

The Water Absorbency of Hydrolyzed Polyacrylonitrile-Grafted Cellulose Fibers

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Synopsis

The water absorbency of a bleached softwood kraft pulp, as measured by its water retention value (WRV), was increased up to 30 times by graft polymerizing polyacrylonitrile (PAN) and subsequently hydrolyzing it to sodium polyacrylate-polyacrylamide copolymer. WRV was found to be related to the initial PAN graft level rather than to the final sodium polyacrylate content, and was independent of the grafting process used. However, the ceric ion process was found superior to both the cellulose xanthate- H_2O_2 and ferrous ion- H_2O_2 redox systems in that it occasioned only a minor loss during the hydrolysis stage and the WRV was less affected by drying. The WRV remained constant as pH was lowered from 9 to 5 but dropped to the level of unmodified pulp at pH 3.5 where the sodium salt is fully converted to poly(acrylic acid). Retention of 1% aqueous NaCl was about 60% of the WRV. The swelling properties of the grafted fibers under various conditions appear to be explained by considering the grafting to act in two ways: (a) the introduction of a potentially hydrophilic component capable of generating swelling pressures and (b) the reduction in the cohesion of the fiber by the interposition of graft polymer chains in the fiber structure.

INTRODUCTION

The ability of cellulose fibers to absorb or retain large amounts of water is important in several applications. Usually, the fibers are in the form of a sheet or pad and the water is held within the fiber wall, in the lumen, and in the interfiber capillaries.

The amount of water absorbed within the fiber wall (fiber saturation point) and that contained within the lumen are both comparable with the fiber weight, i.e., 1-2 H_2O per g solid, and are dependent on fiber history. The interfiber capillary water is dependent on capillary size, thus on the construction of the fiber assembly, and will not be dealt with here.

The amount of water retained by the fiber can be increased somewhat by swelling treatments using sodium hydroxide or phosphoric acid, but much greater increases can be obtained if the cellulose is modified by introducing carboxylate or other hydrophilic groups. Thus, a considerable increase in water absorbency has been reported for sodium cellulose carboxylate obtained by oxidation of wood pulp,¹ while ratios of water to fiber of up to 30 g/g have been obtained with crosslinked carboxymethylated fibers,² after centrifugation under 1500 G.

The work reported here concerns fibers modified by graft polymerization of acrylonitrile followed by hydrolysis of the nitrile groups to give a polyacrylamide-sodium polyacrylate copolymer graft. The modified cellulose fiber is capable of holding more than 30 times its own weight of water, after centrifugation under 900 G.

Graft polymerization onto cellulose of a monomer containing hydrolyzable groups such as acrylonitrile or acrylic esters, followed by alkaline hydrolysis of these groups, was first reported by Adams and Hoftiezer³ who found that the incorporation of these fibers in a paper furnish enhanced the properties of the paper. However, there are no published data on the water absorbency resulting from this treatment. It is the purpose of this paper to present data on the water-holding capacity of hydrolyzed polyacrylonitrile-grafted wood fibers and to discuss how this is influenced by the method of preparation and other variables.

EXPERIMENTAL

Materials

A never-dried bleached kraft softwood pulp (Cellate from Canadian International Paper Co.) was used throughout the work.

Acrylonitrile monomer (Anachemia reagent grade) was washed free of inhibitor with NaOH and then distilled under reduced pressure before use.

Graft Copolymerization

The following three methods were used to prepare polyacrylonitrile (PAN) grafted cellulose fibers.

Cellulose Xanthate Method. Never-dried pulp, 10 g, was steeped in 7% NaOH solution for 15 min. The excess sodium hydroxide was removed by a combination of pressing and filtration. Xanthation was carried out by placing the pressed pulp in a vacuum desiccator kept at constant temperature, evacuating the desiccator to 25 mm Hg and then connecting it to a carbon disulfide ampoule. After 2 hr of xanthation at 27.2°C, a D.S. of 0.18 was obtained. The sodium cellulose xanthate was then ion exchanged with ferrous ion. Finally, the ion-exchanged pulp was transferred to a reaction kettle containing 900 ml water, 3 ml 30% H₂O₂, and the monomer. After 3 hr with constant agitation, the grafted pulp was filtered washed, and dried.

