

## **Water Vapor Absorption and Aqueous Retention of Hydrolyzed Starch Polyacrylonitrile Graft Copolymers – "Superabsorbent Starch"**

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### SUMMARY

Starch copolymers with polyacrylonitrile grafts were prepared using the  $Mn^{3+}$  initiation method and different amounts of acrylonitrile. The product was hydrolyzed in aqueous alkali (nitrile groups to amide and carboxyl groups) to enhance the hydrophilic character of the copolymer and achieve "superabsorbent properties". At relative humidities (RH) up to 95-97 % the modified starch shows "normal" water vapor absorption like cellulose and other polysaccharides. When in contact with liquid distilled water, the modified starch forms a "superabsorbent" gel which retains very large amounts of water (up to 800 g/g). At low and high pH and in aqueous salt solutions (NaCl, CaCl<sub>2</sub>, and synthetic urine) the water retention is strongly reduced. This is interpreted as due to the ionic strength (salt effect) and for Ca<sup>2+</sup> ions probably also crosslinking by salt formation with carboxyl groups on adjacent chains or chain segments.

### INTRODUCTION

Extensive studies have been reported on the altering of structure and properties of polysaccharides by chemical modification, e.g. acetylation or crosslinking, and by physical modification, e.g. mercerization of cellulose. Formation of polysaccharide graft copolymers can add new properties to the polysaccharide with some of the native properties retained. Grafting of polysaccharides in a two-phase system is a common method due to limited solubility of the naturally occurring polysaccharides. Most of the processes reported have included free radical initiation of the polymerization reaction.

Phosphate complexes of  $Mn^{3+}$  as initiator were first described in a patent from 1961 for the grafting of vinyl monomers onto cellulose and cellulose derivatives (RAYONIER 1961). Independently a system of grafting vinyl monomers onto starch using manganic pyrophosphate complex ions as initiator was developed in our laboratories (MEHROTRA and RÅNBY 1977 a, b, 1978 a, b) and also applied to cellulosic fibers (RÅNBY 1978).

Using the  $Mn^{3+}$  complex ions, acrylonitrile is easily graft copolymerized onto starch, in native granular, swollen or gelatinized form and onto starch derivatives. Starch-co-polyacrylonitrile can further be modified by alkaline hydrolysis to a product "super-absorbent" starch (similar to HSPAN, described by WEAVER 1974) capable of absorbing and retaining very large amounts of water and aqueous solutions.

As studied earlier by GUGLIEMELLI et al (1969) alkaline hydrolysis of starch-polyacrylonitrile groups reacts with all nitrile functional groups (analyzed by infrared absorption) and gives rise to amide and carboxyl groups. ROGERS (1953) has reported a maximum conversion to 70 % carboxyl groups. The residual 30 % are amide groups. The incomplete hydrolysis is interpreted as related to steric and polar factors due to hydrogen bonding between neighbouring amide and carboxyl groups on the same chain or on adjacent chains. WEAVER (1971) suggests that condensation reactions also may occur between acid and amide groups to form imide structures. WEAVER (1971) also reports that the carboxyl content varies inversely with the alkali concentration used in the hydrolysis. Raising the hydrolysis temperature from 80°C to 100°C increases the conversion to carboxyl groups somewhat (WEAVER 1971).

## EXPERIMENTAL

### Materials

Most chemicals used were analytical-grade reagents from Merck, Darmstadt, Germany and EKA, Sweden. Native potato starch was supplied by Svenska Stärkelse Föreningen AB (SSF). Acrylonitrile, synthetic grade from Merck, was purified by distillation under reduced pressure in a nitrogen gas atmosphere.

### Graft Copolymerization

Starch-polyacrylonitrile graft copolymers were prepared (MEHROTRA and RÅNBY 1977 and 1978) under the following conditions: Native potato starch (21,5 g dry weight) in granular or gelatinized form, and different amounts of acrylonitrile were slurried in distilled water (465 ml) in a reaction vessel immersed in a thermostatically controlled water bath (30°C). The reaction vessel was equipped with a stirrer, a condenser, an  $N_2$ -bubbler and a dropping funnel. Initiator solution (62,5 ml) and acidified water (62,5 ml) were poured into the dropping funnel. The temperature was set to 30°C. After 30 minutes the  $N_2$ -purged initiator solution and the acidified water were added to the reaction vessel. The reaction was carried out under an atmosphere of purified nitrogen gas at 30°C for 3 hours.

