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Super-absorbent Polymers from Starch–Polyacrylonitrile Graft Copolymers by Acid Hydrolysis before Saponification

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SUMMARY

Graft copolymers (SPAN) of polyacrylonitrile (PAN) onto starch were prepared from gelatinized starch varieties with ammonium ceric nitrate as an initiator. The molecular weight of the PAN branches increased for the varieties of starches in the order high amylose maize starch < maize starch < waxy maize starch. SPAN samples were saponified with aqueous NaOH, and the aqueous solution of the resulting polymer (HSPAN) was cast into film in a forced-air oven at 35°C. The water absorbency of the HSPAN film formed from waxy maize starch was the highest (1200 g H_2O (g dry sample)$^{-1}$) and that from high amylose maize starch was the lowest (530 g g^{-1}). SPAN samples from maize starch were partially hydrolyzed with dilute hydrochloric acid. The resulting polyacrylonitriles with low molecular weight starch end groups (LSPAN) were also saponified. The resulting saponified product (HLSPAN) was cast into film. The absorbencies of HLSPAN films were found to be far larger (up to 6000 g g^{-1}) than those of the corresponding HSPAN films. The absorbency increased with increasing molecular weight of PAN in the initial SPAN up to a molecular weight of 1–1·5 × 10^6. The absorbency decreased significantly when HSPAN and HLSPAN films were subjected to heat treatment at 135°C or above. The crosslinks present in HSPAN and HLSPAN films prepared at 35°C and those formed during heat treatment were considered to have different structures: the former formed between carbohydrate alkoxide ions and nitrile groups at the early stages of saponification and the latter

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formed between carbohydrate and copoly(acrylate–acrylamide) chains and/or between copoly(acrylate–acrylamide) chains.

INTRODUCTION

Super-absorbent polymers, which can absorb several hundred times their weight of water in a few minutes, were first developed by a group at the Northern Regional Research Laboratory, US Department of Agriculture, in the early 1970s (Weaver *et al.*, 1977). They are based on the graft copolymers (SPAN) of polyacrylonitrile (PAN) onto starch. When SPAN is saponified with alkali metal hydroxide, PAN moieties of SPAN are converted into copolymers of alkali metal acrylate and acrylamide. Films made from the resultant saponified graft copolymer (HSPAN) by casting from a dispersion of microgels at ambient temperature are insoluble in water and absorb large quantities of water, to give highly swollen gel sheets which retain water even under pressure (Taylor & Bagley, 1974).

The high absorbency of HSPAN is believed to be due to its very lightly crosslinked polyelectrolyte structure. The chemical structure of the crosslinks has not been determined by spectroscopic analysis because the concentration of the crosslinks is very low. Recently, Fanta *et al.* (1982*b*) reported some evidence that crosslinking took place during graft polymerization and during the early stages of saponification. According to Fanta *et al.*, formation of new crosslinks during drying is not necessary to explain why the films do not disintegrate when put into water.

A number of super-absorbent polymers, either starch-based materials or totally synthetic polymers, are now in commercial production or at a development stage in the USA and Japan (Nukushina, 1980). The most frequent applications of super-absorbent polymers today are for disposable soft goods such as napkins and diapers which are designed to absorb body fluids. Other important applications are in agriculture. For example, seeds coated with super-absorbent polymers hold water at the surface so that the germination rate is improved (Deterling, 1981). Another example is to place plant roots in super-absorbent polymer gel so that the roots are protected against shock during transplanting (Lindsay, 1977).

In this paper, a significantly higher absorbency of the saponified PAN with a low molecular weight polysaccharide end group will be described, which is produced by partial hydrolysis of starch moieties of SPAN in dilute hydrochloric acid, prior to saponification.

EXPERIMENTAL

Materials

Maize starch, waxy maize starch and high amylose maize starch from Nihon Shokuhin Kako (Japan Maize Products, Japan) containing about 12·5% moisture were used. Acrylonitrile was distilled at atmospheric pressure and stored at 5°C before use. Ammonium ceric nitrate was of guaranteed reagent grade and obtained from Koso Chemical, Tokyo, Japan.