Ceric Ion Method. A thick-wall vacuum flask equipped with a nitrogen inlet was used. A typical reaction was carried out by introducing 10 g pulp at 30% consistency into the flask, followed by 20 g acrylonitrile (AN) monomer. After 5 min of contact time, 0.5 g ceric ammonium nitrate dissolved in 140 g 1% HNO₃ was added. The flask was evacuated and flushed with nitrogen. After standing at room temperature for 3 hr with occasional stirring, the grafted cellulose was filtered, washed, and dried.

Ferrous Ion-H₂O₂ Process. Never-dry pulp, 10 g, was stirred in 1 liter 1% ferrous ammonium sulfate solution for 15 min. The ion-exchanged pulp was filtered, washed with 1 liter distilled water, and dispersed in another liter of water containing 50 g monomer. Ten ml 30% H₂O₂ was then added. The reaction mixture was deaerated immediately and flushed with nitrogen. After standing at room temperature for 18 hr, the grafted cellulose was filtered, washed, and dried.

Extraction of Homopolymer and Determination of Graft Level

The grafted pulp was extracted twice with dimethylformamide at room temperature, dried again, and weighed. The percentage weight increase was expressed as *graft level* after suitable correction for the loss in cellulosic material occurring during the sodium hydroxide treatment in the case of the xanthate-H₂O₂ process.

Good correlation was found with values obtained by nitrogen determination.

Hydrolysis of PAN Grafts

Grafted fibers, 2 g, were introduced into 100 ml boiling 3% NaOH solution stirred with a magnetic stirrer. The slurry was kept boiling for 15 to 30 min, and the pulp was filtered while hot on a Buchner funnel and washed with deionized water until pH 9.

Determination of Carboxyl Content

A procedure similar to that used by Weaver et al.⁴ for hydrolyzed polyacrylonitrile starch grafts was used. It consisted of titrating potentiometrically the hydrolyzed PAN fibers with 0.1N H₂SO₄. The amount of H₂SO₄ consumed between pH 8.5 (sodium polyacrylate) and 3.75 (poly(acrylic acid)) corresponds to the carboxyl content.

Determination of Water Absorbency

The water absorbency was measured by a centrifugal technique. After hydrolysis the washed fibers were placed in a basket fitted with a stainless steel screen at the bottom and placed in the centrifuge for 30 min under a centrifugal acceleration of 900 G. After centrifugation, the pads were weighed, dried at 80°C overnight, and weighed again. The amount of water, in grams, retained per gram of dry material was expressed as a water retention value (WRV). As shown in Table I, results were less affected by centrifugal force as the water retention value increased. This test was quite reproducible as the coefficient of variation (within one sample) was of the order of 4% at the 30 g/g WRV level.

TABLE I
Effect of Centrifugal Acceleration on Water Retention Value (WRV)^a

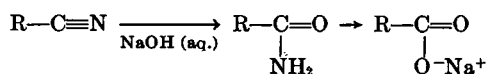
Centrifugal acceleration	Water retention value		
	0% PAN (never-dried pulp)	73% PAN	127% PAN
100 G	—	19.40	35.1
400 G	1.90	17.30	35.0
900 G	1.56	15.80	34.9
1600 G	1.25	—	—

^a The water retention value (WRV) was measured by centrifugation and is expressed as weight of water retained per weight of dry sample.

RESULTS

Hydrolysis of PAN-Grafted Cellulose

Alkaline hydrolysis of the nitrile group to carboxylate group proceeds through the amide intermediate:



However, because of a neighboring group effect,⁵ hydrolysis to carboxyl is never complete, and a combination of carboxyl and amide groups is obtained depending on the reaction conditions and time.

Carboxyl and nitrogen determinations were carried out after hydrolyzing grafted fibers of increasing PAN content. Results are shown in Table II as poly(acrylic acid) and polyacrylamide contents (it being understood that the grafted side chains after hydrolysis are copolymers) versus polyacrylonitrile content before hydrolysis. IR spectra confirmed that no nitrile remained after hydrolysis.

The difference in Table II between the expected polymer content after hydrolysis and the actual polymer content computed from the carboxyl and amide determination is due to the loss of hydrolyzed polymer occurring during the alkaline hydrolysis stage. This loss is quite substantial in the case of the xanthate-H₂O₂ process, less severe with the ferrous ion-H₂O₂ process, and much smaller with the ceric ion process. This loss is attributed in part to the extraction of some of the residual homopolymer which could not be extracted with DMF but can now escape from the highly swollen fiber structure. In the case of the xanthate-H₂O₂ process, where the loss is highest, it is possible that some of the polymer was truly grafted to the cellulosic backbone; but, as suggested by Kraessig,⁶ through —C—S—R linkages which are destroyed during the alkaline hydrolysis.