Another series of grafted samples with equal amounts of starch and acrylonitrile and different amounts of EGDMA (ethylene glycol dimethacrylate) added to the acrylonitrile as a crosslinking agent were prepared in the same way.

% Add-on, grafting ratio and conversion of acrylonitrile to polymer were calculated after drying the grafted samples to constant weight and their water content analyzed. The amount of homopolymer was determined by extraction with dimethylformamide (DMF) for 24 hours. The samples were centrifuged and the clear supernatant was poured into methanol to precipitate the homopolymer.

#### Saponification of Nitrile Groups

The alkaline hydrolysis was carried out at 90°C with a 1% aqueous sodium hydroxide solution (by weight) on never-dried graft copolymer. A deep red colour is developed during the hydrolysis due to intermediate formation of naphthyridine ring structures from adjacent nitrile groups. The intermediate rings are subsequently hydrolyzed causing the red colour to turn into yellow (GRASSIE and McNEILL 1959). The hydrolysis was stopped at the sharp change in color from red to yellow. The product was then recovered by precipitation in methanol and washing to neutrality.

#### METHODS

##### Absorption of Water Vapor

The grafted and hydrolyzed starch samples were dried in vacuum to remove traces of methanol and then exposed to an atmosphere of increasing relative humidity (RH) in a desiccator at 25°C. The RH in the desiccator was controlled with standard aqueous solutions of  $H_2SO_4$ ,  $CaCl_2$  and KOH (STOKES 1949, LB TABLES 1936). The absorption values, based on weighing, were calculated as gram absorbed water per gram modified starch and recorded as function of RH and time of exposure.

##### Retention of Distilled Water and Aqueous Solutions

###### Method 1

The retention measurements were carried out by immersion of a weighed sample of modified starch powder under stirring in a known amount of aqueous medium. After 30 minutes at room temperature ( $\sim 20^\circ C$ ) the slurry was filtered, the amount of not-retained aqueous solution calculated. The retention value is given as amount of retained solution in gram per gram of dry modified starch sample. The retention of the following liquid media was measured: water of different pH and aqueous solutions of NaCl and  $CaCl_2$ .

###### Method 2

A weighed sample of modified starch was immersed by stirring in an aqueous solution in a weighed centrifuge tube. After 30 minutes the tube was centrifuged at 900 G for 30 minutes. The upper clear layer of supernatant was poured off the bottom gel layer and the

tube weighed again. The retention value was calculated as amount of retained solution in gram per gram of dry modified starch charged. The retention was measured for distilled water, 0,9 % NaCl-solution and synthetic urine.

The synthetic urine solution was prepared by dissolving 2,04 g potassium sulfate, 0,85 g calcium chloride dihydrate, 1,14 g magnesium sulfate · 7 H<sub>2</sub>O, 8,20 g sodium chloride, and 20,00 g urea in 700 ml distilled water and adjusting the pH value to 7,00 by addition of dilute hydrochloric acid or dilute sodium hydroxide as required. The solution was then diluted to 1000 ml in a volumetric flask by adding distilled water.

### Results and Discussion

The following definitions of grafting parameters have been used.

% Add-on = per cent synthetic polymer in graft copolymer

Grafting Ratio % = Amount of synthetic polymer in graft copolymer in per cent of the amount substrate.

The first series of experiments with different amounts of acrylonitrile (TABLE I) shows that with a higher monomer concentration in the grafting reaction a graft copolymer with higher add-on and grafting ratio is obtained. The conversion of monomer also increases with increasing amounts of acrylonitrile charged. The amount of homopolymer formed in this series is between 1 and 3 %.

TABLE I

Grafting of acrylonitrile to 25 gram native potato starch (21,5 gram dry weight).

$[Mn^{3+}] = 1.0 \text{ mmol/l}$ ,  $[H_2SO_4] = 75 \text{ mmol/l}$  giving pH  $\sim 1,7$ ,  
temp. 30°C, time 3 hrs

Pretreatment	Acrylonitrile ml	ml AN g STARCH	% Add-on Found	Calculated for complete grafting	Conversion of monomer %	Grafting Ratio %
Starch	6,25	0,25	16	19	72	19
gelatinized	12,5	0,50	23	32	64	30
before	25	1,00	45	48	88	82
grafting	50	2,00	63	65	93	173
Granular starch - no pre- treatment	25	1,00	46	48	88	83

TABLE 2

Grafting of 25 ml acrylonitrile to 25 gram native potato starch (gelatinized) (21,5 gram dry weight) with different amounts of ethylene-glycol dimethacrylate added,

$[Mn^{3+}] = 1.0 \text{ mmol/l}$ ,  $[H_2SO_4] = 75 \text{ mmol/l}$  giving pH  $\sim 1.7$ , temp.  $30^\circ C$ , time 3 hrs.