Graft copolymerization of acrylonitrile onto starch

A slurry of 10.0 g (dry basis) of starch in 127 ml of water was heated with stirring at 95°C for 30 min under nitrogen to promote gelatinization. The gelatinized starch mixture was cooled to 25°C and 10.0 g of acrylonitrile was added to the mixture. After a few minutes, a freshly prepared solution of 0·335 g (corresponding to anhydroglucose units/$Ce^{4+} = 100$) of ammonium ceric nitrate in 6·7 ml of 1 N nitric acid was added. The mixture was kept with stirring for 2 h at 25°C. The reaction mixture was neutralized to pH 6–7 with aqueous sodium hydroxide and a large amount of water was added to the mixture. The product was collected by filtration, washed with water and ungrafted homopolymer of PAN was extracted with dimethylformamide (DMF) at room temperature overnight. The DMF-insoluble product was washed with water, then with methanol, and dried under vacuum at room temperature.

The PAN present as branches in the SPAN was isolated by acid hydrolysis in 1 N hydrochloric acid under reflux for 2 h. The molecular weight of the PAN was obtained from the intrinsic viscosity measured in DMF at 30°C (Fanta *et al.*, 1966).

Partial acid hydrolysis of SPAN

About 4·0 g of SPAN was hydrolyzed in 200 ml of hydrochloric acid of a given concentration under reflux for 2 h. The insoluble polymer was separated by filtration, washed with water and with methanol, and dried under vacuum at room temperature.

Saponification of SPAN and LSPAN and isolation of absorbent polymer

A suspension of 1·0 g of SPAN or LSPAN in 20 ml of 0·7 N sodium hydroxide solution was heated on a steam bath until the mixture

assumed a red–orange color (Fanta *et al.*, 1978; Batty & Guthrie, 1981). Then the mixture was heated in an oven at 100–105°C for an additional 2 h. The reaction mixture was neutralized with glacial acetic acid to pH 6 and the mixture (HSPAN or HLSPAN) was kept stirring at a high speed in a mixer with 300 ml of methanol for 30 s. The precipitated solid was collected and dried under vacuum, at room temperature.

The saponified polymer was placed in about 400 ml of water with stirring. The resulting viscous dispersion was filtered through a G-1 sintered glass filter, cast on a Teflon plate and dried to form a film in a forced-air oven at 35°C.

Approximately 0·1 g of the polymer film was heated in a vacuum oven at 100, 135 or 175°C for 1 h, when necessary.

Measurement of the absorbency

An accurately weighed (50–100 mg) sample of dry polymer film was allowed to swell in 500 ml of distilled water for 30 min at room temperature. The swollen gel film was collected by the use of a tared 200-mesh sieve 16·0 cm diameter. Water among the pieces of gel was allowed to drain away, and the remaining swollen gel was collected and weighed. Absorbency was expressed as grams of water per gram of the dry polymer film.

A similar absorbency test was run with 0·9% sodium chloride solution.

RESULTS AND DISCUSSION

Graft copolymers (SPAN) of starch and polyacrylonitrile (PAN) were prepared by graft copolymerization of acrylonitrile onto starches from different sources, i.e. waxy maize starch, maize starch and high amylose maize starch, with ammonium ceric nitrate as an initiator (see Table 1). Starches were gelatinized in water at 95°C for 30 min prior to the graft copolymerization. In each preparation, ungrafted homopolymer of PAN was removed from the product by extraction with DMF. The weight per cent of the grafted PAN (% PAN) in SPAN was calculated from the nitrogen content of the SPAN determined by the Kjeldahl method. The average molecular weight (M_v) of the grafted PAN was calculated from the intrinsic viscosity of the PAN, which was isolated by acid hydrolysis of the SPAN in 1 N HCl under reflux for 2 h, using the intrinsic viscosity–molecular weight equation given in the literature (Shibukawa *et al.*, 1968). The grafting interval (AGU/chain), i.e. the average number of

