The Preparation and Properties of Acrylic and Methacrylic Acid Grafted Cellulose Prepared by Ceric Ion Initiation. II. Water Retention Properties

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Synopsis

Bleached sulfite softwood pulp and the corresponding paper have been grafted with acrylic and methacrylic acids and a number of other monomers. A practical, all aqueous, ceric ion method was used as described in Part I of this series. The water and saline retention values of the grafted pulps were determined. Super water sorbency, up to 48 g/g, were obtained after suitable post treatments. A number of variables were studied including the effects of pH, counterion, crosslinking, drying, and beating. It was gratifying that drying did not affect the efficiency of water or saline water retention. Useful linear functional relationships were found between the saline water retention values and the logarithm of the percent sodium chloride in the water. The two "model" parameters of the plots also correlated well with the water retention values and with the degree of grafting expressed as the ion exchange equivalents of the pulps. The osmotic pressure approach to the water sorption as developed by Grignon and Scallan[5] coupled with the restraining forces of the grafted polymer itself is used to interpret the process.

INTRODUCTION

In the first paper of this series[1] a practical, completely aqueous, system was developed for the ceric ion grafting of acrylic and methacrylic acids directly to bleached sulfite softwood paper. In this paper a study of the water retention values of the pulped paper under various conditions is described. The development of materials which absorb and retain large quantities of water has been extensively studied in recent years. Such products have found wide use in various sanitary and medical applications. In addition a number of other uses and potential applications have been developed. Essentially the entire subject of superwater absorbency has been discussed in recent monograph,[2] including a chapter on grafting in general and on the chemistry technology of grafted cellulose and starch.[3] Acrylic and methacrylic acid grafts to cellulose, particularly in the form of their sodium salts, are highly suitable as super water absorbents and for water-retaining structures. These may be prepared by grafting polyacrylonitrile, polyacrylamide, or polyacrylates or their α methyl counterparts or copolymers and hydrolyzing[4] or by direct grafting with the acids themselves. The latter is preferred since the hydrolysis step often leads to substantial losses of both polymer and cellulose leading to higher costs. On the other hand, direct grafting and polyacrylic or methacrylic acid and conversion to the sodium salt does not lead to superabsorbency without a

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post-grafting decrystallization step.[5, 6] This approach and other features of the system are discussed in detail in this paper.

EXPERIMENTAL

Materials

The paper, ceric ammonium nitrate (CAN), acrylic acid (AA), and methacrylic acid (MAA) used were described in the previous paper of this series.[1] Acrylonitrile (AN) and methyl acrylate (MA) were obtained from the Eastman Kodak Co., ethylene glycol dimethacrylate (EGDM) was obtained from Polysciences Inc., and the other chemicals from the Fisher Scientific Co. The monomers were purified by distillation and the EGDM by washing with a 5% sodium hydroxide solution before use.

Procedures

The grafting was carried out according to the procedure described previously.[1]

The grafted papers were defibered into pulp form in a Waring Blender at low speed for 1 min prior to the determination of their water retention values (WRV). The WRV values were measured by a centrifugal technique.[4-7] The grafted samples were equilibrated with deionized water for at least 2 h before being subjected to centrifugation. Each grafted sample was then placed in a centrifuge tube and centrifuged at 900 g for 30 min. The centrifuge tube was equipped with a fine mesh stainless steel strainer to allow excess water to drain away from the sample. The centrifuge tubes were also capped to prevent any evaporation of water. The weight of the sample equilibrated with water (WET) was recorded, and the sample was then dried in a vacuum oven at 40°C for 24 h. The oven dry weight of the sample (DRY) was recorded. WR values were calculated as follows:

$$\text{WRV (g/g)} = (\text{WET} - \text{DRY})/(\text{DRY}) \qquad (\text{g water/g oven dry sample})$$

The water sorbencies of the alkaline salts of the polyacrylic acid grafted samples were determined, after conversion of the grafted polyacrylic acid to their respective salts as follows: The polyacrylic acid grafted samples, after defibering in the Waring Blender, were converted into their alkaline salts by equilibrating with their respective alkaline hydroxides (except in the case of zinc salt) for at least 2 h (overnight for multivalent alkaline salts) with mild stirring. These samples were then washed thoroughly with deionized water until the washings were free of alkali.