In addition to a loss in hydrolyzed polymer, there is also a loss in cellulosic material, particularly pronounced in the xanthate and ferrous ion processes

TABLE II
Composition of Hydrolyzed PAN-Grafted Fibers

Time of hydrolysis, min	PAN Before hydrolysis		After hydrolysis		Total polymer content		Total loss in	
	Graft level, %	PAN content, %	PAAc content, %	PAAm content, %	Actual, %	Expected, %	Polymer, ^a %	Cellulose, ^b %
Xanthate-H ₂ O ₂ Process								
30	31	23.6	12.9	9.1	22.0	29.5	48	28
30	59	37.5	20.0	12.7	32.8	44.7	55	25
30	91	47.5	26.2	15.7	41.9	55.2	55	22
30	160	62.4	31.0	19.8	50.8	69.2	59	11
Ferrous Ion-H ₂ O ₂ Process								
15	74	42.5	24.5	20.8	45.3	50.0	33	19
15	91	47.5	26	22.4	48.4	55.2	36	15.5
30	66	39.7	25.6	18.3	43.9	47.4	31	21
30	115	53.5	31	21.3	52.3	60.9	38	12.5
Ceric Ion Process								
15	72	41.8	24.0	23.8	48	49.2	8	4
15	82	45.0	24.2	25.3	49.5	52.4	15	4.5
15	105	51.1	29.7	26.8	56.5	58.5	13	6
20	144	59.0	34.2	29.4	64.1	66.1	13.5	4

^a Based on expected conversion to amide or acid.

^b Calculated on basis of original weight of cellulose.

(where H_2O_2 is used), and is most likely due to oxidative cellulose degradation during grafting in the presence of H_2O_2 . Also, the carboxyl groups introduced by H_2O_2 oxidation make cellulose more susceptible to alkali degradation. In a blank xanthate "grafting" experiment using α -methylstyrene which does not polymerize, followed by hydrolysis in 3% NaOH for 30 min, a loss of 30% of the cellulose was measured.

The influence of time of hydrolysis, NaOH concentration, and temperature was also examined on fibers grafted by the xanthate process, and the results are shown in Table III. Carboxyl content increases quickly at the

TABLE III
Influence of Time of Hydrolysis^a

Time of hydrolysis, min	PAAc content, %	PAAm content, %	PAAc/PAAm Ratio	Loss, ^b %	WRV, g/g
0	0	0	—	—	1.5
5	17.4	—	—	—	6.5
8	24.5	—	—	—	18.6
10	27.5	29.4	0.94	44	33.5
15	30.2	22.8	1.33	48	39.0
30	30.5	19.3	1.58	50	43.0
60	31.6	18.3	1.78	54	—
180	42	16.2	2.59	68	—

^a Conditions: fibers prepared by the xanthate process; initial PAN graft level, 144%; hydrolysis with 3% NaOH at boil.

^b Loss includes both polymer and cellulose.

beginning of hydrolysis and then more slowly. After 3 hr, the hydrolyzed copolymer is composed of 72% polyacrylic acid and 28% polyacrylamide—the composition usually obtained after complete hydrolysis of PAN homopolymer. However, the loss in polymer and in cellulose becomes excessive, 70% and 58%, respectively. Low temperature and low NaOH concentration reduced hydrolysis loss but effected lower conversion of amide to acid. Hydrolysis was also followed by infrared spectrometry. The development of deep red color and its gradual disappearance during hydrolysis of PAN fiber is caused by the formation of naphthyridine ring structures from adjacent nitrile groups which are subsequently hydrolyzed.⁵ The infrared spectra of the hydrolyzed PAN fiber in its sodium form (Fig. 1) showed two distinct bands at 1560 cm^{-1} and 1400 cm^{-1} , indicating the presence of both nonionized and ionized carboxyl. A strong band at 1660 cm^{-1} established the existence of the saponified intermediate, i.e., the amide. With the presence of the characteristic bands from 890 to 1160 cm^{-1} for polysaccharide, the main features of sodium polyacrylate-grafted cellulose are confirmed. On the other hand, residue recovered from the sodium hydroxide solution by precipitating with methanol showed the same absorption bands at 1400 , 1560 and 1660 cm^{-1} , but an absence of the characteristic cellulose bands between 850 and 1200 cm^{-1}

