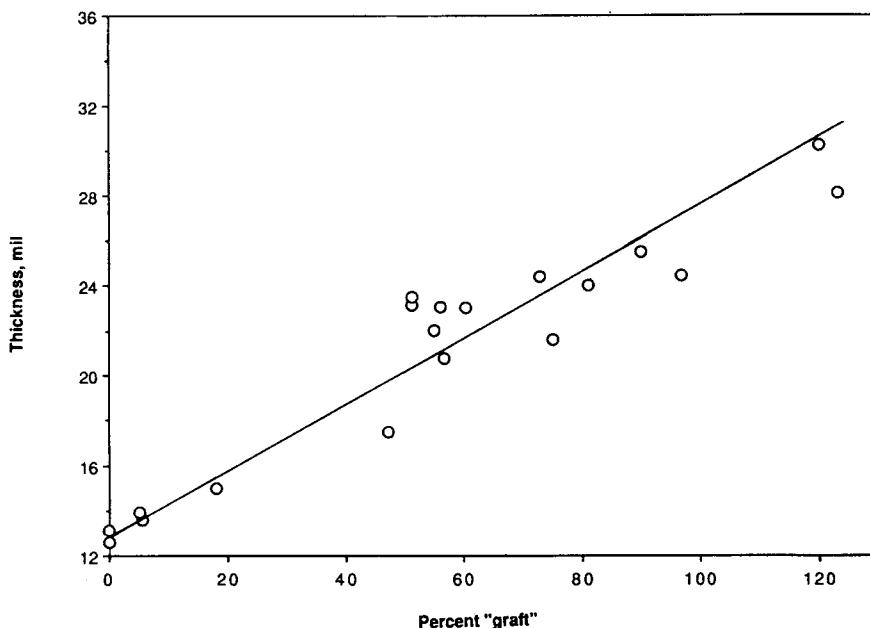


Fig. 3. Effect of percent "graft" on the thickness of the paper.

increase in thickness is much greater. This could, again, be explained in the same way as the permeability results. Interestingly, the one hydrophilic monomer, acrylamide, gave the second greatest increase in thickness. In general, the reduction in area was quite small. This is a general phenomenon except with very large degrees of grafting. The results show that the increase in the fibers is in their diameters and is also true with grafting to textile fibers. It is a consequence of the restraints imposed by their crystallite orientation and structure. Cellophane, on the other hand, tends to grow in all three directions as it is less strongly oriented.

Tensile Strength Properties

The dry tensile strength values are given in Table III. There is a substantial increase with grafting, up to about 45% graft, followed by a gradual decrease. The zero span (fiber) strength, on the other hand, steadily decreased with grafting. The increase in strength is quite general with most monomers.⁶ The subsequent decrease has also been reported for polyacrylamide grafts.⁷ It can be presumed that the increases in dry strength are due to an increase in the fiber to fiber bonding. This should be particularly important with hydrogen bonding grafts such as acrylic acid and acrylamide. The eventual decrease in the present work is most probably due to the observed loss of strength of the fibers themselves. This, again, could reflect the greater penetration into the fibers themselves. It is interesting that acrylamide grafts which should have the same propensity also shows an eventual decrease in dry tensile strength.

The effect of grafting on the wet tenacities is illustrated in Figure 4. Again there is an increase up to a similar maximum as the dry strength followed by a drop in the values. The same general explanation as given for the strengths is

TABLE III
Dry Tensile Properties of Polyacrylic Acid Grafted Papers

Graft (%)	Breaking length (km)	Zero span breaking length (km)	Apparent density (g/cc)
0	2.1	8.6	0.29
0(a)	1.6	9.0	0.30
43	2.8	6.2	0.32
47	2.5	5.7	0.32
78	2.4	5.7	0.33
81	—	5.2	—
89	2.0	5.1	0.28
125	1.8	4.6	—
186	0.9	—	0.25

^aControl, treated exactly as in the grafting process but without monomer.

applicable. The wet strengths decline much more and eventually fall far below the zero graft levels. This would be expected for a hydrophilic monomer. The wet stretch values are illustrated in Figure 5 and increase continually with increasing degrees of grafting. This could be due to the increasing plastization of the fibers. Eventually this effect is overcome by the restraining influence of the fiber crystallinity.