The saline retention values (SRV) of the sodium salts of the various polymer-grafted cellulose samples were determined as follows: The sodium salts of the ionic polymer grafted cellulose pulps were equilibrated with various concentrations of sodium chloride solution at 23°C for at least 4 h. The samples were centrifuged at 900 g for 30 min and the saline retention value was determined, as with WRV, from the retention of water after centrifugation and expressed as g water/g oven dry material.

The decrystallization procedure described by Zahran et al.[7] was adopted here. Samples of the grafted cellulosic filter paper, first defibered in the Waring Blender, were decrystallized by treating with a 70% zinc chloride solution at 40°C for 3 h. The decrystallized samples in the form of their zinc salts were then converted into their sodium salts by equilibrating them with 3% sodium hydroxide solution for 2 h. These samples were then washed thoroughly with water until the washings were free of alkali. Decrystallization of some samples with hot sodium hydroxide was carried out by placing the samples in a boiling 3% sodium hydroxide solution for 30 min. These samples were then washed thoroughly with deionized water until the washings were free of alkali.

Hydrolysis of the polymethyl acrylate–cellulose grafts was carried out according to the method of Richards and White.[8] The hydrolysis was accomplished by treating the samples with a 2.5N sodium hydroxide solution at 15°C for 15 h. The samples, upon hydrolysis, consisted mainly of sodium-poly-acrylate-grafted chains. These were then washed thoroughly with deionized water until the filtrate was free of alkali.

RESULTS AND DISCUSSION

The effect of a considerable number of variables on the water and saline water retention values were investigated. These studies included both acrylic and methacrylic acid grafts and hydrolyzed and nonhydrolyzed methyl acrylate–acrylic acid copolymer systems.

Water Retention Values (WRV)

The WRVs of acrylic and methacrylic acid grafts are presented as a function of percent grafting in Figure 1. With both acids there is a linear increase in WRV with a tendency to level off at very high yields. The free acid forms show only minor changes whereas the sodium salts show considerable increases with methacrylic being lower in each case. The SPMAA grafts are about 15% lower on a molar basis than the SPAA, but the WRVs and the SRVs are up to nearly 50% lower. The same reductions were found by Zahran et al.[7] with radiation-grafted samples. Additional reasons for the differences could be due to polymethacrylic being a slightly weaker acid and with a stiffer and more hydrophobic backbone leading to less expansion with the same degree of ionization. It is probable however that the morphology of the two types of graft copolymers are different since the rates of grafting are different.[1,7] Increasing the pH of the water leads to a sharp increase in the WRVs at the point where ionization begins to become significant. Typical curves of WRV vs pH are shown in Figure 2. The leveling off at high grafting values, also shown in Figure 3, has been observed previously[6,7] and is usually ascribed to the restriction of further sorption by the cellulose crystallites. Decrystallization after grafting has been shown[6,7] to essentially eliminate this effect. The treatment was carried out on the acrylic acid grafts using the method described in the Experimental section. The results are shown in Figure 3. Not only is there no leveling off, but there is a very large increase in the WRVs which now reach super water absorbing proportions. Hot 3% sodium hydroxide solution also brings about considerable increases in the
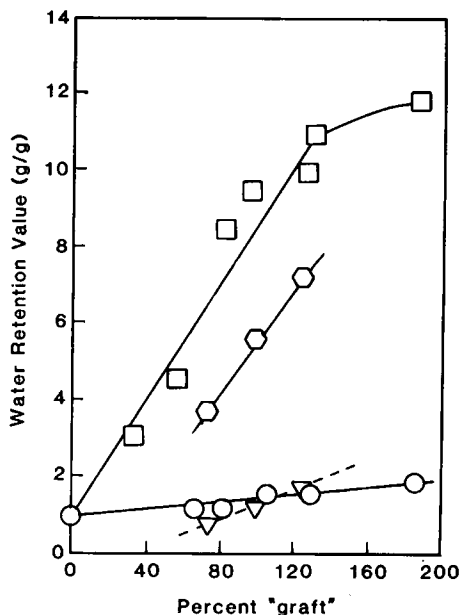
Fig. 1. Relationship between percent "graft" and water retention values (WRV) of grafted pulps: (○) polyacrylic acid PAA; (▽) polymethacrylic acid PMAA; (□) sodium polyacrylate SPAA; (⬡) sodium polymethacrylate SPMA.