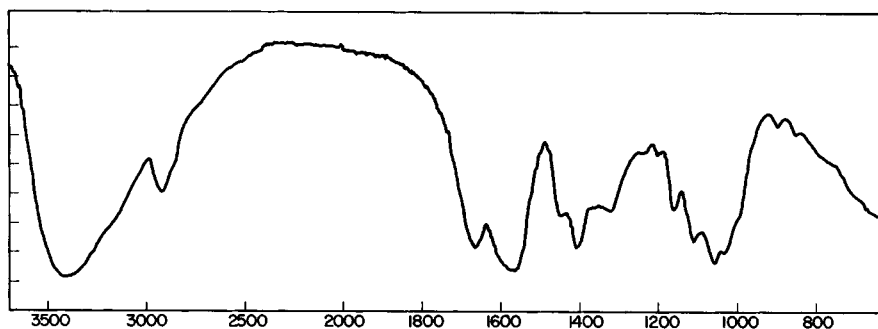


Fig. 1. Infrared spectrum of hydrolyzed PAN-grafted fibers. Xanthate- H_2O_2 process (KBr pellet).

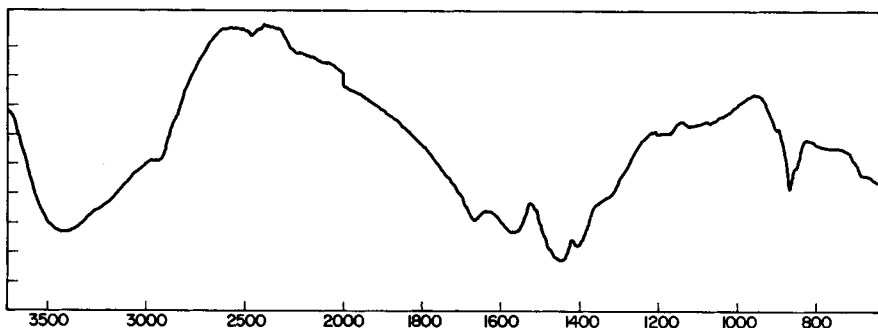


Fig. 2. Infrared spectrum of homopolymer dissolved during hydrolysis of PAN-grafted fibers. Xanthate- H_2O_2 process (KBr pellet).

(Fig. 2). This suggests that the loss of polymer during the hydrolysis of PAN fiber is mainly homopolymer.

Water Absorbency

The absorbency of hydrolyzed PAN-grafted fibers was measured by the water retention value (WRV) method described earlier.

Influence of Graft Level and Grafting Conditions. The influence of initial PAN graft level on the water retention value is shown in Figure 3, where the results obtained with the three grafting processes are plotted. WRV increases almost linearly with PAN graft level up to 25 to 30 g/g. Above this range, the points are scattered. Some of the scatter may be due to the fragility of these highly swollen fibers which can be broken down mechanically by too much agitation, and this may result in variations in the packing of the mat formed during centrifuging and thus affect the WRV.

Fiber saturation points were measured on some of these fibers, using the dextran solute exclusion technique developed by Stone and Scallan.⁷ As shown in Table IV, agreement between water retention values and fiber saturation points was very good where the values of each lay below 30 g/g, thus confirming the equivalence shown by Scallan and Carles⁸ on ungrafted

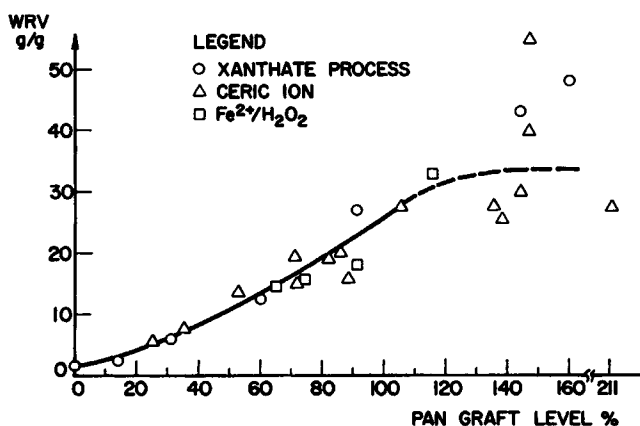


Fig. 3. Water retention value vs. initial (before hydrolysis) PAN graft level.

pulps. Further, good agreement was found between the ratio of the volumes of the wet cell wall before and after the swelling treatment as calculated from the water retention values and the ratio as determined by optical microscopy (18:1 and 20:1, respectively).

