Role of Polyacrylate Starch Copolymer in Water Sorption*†

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Synopsis

Water sorbence by saponified polyacrylonitrile-grafted polysaccharides was studied in relation to practical end uses. Graft copolymers prepared from wheat flour, corn flour, cotton wool, and rayon fibers swelled to a gel, exhibiting a 10- to 20-fold increase in sorbency over the starting materials. A further enhanced water capacity was obtained when homopolymer was not removed. Soaking the wheat flour copolymer in salts or dilute mineral acid nullified the enhanced water sorbence, which could be reversible restored by neutralization of acrylic acid functions with alkali. Swelling the copolymer in aqueous D-glucose did not impair its water capacity. The mechanism of swelling to a gel appears to involve electrolyte osmotic pressure generated by a Donnan equilibrium. Grafting starch elevated its heat of water vaporization above that of pure water, and increased its capacity to absorb water from ethanol-water vapor at 40° above that of native starch. At higher temperatures, however, the dehydrating capacity decreased to that of native flour.

INTRODUCTION

Because of the paramount importance of water as the major functional component of biological and inanimate systems on Earth, particular interest has been aroused by the development[2-4] of a saponified polyacrylonitrile (PAN)-grafted starch (II) exhibiting extremely high water sorbency, which is marketed particularly for agricultural and horticultural end uses.[5,6] While the graft polymerization of this product is initiated[1-4] with Ce^{4+}, others[7] have reported the use of Mn^{3+} initiation. Water-absorptive celluloses have been prepared[8] by a supposed "postdecrystallization" of direct polyacrylic acid grafts (see Discussion).

Saponification of PAN-grafted starch (I) yields a mixture of pendant carboxylate and carboxamide functions.[2,3] By analogy with other hydrogels,[9] the hydrophilic property of the product should depend critically on its polyelectrolyte nature, the water absorbency decreasing tenfold in the presence of simulated urine.[2] Accordingly, we first examined the effect of various solutes on absorbency in order to clarify its mechanism. The heat of water vaporization from the saponified graft copolymer was determined, too.

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*Dedicated to the memory of Mrs. Bella Hirschmann, our late colleague who contributed to this research.

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Fig. 1.

These properties of the absorbent are also relevant to its possible use in drying ethanol (gasohol program[10]), as a functional ingredient of disposable softgoods for hygienic and medical purposes,[11] or as a medicant for treating both diarrhea and constipation (cf. calcium polycarbophil[12]). Besides wheat and corn flours, saponified PAN graft copolymers were also prepared from cotton wool and rayon fibers, in view of their potential value as an advantageous strengthening agent in cement.

The chemical reactions presumably involved in formation of the saponified PAN copolymer are depicted in Fig. 1, in accordance with the account of Ranby and Rodehed.[13]

EXPERIMENTAL

Preparation of Saponified Graft Copolymers. Starting materials were commercial white wheat flour, corn flour, rayon fiber, and surgical cotton wool.

The polysaccharides were reacted in water with acrylonitrile in the presence of ceric ammonium nitrate, as described by Fanta et al.[3] Saponification was performed at 100°C in aqueous sodium hydroxide (0.7 N), and the product was separated by stirring with methanol.[3]

Measurement of Water Sorbency. Water sorbency, defined as the weight of water (g) absorbed by one gram of material after 30 minutes, was determined as described by Fanta et al.[3] Saponified copolymers (20 mg) swelled to a gel, which was separated from supernatant on a 170 mesh sieve and weighed.

Thermal Analysis After drying in an oven (105°C), the material was equilibrated with the designated vapor and then examined in a Du Pont-900 Differential Thermal Analyzer and a Du Pont-950 Thermogravimetric Analyzer (nitrogen flow 0.4 L/min and rate of heating 5°C min^{-1}). Using the percentage weight loss in thermogravimetric analysis (TGA) together with the corresponding chart area in differential scanning calorimetry (DSC), it was possible to calculate the heat of vaporization.

Removal of Water from Ethanol-Water Vapor. This system was developed by Basch and Wasserman.[14]

After being dried in an oven, the test material (30–50 g) was packed in a jacketed (thermostat) horizontal tube, through which was then passed a stream of nitrogen gas (15 mL/min) that had been bubbled through an ethanol-water (4:1) mixture maintained at 60°C. Thereafter, the vapor was condensed from the nitrogen stream and collected in a benzine trap until first turbidity appeared. The weight increase in the trap measured the amount of pure ethanol obtained.

RESULTS AND DISCUSSION

Sorbency of Saponified PAN-Grafted Copolymers. The copolymeric derivatives prepared from wheat flour, corn flour, cotton wool, and rayon were all highly absorbent (Table I). When the crude grafted copolymer was not extracted with dimethylformamide (DMF) before saponification, the saponified product exhibited considerably enhanced swelling, indicating that saponified PAN remaining contributed to this property.