WRVs but not as large as with the zinc chloride solution followed by conversion to the sodium salt. Typical results are shown in Table I. The results agree with those reported previously with radiation-grafted rayon fibers.[7] It is gratifying that the ceric ion grafting technique gives essentially the same type of result as the preirradiation method. The more practical hot sodium hydroxide treatment is, however, much more effective with preirradiation grafts.[7] This is presumably due to the grafting being throughout the fibers enabling the alkali to penetrate more deeply and decrystallize more
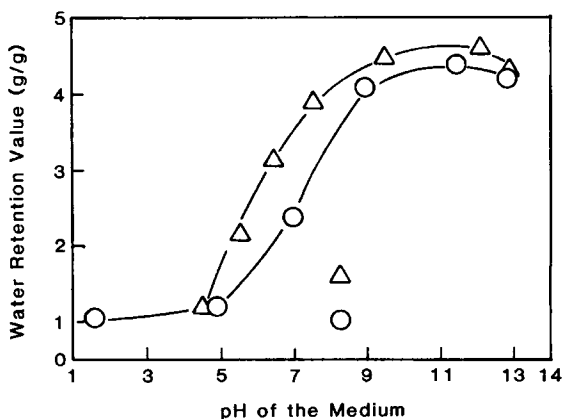

Fig. 2. Effect of pH on the WRV's of polyacrylic acid grafted pulps: (○) 56% graft; (△) 81% graft.
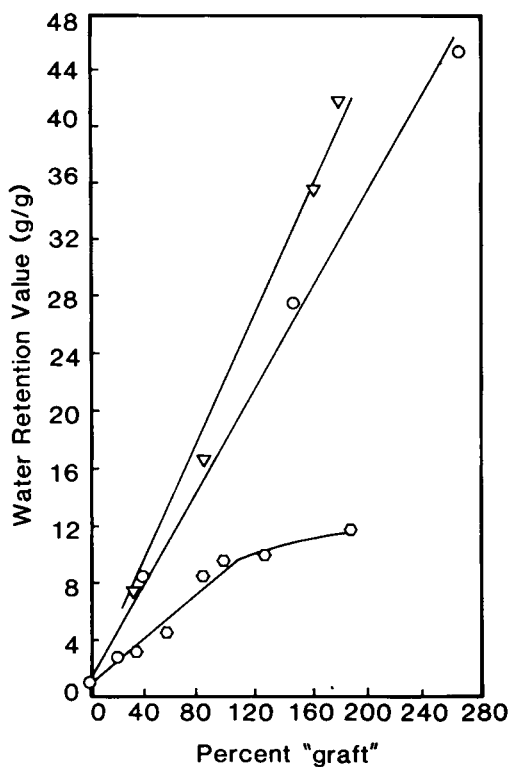
Fig. 3. WRVs as a function of percent grafting: (○) SPAA; (▽) decrystallized SPAA; (○) hydrolyzed copolymers of methyl acrylate and acrylic acid, as sodium salts.