Noteworthy is the fact that there is very little difference between the three processes investigated although the molecular weight of the grafted side chains, and thus the grafting frequencies are different. Xanthate and ferrous ion grafting yield molecular weight of the order of $0.2\text{--}0.5 \times 10^6$, compared with $3\text{--}5 \times 10^5$ for the ceric ion process.

Influence of Drying. Water retention values ("Rewet" WRV) were measured on samples air dried and then vacuum dried at 40°C in sheet form. The results are given in Table V.

It is well known that dried cellulosic fibers, when placed in water, never swell back to the original level. This is attributed to a permanent collapse of some of the water-filled voids present in a never-dried fiber. It was expected that this irreversible phenomenon would still be present in grafted fibers but that the permanent loss in swelling would decrease as graft level increased, i.e., as cellulose content decreased. In fact, this expectation

TABLE IV
Fiber Saturation Point Versus Water Retention Value of Hydrolyzed PAN-Grafted Fibers

PAN graft level before hydrolysis, %	WRV	FSP ^a
31	6.0	6.0
72	16.0	15.6
105	18.0	29.5
144	31.8	26.5
147	54.8	32.5

^a FSP is measured as the amount of water, held by the fiber, which is not available as solvent for high molecular weight polymer (Dextran 2000).⁶

TABLE V
Influence of Drying on Water Retention Value

PAN graft level before hydrolysis	WRV before drying	WRV after drying	Ratio
Xanthate-H ₂ O ₂ Process			
14	2.5	1.95	0.78
31	6.0	5.50	0.91
60	13.0	9.75	0.75
91	27.0	19.25	0.71
160	48.0	24.00	0.50
Ceric Ion Process			
72	15.0	15.0	1.0
89	15.8	20.0	(1.26)
105	28.0	25.0	0.90
211	34.2	33.7	0.98
Pulp			
	1.5	1.0	0.66

proved to be correct in the case of fibers grafted by the ceric ion method but not with the xanthate-H₂O₂ process.

No doubt, this is related to the wet strength observed with handsheets from xanthate-grafted fibers which indicate some irreversibility in interfiber bonding and, by extension, an irreversibility in intrafiber bonding. In addition, the less irreversible collapse after drying of ceric ion-grafted fibers compared to xanthate grafts is consistent with the physical aspect of the dried fiber mats. Hydrolyzed xanthate-grafted fibers when dried from water form a very dense, compact, and somewhat brittle sheet with poor tear strength. On the contrary, ceric ion-grafted fibers dry as bulky structures as though the fibers had a higher inherent stiffness that prevents them from conforming and bonding to adjacent fibers as water evaporates from the interfiber capillaries. It can be hypothesized that this higher stiffness and lower conformability also exist at the submicroscopic level, thereby preventing full collapse of the fiber during drying. This may be related to the large difference in the molecular weight of the grafted chains produced by the two processes.

Influence of Homopolymer Extraction. The normal procedure used in this work was to dry the grafted fibers to determine total polymer add-on (homopolymer plus graft), then to extract the homopolymer, and finally dry again to determine graft level.

In a commercial process it would not be economical to extract the homopolymer (which forms about 10% to 20% of total polymer add-on) before alkaline hydrolysis. It is thus of interest to know how this would affect the WRV. The few available results are shown in Table VI where the WRV of never-dried, unextracted fibers are compared to the WRV obtained after the extraction step (which includes two overnight dryings at 80°C). The water retention value of extracted samples was always lower

TABLE VI
Influence of Homopolymer Extraction on Water Retention Value

PAN graft level before hydrolysis	WRV, never dry, unextracted	WRV, dry and extracted before hydrolysis	Ratio
23	10.8	5.8	0.54
88	20.0	15.7	0.79
135	27.5	26.2	0.95
138	30.0	26.0	0.87
144	34.3	31.7	0.92
144	42.7	40.5	0.95
211	34.0	27.2	0.80

than that before extraction but the difference is larger at low grafting level, and the drop could be ascribed either to homopolymer extraction per se or to the two drying steps involved with it.

Water Retention Value in 1% NaCl or Saline Retention Value. For many applications, it is important to know the behavior of absorbent fibers in a physiologic solution, usually simulated by 1% aqueous NaCl.

