

The Water Absorbency of Poly(2-dimethylaminoethyl Methacrylate)-Grafted Cellulose Fibers

In an earlier publication,¹ we showed that the water absorption of cellulose fibers can be substantially increased by the introduction of an anionic polyelectrolyte (alkaline hydrolyzed polyacrylonitrile, HPAN) by graft copolymerization. This increase in water absorbency was ascribed to the interposition of the hydrophilic polymer chains between the fiber structural elements leading to a reduction in their cohesion and generating additional swelling pressure when the modified fiber comes in contact with water. In this work we describe the preparation and water absorbency characteristics of cellulose fibers grafted with a cationic polyelectrolyte.

EXPERIMENTAL

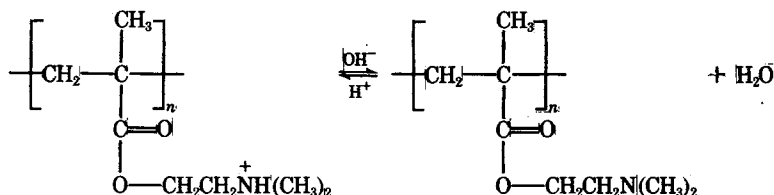
The monomer used in this work was 2-dimethylaminoethyl methacrylate hydrochloride (DMM). This cationic monomer was prepared by neutralizing 2-dimethylaminoethyl methacrylate with hydrochloric acid.

Graft copolymerization was carried out according to the method developed by Faessinger and Conte.² A never-dried pulp was first steeped in 7% sodium hydroxide solution and then exposed to carbon disulfide vapor for 2 hr until a xanthate with a degree of substitution of 0.18 was obtained. The sodium cellulose xanthate was then ion exchanged with ferrous ion. Polymerization was carried out for 2 hr at a 2% concentration of the ion-exchanged pulp in the presence of hydrogen peroxide (0.15%) and DMM monomer. The poly(DMM) obtained was expected to carry a wide variety of anions; and in order to replace these by a single anion (e.g., chloride), the poly(DMM)-grafted fiber slurry was first brought to pH 12 using sodium hydroxide, washed, and then acidified with hydrochloric acid to pH 3.5. An infrared spectrum showed a characteristic peak at 1730 cm^{-1} , indicating the presence of the carbonyl group of the poly(DMM). Graft level was determined by the nitrogen analysis (Kjeldahl method).

The water absorbency was measured by a centrifugal technique³ using a centrifugal acceleration of 900 G and was expressed as the water retention value (WRV), i.e., the weight of water retained per gram of fiber.

RESULTS AND DISCUSSION

Except at low monomer concentrations, the graft level increased linearly with monomer concentration, as depicted in Figure 1. Poly(DMM) may exist either as an amine or in the ammonium salt form depending on the pH:



The graft level was calculated from the nitrogen analysis of the ammonium chloride form. The calculated polymer contents from nitrogen analysis were in good agreement with those determined by potentiometric titration using hydrochloric acid, as shown in Table I.

The interconversion between the amine and ammonium salt form by changing pH is expected to have significant effects on the swelling of the grafted fiber as measured by WRV. Plots of the WRV at various pH's for three different graft levels of the poly(DMM)-g-cellulose are shown in Figure 2.

The influence of pH on water retention value can be explained in the following way. At pH 8.0 to 9.0, the polymer is present in the nonionized amine form, and the fibers exhibit water retention values similar to that of the unmodified fiber (WRV \approx 1.6). As the pH moves toward

TABLE I
Determination of Graft Level

Kjeldahl method		Potentiometric titration		
N Found, %	Calculated polymer content, %	HCl required, ^a meq	Calculated polymer content, %	Graft level, %
3.53	48.8	2.62	50.8	95.3
2.38	32.9	1.73	33.5	49.0
1.57	21.7	1.05	20.4	27.7

^a Amount of acid needed (in meq) to bring 1 g poly(DMM)-g-fiber from pH 9.0 to pH 4.25.

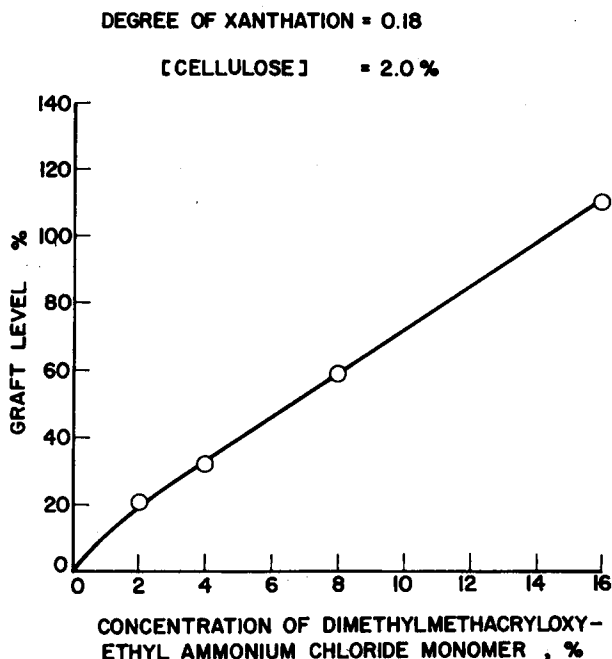


Fig. 1. Effect of monomer concentration on poly(DMM) graft level using the xanthate-H₂O₂ process.

the acid side, the nonionized amine groups are converted into the ionized ammonium salt form, and swelling increases sharply to reach a maximum value at pH 4.0, where conversion is complete. This reduction in pH leads to an increase in both the degree of ionization and the number of ionized ammonium groups. The net effect gives rise to (a) an expansion of the polymer chains within the cellulose fiber and (b) an increase in the affinity toward water molecules through hydration of both the quaternized polyions and the chloride (counterions).