A larger-scale preparation with wheat flour (35 g) was conducted without isolation of the PAN-grafted intermediate, while applying enhanced mechanical agitation. The add on was 60% and the water absorbency 340 g/g: this product (P) was used in the subsequent experiments.

TABLE I
Yield and Sorbency of Copolymerized Polysaccharides

Polysaccharide		Polymerization add-on (%)		Saponified product[b]	
Material	Sorbency (g/g)	Homo-PAN[a]	PAN-copolymer[b]	Add-on[c] (%)	Sorbency (g/g)
Wheat flour	23	22	35	{ 57[d] { 35	500[d] 280
Wheat flour[e]	23	—	—	60[d]	340[d]
Corn flour	29	14	129	150[d]	600; 700[d]
Cotton wool	47	5	63	114	500
Rayon fibers	26	9	79	87	420

[a] DMF-solubles.
[b] After DMF extraction, unless otherwise stated.
[c] As percentage of polysaccharide starting material.
[d] Without DMF extraction before saponification.
[e] 35 g reacted without isolation of PAN-grafted intermediate.

Effects of Solutes on Swelling (Tables II and III). Immersion in dilute solutions of sodium or magnesium chloride diminished the enhanced sorbency of product P: the decrease was progressively greater as the salt concentration was raised, until no further drop was obtained at concentrations above 0.6% and 0.03%, respectively. No change in chloride ion concentration was detected by titration, indicating that the gel would not be useful for separatory processes such as desalination.

On soaking P in dilute hydrochloric acid, the acidity of the solution decreased and the sorbency dropped to that of ungrafted starch. However, after neutralization of the free acrylic acid functions with alkali, the enhanced water capacity was restored. The critical functionality of ionized carboxylate groups in maintaining enhanced sorbence is thereby demonstrated.

Immersion in D-glucose solutions of a wide range of concentrations did not change the enhanced sorbence of P, and no change in sugar concentration was found. Thus, the osmotic pressure of the medium, as such, does not influence the swelling of the materials.

These qualitative findings accord well with a mechanistic model of the enhanced water sorbence of acrylate-grafted polysaccharides that is essentially the same as that described[15] for the swelling of cellulose gels. Swelling is accordingly considered to be caused by an osmotic pressure differential resulting from a difference in concentration of mobile ions between the interior of the gel and the external solution. The fundamental feature within the gel, bringing about the unequal distribution, is the presence of ionizing acidic groups attached to the macromolecular network. Using the Donnan theory to describe the distribution of ions, the experimentally observed variations in swelling can be explained.[15]

Thus, the degree of swelling is proportional to the osmotic pressure differential generated, which is, in turn, determined by the excess (E) of diffusible ions in the gel, and

$$E = \frac{\lambda - 1}{\lambda + 1} c\alpha$$

where $c\alpha$ is the concentration of bound ionized acrylate groups, and

$$\lambda = \frac{[\text{cations}]_{\text{gel}}}{[\text{cations}]_{\text{medium}}} = \frac{[\text{anions}]_{\text{medium}}}{[\text{anions}]_{\text{gel}}}$$

Consequently, for a polyanionic gel, there will be an excess of cations in the gel, excess anions in the medium and the pH in the medium is always greater than within the gel.[15]

This type of mechanism also explains the behavior of super-absorbent carboxymethylated cotton and of conventional wood pulps during alkali swelling and during potentiometric titration.[15]

Williams and Stannett[8] have reported that, after immersion in 70% aqueous zinc chloride, followed by a thorough water wash, acrylic acid-grafted cellulose (water sorbency = 0.5 g/g) were transformed into a water-absorptive form (water sorbency = 30 g/g). The change was ascribed[8] to a supposed

TABLE II
Effect of Salts and D-Glucose on Swelling of Saponified PAN-Grafted Wheat Flour[a]

Solute		Water content
Name	Concentration	(g/g)
None	—	340
Sodium chloride	10^{-3}M	180
Sodium chloride	10^{-2}M	103
Sodium chloride	10^{-1}M	55[d]
Sodium chloride	0.5 M[c]	41[e]
Magnesium chloride	0.0036M	35
Magnesium chloride	0.036M[c]	28
None	—	225[b]
D-glucose	0.08M	250[b]
D-glucose	0.55M	220[b]

[a]Untreated wheat flour sorbency in distilled water 23 g/g.
[b]Different batch of grafted floor.
[c]Concentration in sea water.
[d]After 5 h immersion in solution, the value was 56.
[e]After 5 h immersion in solution, the value was 46.