Washed, hydrolyzed fibers were dispersed in 1% aqueous NaCl and centrifuged under 900 G to obtain a "saline retention value" (SRV) which was corrected to take into account the NaCl present in the fibers after drying. The counterion effect was larger as graft level (i.e., carboxylate content) increased, as evidenced by the ratio SRV/WRV shown in Table VII; but even at high graft level (ca. 150%), the salt retention value is still 60% of the water retention value.

Influence of pH, or Carboxylate/Carboxylic Ratio, on Water Retention. The influence of a change in pH is equivalent to a change in the ratio of sodium carboxylate to carboxylic acid groups. As the fibers are neutralized by HCl, however, there is formation of NaCl which depresses the WRV. In order to eliminate its influence, it was decided to operate at constant NaCl content, corresponding to that obtained after full conversion to acid. Samples of fibers were neutralized to pH 7.6, 5.4, and 3.5, and the NaCl concentration adjusted in each case by adding NaCl crystals. In addition, in three experiments, after adjusting the pH to 7.6, 5.4, and 3.5, the NaCl

TABLE VII
Saline Retention Value (SRV) in 1% NaCl Solution*

PAN graft level before hydrolysis	SRV	SRV/WRV
72	10.0	0.66
82	12.7	0.63
99	10.1	0.64
104	14.4	0.58
144	15.0	0.60
0	1.0	1.0

* SRV and WRV determined after drying the fibers at 40° in vacuo.

TABLE VIII
Influence of pH or NaCOO⁻/COOH Ratio on Water Retention Value

pH	NaCl in solution, %	NaCOO ⁻ /COOH	WRV, g/g
8.9	0.1	1.0	18.6
7	0.1	0.88	17.8
6	0.1	0.65	17.8
5	0.1	0.37	17.4
4	0.1	0.05	3.2
3.5	0.1	0	1.6
8.9	0	1.0	22.5
7	0 ^a	0.87	23.9
5	0 ^a	0.37	23.9
3.5	0 ^a	0	1.6

^a NaCl formed during neutralization of fibers was washed out with water.

formed was removed by washing, the carboxylate content determined, and WRV measured. The washing step did not significantly change the carboxylate content.

Results are shown in Table VIII and indicate that, even at pH 5 where 63% of the carboxylate groups have been converted to acid, WRV has not changed.

The WRV of a hydrolyzed PAN graft in its acid form at pH 3.5 is similar to that of an untreated pulp which indicates that the polyacrylamide and cellulosic parts contribute little to the overall WRV.

Ion Exchange Properties

Several workers have grafted acrylic acid to cellulose to confer ion exchange properties.^{9,10} A few experiments were carried out to examine the exchange of sodium by calcium ions on hydrolyzed PAN fiber of two carboxyl contents using the elution method. Experiments were carried out by passing a known concentration of calcium ion through a packed column of fibers, and the eluent was collected in fractions. The concentrations of Ca and Na in the eluted fractions were followed by atomic absorption spectrophotometry. As shown in Table IX, the exchange was almost quantitative

TABLE IX
Ion Exchange Capacity of Hydrolyzed PAN Graft

Batch no.	Graft level, %	Hydrolysis conditions	Carboxyl content, %	Na present, mg/g fiber	Na exchanged, mg/g fiber	Exchange efficiency, %
260	166	3% NaOH 30 minutes	30.0	95.9	95.6	99.5
286	59.4	3% NaOH 30 minutes	19.3	61.8	61.3	99.4

when the sodium salt form and highly swollen fibers were used. On the other hand, attempts to exchange calcium on the acidified, deswollen fibers were unsuccessful. It is interesting to note that WRV was not affected by the calcium exchange.

DISCUSSION OF RESULTS

The swollen fiber may be considered as a system in which, at equilibrium, swelling forces are balanced by restrictive forces. The swelling forces are believed to arise from osmotic pressure effects and possibly other effects related to the solvation of polyions and their configurational properties.

The restrictive forces are those arising from the inherent structure of the fiber. In native fibers the microfibrils form a coherent structure that limits swelling and resists mechanical disintegration.