EGDMA ml	ml EGDMA / ml AN	% Add-on	Grafting Ratio %	Homopolymer %
0	0	45	88	---
0,05	0,002	41	68	1,3
0,125	0,005	47	88	0,7
0,25	0,010	44	80	0,8
0,375	0,015	42	71	2,6
0,5	0,020	42	74	0,6

Calculated add-on = 48 % for complete grafting.

Table 2 gives the result from a second series of graft copolymerizations with equal amounts of starch and acrylonitrile and different amounts of crosslinker added in the grafting reactions.

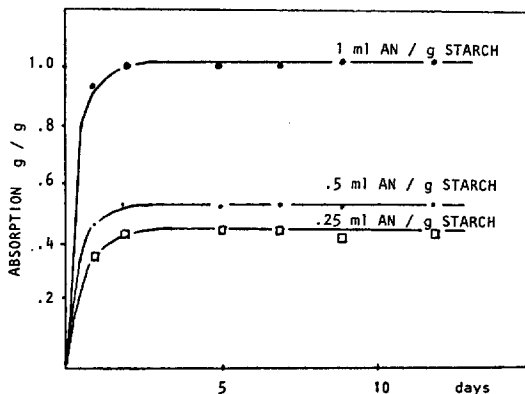


FIGURE 1.

Absorption at 95 % Relative Humidity as a function of time for samples of modified starch prepared with different amounts of acrylonitrile.

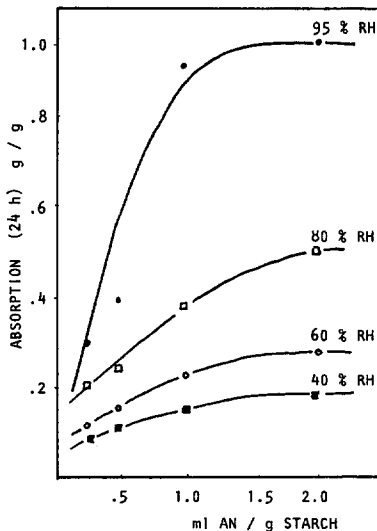


FIGURE 2. Water vapor absorption of modified starch as a function of the amount of acrylonitrile used in the preparation. The measurements are made at four different relative humidities (RH).

The absorption of water vapor at 95 % relative humidity was measured during 2 weeks to determine the time dependence of the absorption (Figure 1). Equilibrium is reached in a few days.

Figure 2 shows the absorption of water vapor at different relative humidities after 24 hrs exposure as a function of the amount acrylonitrile used in the preparation of the modified starch samples. The absorption seems to level out at a high value after increasing the amount of acrylonitrile to 2 ml AN per gram starch.

Water vapor absorption vs. relative humidity for modified starch prepared with different amount of acrylonitrile after 2 weeks exposure is shown in Figure 3. There is a very sharp increase in the absorption above 95 to 97 % humidity. For higher substituted starches the bend is sharper and the increase is faster.

Figure 4 shows that the capability of retaining distilled water increases with the degree of substitution in the hydrolyzed graft copolymer as measured by method 2. Addition of the crosslinker has a small effect and gives a minor decrease in the retention value. This may be due to the probable hydrolysis of the ester groups of the crosslinking agent (EGDMA). Addition of salts to the water solution decreases the retention markedly. Graft copolymer from granular starch has lower retention of distilled water and salt-solutions than the same product from gelatinized starch.

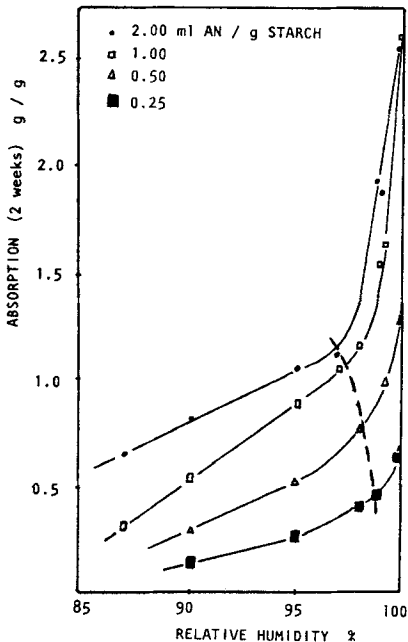


FIGURE 3.