TABLE I
Effect of Decrystallization (DC) after Grafting on Water Retention
Value of Polyacrylic-Acid-Grafted Pulps

| % "graft" | Decrystallization conditions | WRV (g/g) | | | Zinc form[c] |
		Before DC[a]	After DC[b]	Ratio	
00	70% zinc	1.0	—	—	—
33	chloride at 40°C	3.1	5.8	1.9	—
96	for 3 h	9.5	19.0	2.0	—
129		11.5	17.4	1.5	0.9
186		11.8	40.9	3.5	0.8
204	70% zinc	19.1	47.8	2.5	0.7
56	at 40°C for	4.6	7.4	1.6	—
125	4.5 h	8.6	15.2	1.8	—
129	Hot 3% NaOH	11.5	14.4	1.2	—
186	for 0.5 h	11.8	19.4	1.6	—

[a] Before decrystallization, in their sodium salt form.
[b] After decrystallization, the pulps were reconverted to sodium aslts.
[c] Measured after the decrystallization stage, before converting to their sodium salts.

TABLE II
Effect of Hydrolysis on Water Retention Value of Poly(acrylic Acid-co-Methyl Acrylate)-
Grafted Pulps

| | Composition of graft copolymer (%) | | Water retention value (g/g) | | |
| | | | Before hydrolysis | | After Hydrolysis, sodium form |
% "Graft"	AA	MA	Hydrogen form	Sodium form	
8	87.6	12.4	0.7	1.0	—
21	94.3	5.7	0.6	2.2	2.7
38	—	—	1.3	—	8.5
144	71.0	29.0	1.2	—	27.5
261	58.3	41.7	0.4	19.1	45.4
335	—	100	0.2	—	32.5

effectively. The explanation of decrystallization, although not proven, is reasonable in view of the huge increases in water retention and sorption, even with cellophane.[6,7] Decrystallization was also shown directly by X-ray analysis to take place in similar systems with ethyl acrylate as the grafted monomers.

The "classical" method of achieving high water sorption and retention has been to graft monomers such as acrylontrile, acrylamide, acrylate esters, or their α methyl equivalents followed by alkaline hydrolysis.[3,4] This double process undoubtedly disrupts the crystalline structure causing the onset of supersorbency. A series of acrylic acid–methyl acrylate copolymer grafts were prepared by the same technique as used for the acid monomers and their WRVs determined. The results are shown in Table II and are also included in Figure 3. Supersorbent properties are clearly displayed. It is interesting that all the different copolymers lay on the same straight line, showing, presumably, their complete hydrolysis to the corresponding sodium polyacrylates. The consistently superior performance of the decrystallized sodium polyacrylate grafts is also noteworthy, for example, at 140% grafting the WRVs are 36 and 28 g/g, respectively. Table II also includes one sample of a pure methyl acrylate graft. The WRV is considerably less than much lower grafted

TABLE III
Effect of Drying on Water Retention Value of Sodium-Polyacrylate-Grafted Pulps

| Percent graft | Water retention value (g/g) | |
	Never dried	Oven dried[a]
33	3.1	2.9
56	4.6	4.9
81	8.5	8.2
96	9.5	10.9
125	8.6	9.3
186	11.8	12.9

[a] Dried at 40°C in vacuum oven for 24 h.

TABLE IV
Effect of Beating on Water Retention Value of Sodium-Polyacrylate-Grafted Pulps

Percent "graft"	Water retention value (g/g)		After oven drying[a]
	Before beating	After beating	
33	3.1	3.9	3.6
56	4.6	7.8	7.3
96	9.5	13.0	11.3
125	10.0	13.1	14.2
186	11.8	21.5	19.3
204	19.1	26.5	27.4

[a]After determination of WRV, the fibers were redispersed in water and the WRV was determined again.

copolymer samples. It is possible that the acrylic acid component of the copolymers, always more than 50%, facilitate a greater disruption of the cellulose structure on hydrolysis.

A number of other variables were studied including the effects of drying, beating, and crosslinking.

The effect of drying the grafted pulps as their sodium salts is shown in Table III. The pulps dried at 40°C in a vacuum oven for 24 h showed essentially no change in the WRVs. The effect of beating was studied using a Waring Blender at high speed for one minute. The results are shown in Table IV. Rather substantial increases in the WRVs were found. These higher values were also retained after oven drying and redispersing as shown also in Table IV. The results are not surprising since it is well known that beating increases fiber swelling.[5,9,10]

Finally the effect of crosslinking by the addition of 0.5% of EGDM during the grafting process was investigated. This process is well known as a method to further reduce homopolymer formation. The results (Table V) show that the addition of EGDM reduces the percent grafting a little but essentially eliminates homopolymer formation, unfortunately as might be expected the WRV is also greatly reduced. More data on the effect of crosslinking will be presented with the SRV studies.