TABLE 1
Graft Copolymerization of Varieties of Starch and Absorbencies of the Saponified Graft Copolymers (HSPAN)[a]

Sample no.	*Starch variety*	*Starch-g-PAN (SPAN)*				*HSPAN*	
		Yield (%)	*% (SPAN)*	*M_v of PAN*[c]	*AGU*[d]*/chain*	*WA*[e] *DW*[f]	*(g H_2O g^{-1}) 0·9% NaCl*
1	Waxy maize	86·3	50·8	1 429 000	8 800	1 149	80
2	Maize starch	85·7	48·9	883 000	5 696	784	69
3	High amylose	98·1	45·3	575 000	4 286	525	60

[a] Polymerization was obtained using 10 g starch (db), 127 ml water and 10 g acrylonitrile (AGU/Ce^{4+} = 50).
[b] Calculated from % N by Kjeldahl analysis.
[c] Calculated from intrinsic viscosity in DMF at 30°C.
[d] Anhydroglucose units.
[e] Water absorbency.
[f] Distilled water.

anhydroglucose units (AGU) per grafted PAN chain, was calculated from the % PAN and the molecular weight of the grafted PAN.

All the starch varieties gave SPANs of nearly equal % PAN values (45–51%) in high yields (86–98%). The molecular weight of the grafted PAN varied with the starch varieties, being the highest with waxy maize and the lowest with high amylose maize starch. High amylose maize starch is the least susceptible to gelatinization (Leach, 1965) due to its strongly hydrogen-bonded structure of high crystallinity. Incomplete gelatinization of the high amylose maize starch probably resulted in the formation of the lowest molecular weight of the grafted PAN. Fanta *et al.* (1982*a*) and Burr *et al.* (1967) reported that the molecular weight of the grafted PAN onto gelatinized maize starch was much higher than that onto granular maize starch.

SPAN samples were saponified with 0·7 N NaOH at 100–105°C (for more details, see the 'Experimental' section). PAN moieties are known to be converted to copolymers of acrylamide and sodium acrylate by alkaline hydrolysis. The saponified product in the reaction mixture was neutralized to pH 6 and poured into a large volume of methanol. The precipitate (HSPAN) was dispersed in water and the resulting viscous dispersion was cast into film by drying in a forced-air oven at 35°C. The HSPAN-formed films did not disintegrate into a gel dispersion when placed in water.

The water absorbencies of the HSPAN films were measured in distilled water and 0·9% aqueous NaCl. As shown in Table 1, the HSPAN films absorb a large amount of distilled water (1200–530 g H_2O (g dry sample)$^{-1}$) and a considerably lower amount of 0·9% aqueous NaCl (80–60 g g^{-1}). The HSPAN from waxy maize starch absorbs twice as much water as that from high amylose maize starch. The difference in the absorbencies of the two HSPAN samples towards 0·9% aqueous NaCl is not as great as that towards distilled water.

During the course of the study, it was found that PAN prepared in the presence of low molecular weight polysaccharide and ammonium ceric nitrate gave super-absorbent polymers, which could absorb more than 1000 g g^{-1}, after saponification, neutralization and casting. It is interesting, therefore, to see if SPAN would give such a super-absorbent polymer when starch moieties of SPAN were partially hydrolyzed under acidic conditions and the resulting PAN with low molecular weight polysaccharide (LSPAN) was saponified.