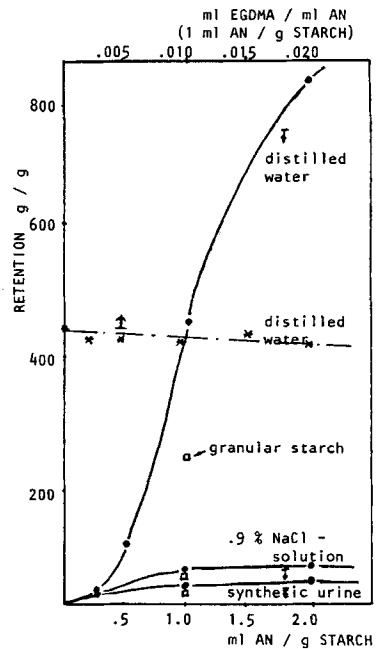


FIGURE 4.

Water vapor absorption as a function of relative humidity for hydrolyzed grafted starch prepared with different amount of acrylonitrile. Limit of "normal" water absorption for polysaccharides is indicated.

Retention of distilled water and aqueous solutions of NaCl and synthetic Urine as a function of amount acrylonitrile and ethyleneglycol dimetacrylate added (method 2)

The retention for hydrolyzed graft copolymer (1 ml AN/g S) vs. pH is shown in figure 5. The retention increases rapidly between pH 3 and pH 4 and stays on the level of about 800 g/g from pH 5 to 9. At further increase of pH, the retention decreases rapidly and reaches about 100 g/g at pH 13-14. These effects are interpreted as related to the ionic strength of the solutions, i.e. salt effects, and the dissociation of the carboxyl groups as a function of pH of the solutions.

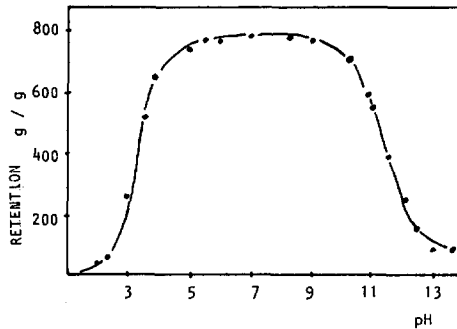


FIGURE 5. Retention of water ( method 1) as a function of pH for a sample of modified starch prepared with 1 ml AN/g starch.

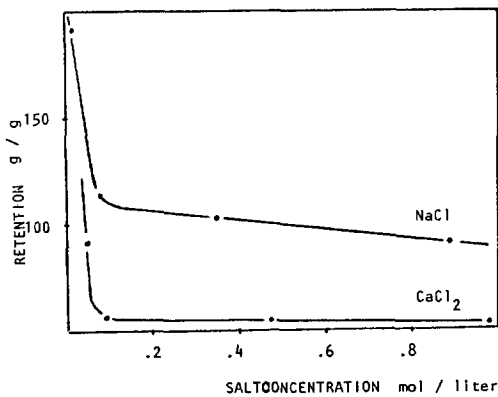


FIGURE 6. Retention of aqueous solutions as a function of salt concentration measured by method 1 for a modified starch sample prepared with 1 ml AN/g starch.

Figure 6 gives the retention as a function of salt concentration. There is a very sharp decrease in the retention with even small amounts of salts. As shown in the figure there is a large difference between NaCl and CaCl<sub>2</sub> as solute. The two-valent Ca<sup>2+</sup> ions almost prevents the swelling of the gel. This is probably due to the ionic strength of the aqueous solutions. In addition the Ca<sup>2+</sup> ions may crosslink the gel by salt formation with the carboxyl groups on adjacent grafted chains.

These investigations will be reported in a more complete form elsewhere.

#### CONSLUIONS

The modified starch, prepared by Mn<sup>3+</sup> initiated grafting of acrylonitrile onto starch followed by alkaline hydrolysis, absorbs water vapor like other polysaccharides at relative humidities (RH) up to 95-97 %. At higher RH the water vapor absorption increases very rapidly. In contact with liquid distilled water the modified starch becomes "superabsorbent" by retaining very large amounts of water (up to 800 g/g). Water vapor absorption and liquid water retention apparently occur by different mechanisms: hydrogen bonding of water molecules to the substrate and immobilizing water clusters by weaker forces respectively. The effects of pH and addition of salts to the aqueous solutions on the water retention supports these views.

#### ACKNOWLEDGEMENT

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