TABLE V
Effect of Crosslinking on Water Retention Value of Sodium-Polyacrylate-Grafted Pulps[a]

Ethylene glycol dimethacrylate in initial monomer (%)	Polymer weight increase (%)		% Homopolymer	Water retention value (g/g)
	Before extraction	After extraction		
0.0	170	150	11.8	11.3
0.5	159	158	0.6	4.4

[a]Pretreatment conditions: CAN concentration = 25 mmol/L; time = 2 h: temp = 25°C.
Reaction conditions: monomer concentration = 5% by volume; time = 5 h; temp = 25°C.

Saline Retention Values (SRV)

Most of the commercial uses for the superabsorbents are concerned with blood, urine and other fluids rather than pure water.[11] The effect of salts, usually sodium chloride, are therefore also studied with such systems; the results are termed saline retention values (SRV).

The effect of sodium chloride concentration on the retention values have been determined for all the systems studied for their WRVs. The results are presented in Figure 4 for sodium polyacrylate grafted pulps in the form of semilog plots. Interestingly the SRVs give good linear relationships for all the systems studied; i.e.,

$$SRV = K \log(NaCl) + C$$

where SRV is the saline water retention value (g/g oven dry pulp) and K and C are the model empirical parameters. (NaCl) is expressed as percent salt by weight per volume. C is defined as the SRV at 1% NaCl solution.

The model parameters K and C are linearly related to the percent grafting expressed here in terms of the ion exchange capacities, of the pulps. This is illustrated clearly in Figure 5 for all the systems studied.
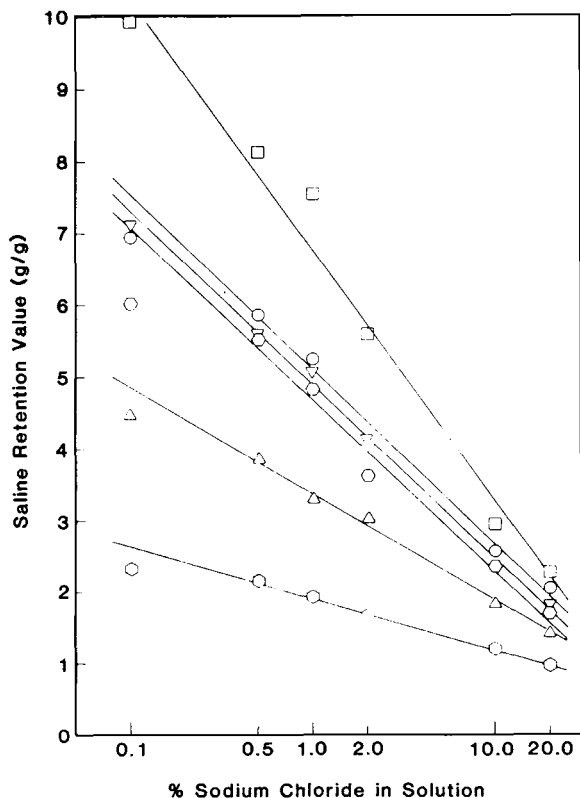