Grafted Wet Strength Papers

The wet tensile results reflect the lack of ionization of the grafted carboxylic acid groups under the near neutral conditions of the tests. When the pH is raised and more and more sodium salt formed, the wet strength drops drastically and eventually the paper is essentially unusable under wet conditions. Since such papers have potential application for filtration of fruit juices

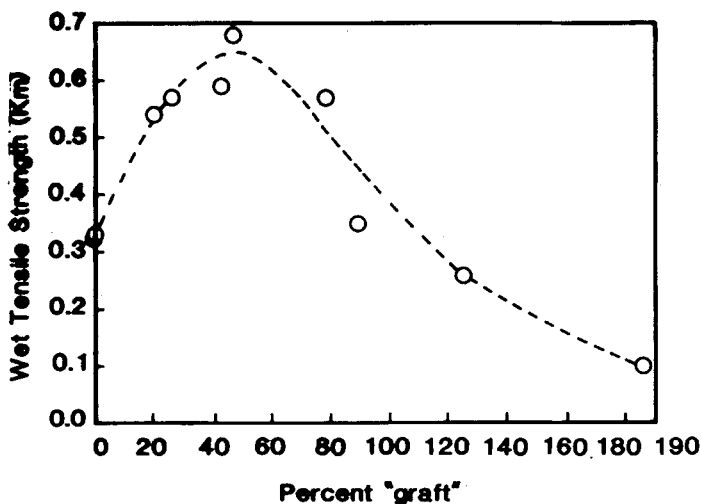


Fig. 4. Effect of percent "graft" on the wet tensile strength of the paper.

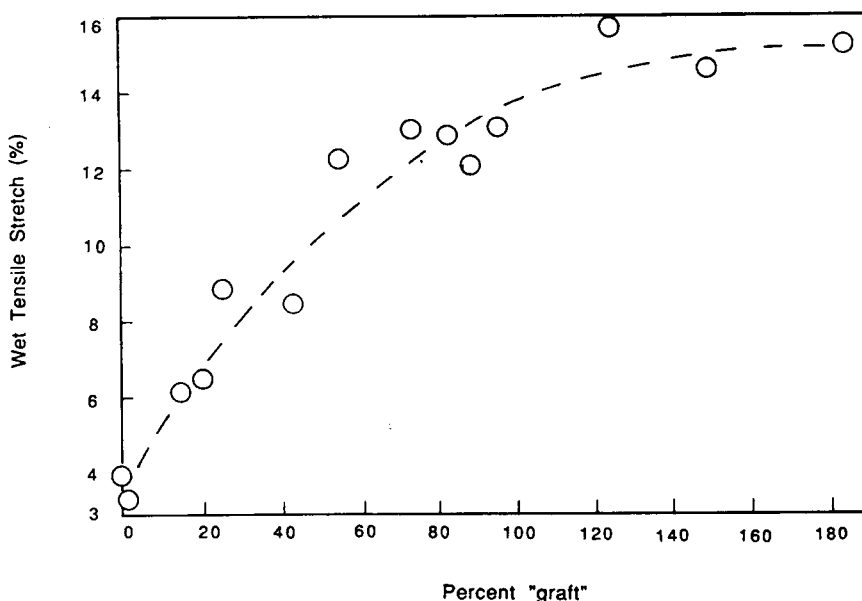


Fig. 5. Effect of percent "graft" on the wet tensile strength of the paper.

and beverages, and, for combined filtration and ion exchange uses, higher wet strengths are needed. Some preliminary experiments have been conducted using melamine-formaldehyde wet strength resins. Grafting can be carried out satisfactorily with such wet strength papers but with reduced yields as reported in Part I of this series.¹

The wet and dry strengths of the papers are presented in Table IV. The results show that better wet strength retention can be obtained in this way. Treating the grafted papers by dipping in the melamine-formaldehyde solution and coating gave excellent wet strength in the one experiment which was conducted. The resin-treated papers all gave coherent strengths under alkaline conditions and maintained their ion exchange properties. Although only

TABLE IV
Strength Properties of Melamine Resin Treated Papers

Melamine resin in paper (% based on dry paper)	Tensile strength of ungrafted paper (lb/in.)			% "Graft"	Tensile strength of grafted paper (lb/in.)			Drop in wet strength upon grafting (%)
	Wet	Dry	Wet/dry ($\times 100$)		Wet	Dry	Wet/dry ($\times 100$)	
0.00	1.7	11.1	15.3	0	—	—	—	—
0.69 ^a	2.4	11.9	20.1	9	2.1	—	—	14.3
2.04 ^a	5.6	11.6	48.3	20	2.4	7.8	30.7	57.1
4.38 ^a	7.0	15.6	44.9	78	1.6	12.4	12.9	77.1
5.97 ^b	—	—	—	83	5.2	—	—	—

^a Polyacrylic acid grafting was carried out on melamine resin treated papers.

^b Polyacrylic acid grafting paper was dipped in melamine resin solution and then cured.

preliminary results have been obtained, the approach appears to be very promising for combined filtration and ion exchange applications.

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