TABLE III
Effect of Hydrochloric Acid and Neutralization
on Swelling of Saponified PAN-Grafted Wheat Flour

10^{-3}N.HCl[c] (mL)	Immersion time (h)	Final pH	Water content[a] (g/g)
50	0.5	3.7	165
50	72	5.5	175
20	2	6.3	210
50	48	5.7	180
20	48	6.9	150
10	48	7.2	150[b]

[a]In the acid. The water content in distilled water (sorbency) was 225 g/g.
[b]After a second immersion in hydrochloric acid (final pH = 3.2, water content 10 g/g), this gel was transfered to water (pH 6.2, water-sorbency 35 g/g). Another twice acidified sample (final pH 3.2, water content 14 g/g) was immersed in aqueous sodium hydrogen carbonate (25 g/L, 50 mL, pH = 8.8) for 18 h (final pH = 9.0, water content 36 g/g) and then washed with water (final pH 6.2, water sorbency 225 g/L).
[c]Initial pH = 3.1.

TABLE IV
Thermal Analysis of Corn Flours Equilibrated with Water Vapor

Test material	Weight loss[c] %	Peak position in DSC (°C)	Heat of vaporization (cal/g H_2O)
Grafted	34.5	105	637
Grafted[a]	46.4	105	596
Ungrafted[b]	15.6	88	438

[a] Equilibrated with ethanol vapor before equilibration with water vapor.
[b] Not dried in oven before equilibration with water vapor.
[c] At 200°C.

"postdecrystallization" process, involving the zinc salt. The present results (Table III, note b) and above discussion would indicate an additional explanation. The zinc salt would, accordingly, act so as to neutralize the acrylic acid functions, thereby converting the copolymer into the polyanionic form which would be water absorptive.

Thermal Analysis of Water Vaporization from the Starches (Table IV). Two samples of P were analyzed by DSC and TGA: one after equilibration with water vapor alone, and the other after equilibration with ethanol vapor followed by water vapor.

The DSC peak was at 105°C for both the samples of grafted starch examined, and the corresponding values calculated for the heat of vaporization were very close, considering the heterogeneity of the material and the inaccuracy of measuring chart areas. The value obtained (616 cal/g water ± 20) was much greater than for ungrafted starch (438 cal/g water), and contrasted with the value of 540 cal/g for pure water.

The DSC peak for ungrafted starch was at 88°C. Grafting greatly increases the water capacity, and pre-equilibration with ethanol may engender a further increase, as evidenced by TGA-data of weight loss (Table IV). According to the location of the DSC peaks and the calculated heats of vaporization, it appears that water is held more strongly in the derivatized starch. Thus, more energy (higher temperature and/or longer drying time) would be required for its removal.

Absorption of Water from Ethanol-Water Mixtures. The gasohol program[10] requires new nondistillative techniques for a less costly and less energy-consuming conversion of the ethanol-water mixture formed in fermentation to absolute alcohol. Vapor-phase systems investigated have been based on the use of water absorbants, such as rayon fiber[16] and milled corn grain,[14,17] while selective liquid-phase absorptions have utilized cellulose,[18] milled corn grain,[19] synthetic ion-exchange membranes for electrodialysis,[20] and, more recently, synthetic pervaporative polar membranes.[21]

Three techniques that were applied to superabsorbent saponified PAN-grafted wheat flour did not produce enrichment in the ethanol content of the product. Batchwise shaking in aqueous alcohol mixtures at ambient temperatures was ineffectual (Table V), as were liquid chromatographic column treatments at ambient temperatures and vapor-phase chromatography of ethanol-water azeotrope in a tube heated above the boiling point.

TABLE V
Treatment of Ethanol-Water Mixtures
with Saponified PAN-Grafted Wheat Flour[a]

Aqueous ethanol		Copolymer (mg)	Time (h)	Sorbency (g/g)	Refractive index of liquid[b]
Composition (% ethanol)	Vol. (mL)				
0	—	0	0	—	1.333
0	50	20	0.5	400	ND
20	50	20	0.5	270	ND
20	15	40	3	263	1.341
20	25	80	20	210	1.341
20	50	80	3	267	1.341
20	100	82	3	313	1.341
80	5	78	5	5	1.3622
80	50	82	24	6	1.3622
80	100	40	0.5	8	ND
96	15	40	3	13	1.363
100	50	20	0.5	6	1.359

[a] Mechanical shaking at ambient temperature.
[b] Some final liquids were also determined to be unchanged in composition by specific gravity determination.
ND not determined.