Fig. 4. Effect of sodium chloride concentration, wt% on the SRVs of SPAA grafted pulps: (□) 186% grafting; (○) 125%, (▽) 96%, (○) 81%; (△) 56%; (○) 33%.
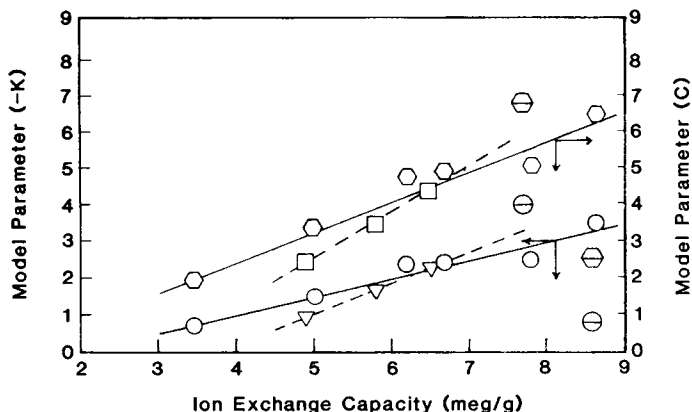
Fig. 5. Relationship between ion exchange capacity of the grafted pulps and the model parameters: (○) SPAA; (△) SPMA; (□) crosslinked SPAA CLSPAA.

A linear regression analysis was performed and the correlations found to be as follows:

SPAA grafted pulps $-K = 0.48 \,(\text{IEC}) - 0.89$ $(r^2 = 0.927)$

$\qquad\qquad\qquad\qquad\quad C = 0.81 \,(\text{IEC}) - 0.68$ $(r^2 = 0.953)$

SPMA grafted pulps $-K = 0.80 \,(\text{IEC}) - 2.94$ $(r^2 = 0.996)$

$\qquad\qquad\qquad\qquad\quad C = 1.24 \,(\text{IEC}) - 3.59$ $(r^2 = 0.999)$

where IEC = ion exchange capacity (meq/g pulp). The correlations are valid for IEC values between 3 and 9 meq/g. The SRVs are higher with the sodium polyacrylate than the sodium polymethacrylate grafts, but the latter increase at a faster rate. The reasons for this are not really clear at this time.

The effect of salt concentration on the water retention values are best explained in terms of the swelling of cellulose gels containing anionic groups. This treatment was first proposed by Proctor[12,13] and extended and further clarified by Scallan and Grignon[9,10] in terms of the swelling of such gels, i.e. pulps, in the context of this paper. Briefly this approach may be summarized in the following way:

The ions attached to the macromolecular network in the gel are immobile and are considered to be separated from the external solution by a semiperme-able membrane, which confines the immobile ions, but gives passage to water and all simple ions. The excess concentration of mobile ions in the gel phase is calculated using Donnan's equilibrium model. This excess concentration is directly proportional to the osmotic pressure differential as stated in van 't Hoff equation, and this, in turn, is assumed to be directly proportional to the degree of swelling, i.e., to the water sorption itself.

Grignon and Scallan[10] have also attempted to apply the above theoretical treatment to supersorbent cellulose gels. Although a good qualitative agreement on the effect of pH and neutral salt has been obtained, it falls short of quantitative agreement. This may be due to the following reasons: (1) The concentration of ionizable groups in the cellulose gel was assumed constant
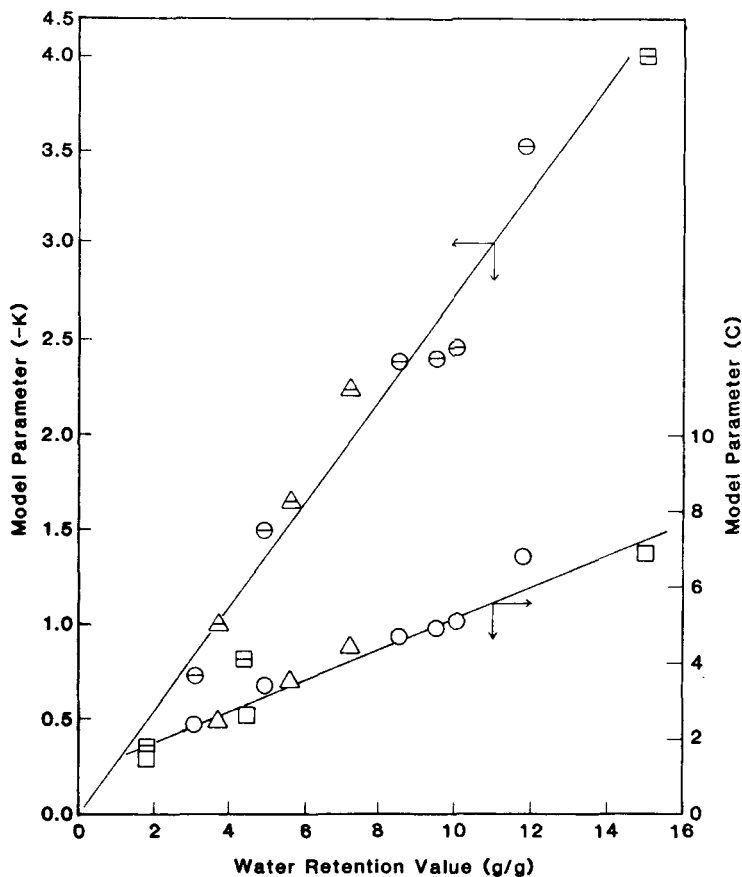
Fig. 6.   Relationship between the WRVs and the model parameters: (○) SPAA; (△) SPMA; (□) CLSPAA.