The WRV also increases with graft level, reflecting the increase in the total number of ionized groups per fiber.

It is interesting to compare these results with those obtained with fibers grafted with an anionic polyelectrolyte (hydrolyzed polyacrylonitrile, HPAN) of similar graft level, i.e., of similar extent of polymer intrusion, as shown in Figure 3. The effect of pH on WRV is reversed. This is simply because HPAN comprises a copolymer of sodium polyacrylate and polyacrylamide. At pH 3.8, the carboxyl groups are present in the nonionized acid form with WRV about the same as that of the untreated fiber. As pH is increased by adding sodium hydroxide, the conversion of the acid form into the ionized sodium carboxylate begins. One difference, however, is immediately apparent: the degree of swelling as measured by WRV is considerably higher for the anionic fibers than for the cationic ones. This may partly be attributed to a higher carboxyl content (3.92 meq/g) for the HPAN fiber than the quaternized

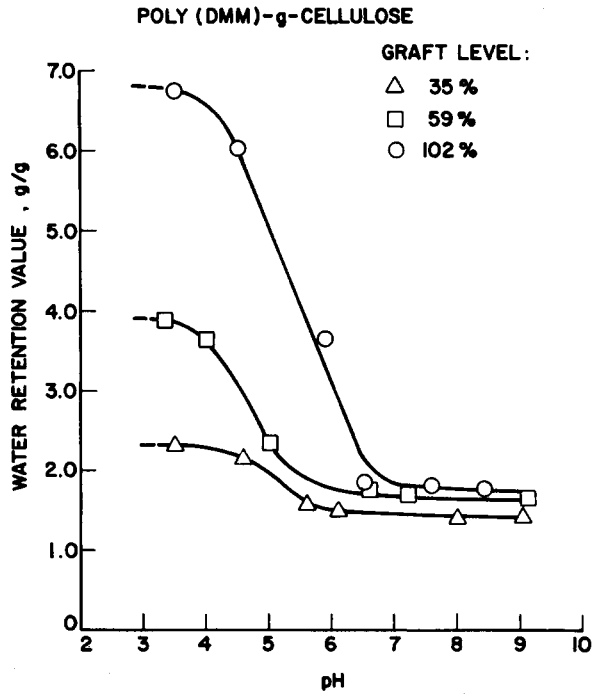


Fig. 2. Effect of pH on water absorbency of poly(DMM)-g-cellulose.

- POLY (DMM) - g - CELLULOSE GRAFT LEVEL : 102 %
- △ HPAN - g - CELLULOSE GRAFT LEVEL : 108 %

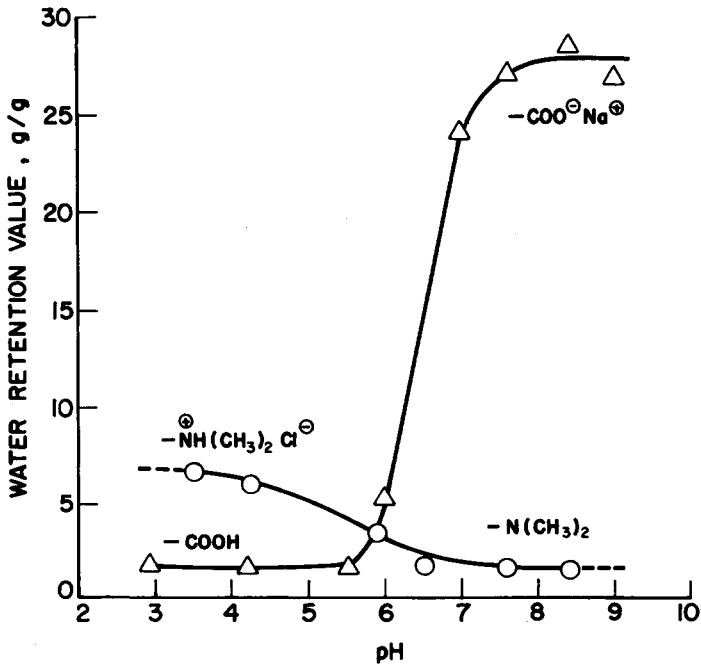


Fig. 3. Comparison of water absorbency of HPAN-g-cellulose and poly(DMM)-g-cellulose.

ammonium content (2.56 meq/g) for the poly(DMM)-grafted fiber (when compared on the same milliequivalent basis, a 2.6 meq/g HPAN fiber would have a WRV of about 16 g/g). In addition, the hydration of the carboxylic and sodium ions by water molecules may be more favorable than that of the alkyl substituted ammonium and chloride ions. Both factors would account for an overall higher WRV for the HPAN fiber than for the poly(DMM)-g-fiber.

In conclusion, the ability of cellulose fibers to absorb water can be substantially increased by the grafting of a polyion. Such an increase in water absorbency is, however, related to both the amount and nature of the ionic groups.

References

1. P. Lepoutre, S. H. Hui, and A. A. Robertson, *J. Appl. Polym. Sci.*, **17**, 3143 (1973).
2. R. W. Faessinger and J. S. Conte, U.S. Pat. 3,330,787, July 11, 1967.
3. A. M. Scallan and J. Carles, *Svensk. Papperstidn.*, **75**, 699 (1972).

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