Positive results were obtained in a vapor-phase system when a carrier-gas stream was used to propel 80% ethanol vapor over a heated sorbent (Table VI): this design permits a more efficient exploitation of the sorbent, since lower temperatures, below the desorbing temperature, may be chosen. At 40°C, the copolymer produces twice the amount of absolute alcohol as the crude flour. At higher temperatures, however, the water sorbency of graft decreases to the level shown by native flour. This result was obtained with samples previously oven dried at 110°C. Drying at 87°C gave a highly absorbent native flour, but it was insufficient to condition an active copolymer. These differences between the behavior of native and grafted flours can be explained by the stronger binding of water to the grafted copolymer, as revealed by the heats of vaporization of 438 and 637 cal/g, respectively.

TABLE VI.
Production of Absolute Ethanol from 80% Ethanol Vapor

Temperature of sorbent (°C)	Native corn flour		Copolymer	
	Distiln (h)	Alcohol yield (%)[a]	Distiln (h)	Alcohol yield (%)[a]
40[b]	12	27	14	49
50[b]	8	36	6	32
60[b]	2.5	24	3	30
50[c]	9.5	43	< 1	10

[a] As percentage of sorbent weight (native 50 g; copolymer 30 g).
[b] Sorbent previously dried at 110°C.
[c] Sorbent previously dried at 87°C.

The copolymer absorbent activity could be regenerated afresh each time by drying after repeated sorptions, indicating the essential reversibility of the sorption process, and also suggesting its potential suitability in a recycling batch process.

Note added in proof. Related studies of Mn^{++}-initiated PAN grafts on starch have been reported by C. Rodehed and B. Ranby (*Polymer*, **27**, 313 (1986) and references therein).

Agricultural and horticultural applications are considered in I. I. Ziderman and J. Belayche, "Soil Improvement with Starch–Polyacrylate Graft Copolymor," 52nd Meeting, Israel Chemical Society, Ramat-Gan, Israel, 28 October, 1986.

References

1. I. I. Ziderman and J. Belayche, in *Book of Abstracts, 30th I.U.P.A.C. International Symposium on Macromolecules*, The Hague, Netherlands, August, 1985, p. 215.

2. M. O. Weaver, R. R. Montgomery, L. D. Miller, V. E. Sohns, G. F. Fanta, and W. M. Doane, *Die Staerke*, **29**, 413 (1977).

3. G. F. Fanta, R. C. Barr, W. M. Doane, and C. R. Russell, *Die Staerke*, **30**, 237 (1978).

4. G. F. Fanta, E. B. Bagley, R. C. Burr, and W. M. Doane, *Die Staerke*, **34**, 95 (1982).

5. WATER-LOCK, Grain Processing Corporation, Muscatine, Iowa.

6. AGRI-GEL, Super Absorbent Company, Lumberton, NC.

7. R. Mehrotra and B. Ranby, *J. Appl. Polym. Sci.*, **21**, 1647 and 3407 (1977).

8. J. L. Williams and V. T. Stannett, *J. Appl. Polym. Sci.*, **23**, 1265 (1979).

9. R. L. Whistler, *Tappi*, **60**, 64 (1977).

10. C. R. Kelm, *Ind. Eng. Chem. Prod. Res. Dev.*, **19**, 483 (1980).

11. W. F. Lindsay, *Tappi*, **59**, 126 (1976).

12. "MITROLAN Tablets. Drug Monograph for Detail Manual," A. H. Robins Co., Richmond, Va, 1980.

13. B. Ranby and C. Rodehed, in *Polymer Sci. Overview: A Tribute to Herman F. Mark*, G. A. Stahl, Ed., ACS Symposium Series, No. 175, 1981, p. 253.

14. A. Basch and A. Wasserman, unpublished results.

15. J. Grignon and A. M. Scallan, *J. Appl. Polym. Sci.*, **25**, 2829 (1980).

16. B. Miller, H. L. Friedman, and C. H. Meiser, *Text. Res. J.*, **50**, 10 (1980).

17. G. H. Robertson, L. R. Doyle, and A. E. Pavlath, *Biotech. Bioeng.*, **25**, 3133 (1983).

18. G. W. Brant, U.S. Patent 2,253,755 (26 Aug., 1941), cit. ref. 19.

19. G. H. Robertson, R. A. Kahlstrom, and A. E. Pavlath, "Intensive Grain Use in Ethanol Fermentation and Separation: Simultaneous Liquid-Phase Absorption of Water from Ethanol and Extraction of Oil," presented at the Meeting of the American Society of Agricultural Engineers, June, 1983, Bozeman, Montana.

20. Ch. Forgas and M. Parchi, "Report on Separation of Ethanol from an Ethanol-Water Mixture by Selective Electro-Osmotic Transport Through Membrances," Ben-Gurion University, Beersheba, Israel, December, 1980, 7 pp. (in Hebrew).

21. T. Itoh, H. Toya, K. Ishihara, and I. Shinohara, *J. Appl. Polym. Sci.*, **30**, 179 (1985).