over the whole range of swelling, which is not correct, since swelling of these fibers clearly causes changes. The authors did, indeed, recognize and acknowledge this point. (2) Degree of swelling is expressed in terms of the ratio of water to solid material in the swollen gel, which should be modified and expressed in terms of the ratio of weight of water and electrolyte (salt) to the weight of cellulose gel, excluding the weight of salt.

The swelling forces due to osmotic pressure effects are counteracted by the cohesive forces of the crosslinked gel which also presumably still retains some residual crystallinity. Eventually an equilibrium is reached leading to the observed WR and SR values. When a crosslinking agent is introduced these values are lowered as shown, for example, in Figure 5.

It is interesting that the model parameters K and C are also related to the WRV vlaues themselves. This is clearly shown in Figure 6 for SPAA grafted pulps. The actual correlations are:

$$-K = C'\ \ (\text{WRV}), \qquad C' = 0.22, \qquad r^2 = 0.952$$

$$C = C''\ \ (\text{WRV}), \qquad C'' = 0.42, \qquad r^2 = 0.961$$

TABLE VI
Effect of Counterion's on the WR Values of a 129% Polyacrylic-Acid-Grafted Pulp

Counterion	WRV
H^+	1.6
Li^+	12.9
Na^+	11.5
K^+	11.6
$Mg\ (2+)$	1.3
$Ca\ (2+)$	1.1
$Zn\ (2+)$	0.9
$Cu\ (2+)$	0.8
$Al\ (3+)$	0.7

C' and C'' are constants for all the grafted pulps. It is clear from these expressions and the earlier correlation that $SRV = K \log(NaCl) + C$ that the SRV at a particular correlation is only dependent on the WRV value and independent of the percent grafting of the pulp.

K is dependent on the ion exchange capacity of the pulp and the cohesive forces of the fibers. The latter is complex and hard to quantify. The treatment of Gregor[14] is an interesting approach to this problem.

Finally the effect of the actual counter ion was studied. The results are presented in Table VI. The WRVs increased in the order

$$Al^{3+} < Cu^{2+} < Zw^{2+} < Ca^{2+} < Mg^{2+} < H^+ < Na^+ < K^+ < Li^+$$

Various orders have been reported for the effect of counterions on the strength of papers made from carboxymethylated pulps and the corresponding swelling values.[9,10] The degrees of dissociation of the corresponding acetate salts are also known from conductivity measurements.[9,10] Although the various orders are not consistent it was clear that Al^{3+} was the lowest, then Ca^{2+}, Mg^{2+}, and H^+; Na^+, Li^+, and K^+ were always the highest. Consistent with this picture increasing the pH of the water causes a marked increase in the WR values when dissociation becomes significant as shown in Figure 2. In our system the multivalent ions probably also cause ionic crosslinks increasing the cohesive forces and reducing swelling.

The work presented in this paper has been taken in part from a fuller report contained in the dissertation of Vitta.[15]

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