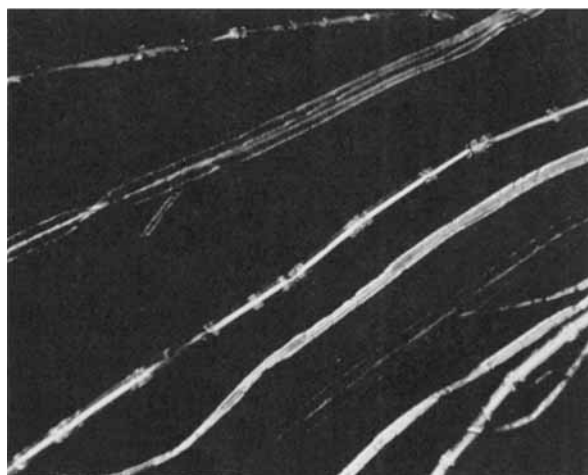
Before explaining how swelling occurs, it should be stated first that graft polymerization of acrylonitrile takes place uniformly throughout the fiber structure. This is supported by the microscopic observation that the presence of as little as 10% PAN graft (unhydrolyzed) prevents the dissolution of the fiber in cupriethylene diamine, although uniform swelling occurs.

There is some experimental evidence that grafting *per se* reduces the cohesion of the fiber structure. Swelling of the fibers *during* grafting is suggested by the observation that the volume of water retained *per fiber* after centrifugation is higher for polyacrylonitrile-grafted fibers (unhydrolyzed) than for untreated fibers and increases as graft level increases. Further, the moisture regain at high relative humidity is increased by PAN grafting, when calculated on the basis of cellulose content.

It is therefore suggested that an interposition of grafted PAN polymer chains between fiber elements occurs throughout the fiber cross section, reducing the cohesion between fiber elements and permitting swelling. After hydrolysis, the grafted chains, now water soluble, produce much greater swelling without destroying the integrity of the fiber (Fig. 4).

The hypothesis of this dual effect of grafting—the reduction of fiber cohesion and thus of the forces opposing swelling and the introduction of a potentially hydrophilic polymer capable of generating swelling pressures—appears to be sufficient to explain qualitatively the experimental observations.

The water retention value (WRV) increases with hydrolysis time as shown in Table III. This represents a correlation of swelling with carboxyl content when the initial graft level is held constant. On the other hand, Table X includes data in which the *same* carboxyl content (15–17%) was achieved by grafting 21% poly(acrylic acid), 48% acrylonitrile, and 71% poly(ethyl acrylate), respectively, followed by hydrolysis. The water retention values differed widely but were found to correlate with the initial graft level (Fig. 3). The influential factor here appears to be the reduction in fiber cohesion and its relationship to the level of graft polymer intrusion.



(a)



(b)

Fig. 4. Microphotographs of (a) unmodified pulp fibers (b) hydrolyzed polyacrylonitrile-grafted fibers of 90% graft level and 26 g/g WRV. Note the intact section of fiber, probably ungrafted (magnification 100 \times).

Addition of sodium chloride (which has been shown¹¹ to depress the viscosity of hydrolyzed PAN-grafted starch) presumably causes the grafted polyion chain to undergo configurational changes related to a reduction in the swelling forces. Decreasing the pH to 3.5 causes the nonionized poly(acrylic acid) to "precipitate," thereby reducing the swelling forces to a minimum. On the other hand, the reason for the constancy of WRV in the pH range 9-5 is not clear at present, as it does not seem to correlate with solution properties of sodium polyacrylate.

TABLE X
Water Retention Values of Sodium Polyacrylate
and Hydrolyzed Poly(ethyl Acrylate) Grafts

Polymer	Graft level, %	Carboxyl content as poly-(acrylic acid), %	WRV, g/g
Poly(acrylic acid)	21	17	310
Polyacrylonitrile	48 ^a	17	1000
Poly(ethyl acrylate)	71	15 ^b	1950
Polyacrylonitrile	21 ^a	9	350
Polyacrylonitrile	71	22	1750

^a Interpolated from Fig. 1.

^b Expected carboxyl content was 32%, but a considerable amount of polymer was lost during hydrolysis.

Finally, the lower WRV obtained after drying can be explained by the usual hysteresis effects. The reason for the difference between the xanthate-H₂O₂ process and the ceric ion process (40% and 10% drop in WRV, respectively) is believed to be due to the fact that the portion of the polymer lost during hydrolysis (more than 50% for the xanthate process) is no longer there to prevent the cellulosic fibrils coming into close contact and reforming irreversible bonds during drying.

Fiber Saturation Points were obtained through the courtesy of Dr. A. M. Scallan.

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