The SPAN samples were treated with refluxing hydrochloric acid of various concentrations (0·001–6 N) for 2 h. The nitrogen contents of the resulting LSPAN samples were determined, from which the % PAN values were calculated (see Fig. 1). When the concentrations of hydro-

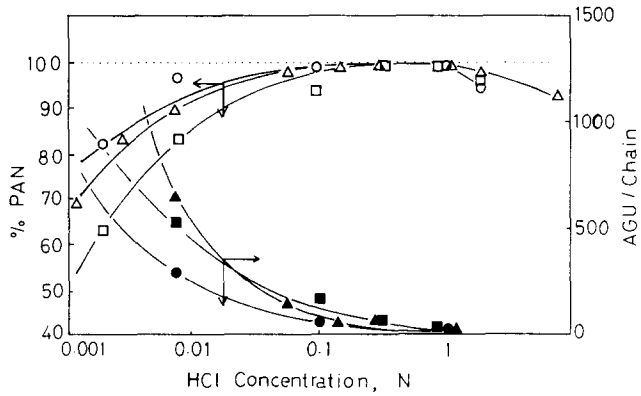

Fig. 1. Change in % PAN and AGU/chain by acid hydrolysis of SPAN in hydrochloric acid of different concentrations under reflux for 2 h: ○, ●, waxy maize starch-g-PAN; △, ▲, maize starch-g-PAN; □, ■, high amylose maize starch.

chloric acid used were between 0.5 and 1 N, the % PAN of the LSPAN was almost equal to 100%. In other words, a homopolymer of PAN was obtained. The PAN isolated was soluble in DMF. When hydrochloric acid of higher concentrations (2 N) was used, the apparent % PAN of the product became lower. Probably, under these conditions, the PAN moieties were chemically modified to some extent. When hydrochloric acid of a lower concentration (0·5 N) was used, LSPAN samples of varieties of % PAN were obtained. The degrees of polymerization of lower molecular weight starches of AGU/chain were calculated for LSPAN samples from the % PAN values (see Fig. 1)

The LSPAN samples originating from maize starch were treated with alkali, in a similar manner to the preparation of HSPAN, to prepare saponified LSPAN or HLSPAN. The water absorbencies of HLSPAN samples of various lengths of polysaccharides are shown in Fig. 2. It is clearly shown that the acid pretreatment is a very effective way to increase the water absorbency. An HSPAN with 5700 AGU/chain absorbs only 800 g g^{-1} water while an HLSPAN with 22 AGU/chain made from the HSPAN absorbs 4500 g g^{-1} water. The shorter the starch moieties, the higher the water absorbency. The highly swollen gel films containing more than 4000 times their weight of water were mechanically very weak.

Figure 2 also shows the effect of heating on the HSPAN and HLSPAN films. It is well documented that the water absorbency is lowered by heating HSPAN (Weaver *et al.*, 1977). This decrease is considered to be due to the formation of new crosslinks between saponified PAN chains

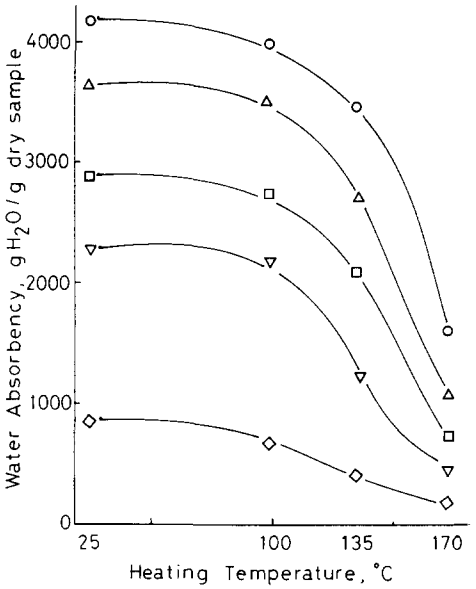

Fig. 2. Effect of heat treatment on the water absorbency of HLSPAN under different AGU/chain made by acid hydrolysis of SPAN followed by saponification, neutralization and casting: AGU/chain: ○, 22; △, 87; □, 157; ▽, 672; ◇, 5696.

and/or between starch chains and saponified PAN chains upon heating. The decrease in the absorbency is more significant for heat treatment at temperatures higher than 135°C. The HLSPAN films with $DP = 157$ (DP is the degree of polymerization) show higher absorbencies, even after heating at 170°C, than the HSPAN film without heating.

Figure 3 plots water absorbency against % PAN. The lower the carbohydrate content in HLSPAN, the higher the water absorbency. Figure 4 plots water absorbency against AGU/chain. The lower the molecular weight of the starch chains or AGU/chain, the higher the absorbency. Saponified PAN film prepared from homopolymer ($M_v = 553\,000$) made with potassium persulfate as an initiator was found to be soluble in water.

These results are consistent with the proposal of Fanta *et al.* (1982*b*) that the crosslinking takes place between starch alkoxide ions and nitrile groups as the initiation reaction of nitrile polymerization at the early stages of saponification. It is also possible to deduce from the results that strong hydrogen-bonded networks are formed between carbohydrate chains during drying, which contribute to the additional stabilization of the films in water.

The effect of the molecular weight of the PAN component on the absorbency of HSPAN and HLSPAN was studied. SPAN samples with different molecular weights of the grafted PAN were prepared by Ce^{4+}-

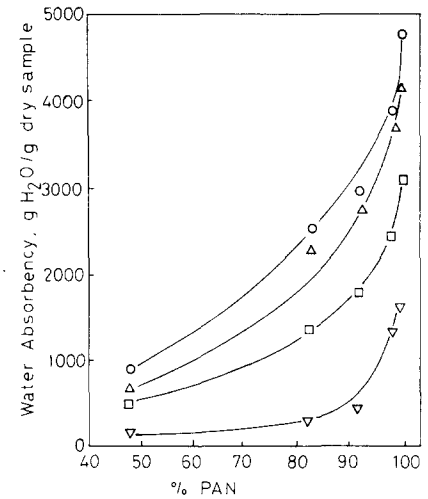

Fig. 3. Water absorbency of HSPAN samples of different % PAN made by acid hydrolysis of SPAN followed by saponification, neutralization and casting: ○, as cast; △, heated at 100°C for 1 h; □, heated at 135°C for 1 h; ▽, heated at 170°C for 1 h.

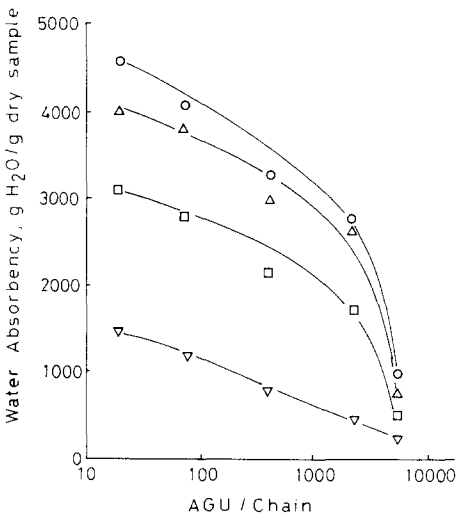

Fig. 4. Water absorbency of HSPAN samples of different AGU/chain made by acid hydrolysis of SPAN followed by saponification, neutralization and casting: ○, as cast; △, heated at 100°C for 1 h; □, heated at 135°C for 1 h; ▽, heated at 170°C for 1 h.

initiated graft copolymerization of acrylonitrile onto granular and gelatinized corn starch with different ratios of AGU/Ce^{4+} (25–400). SPAN samples of % PAN of 42–51% were obtained in high yields (80–93%). The results are shown in Table 2. The molecular weight of the

TABLE 2
Preparation of SPAN[a] and LSPAN[b] from Maize Starch

Sample no.	*Starch granule type*	*AGU/Ce*$^{4+}$	*Starch-g-PAN (SPAN)*			*Corresponding LSPAN*	
			Yield (%)	*% PAN*[c]	M_v *of PAN*[d]	*% PAN*	*AGU/chain*
4	Granular	200	93·3	42·3	120000	97·66	18
5	Gelatinized	25	91·3	51·1	574000	99·04	34
6	Gelatinized	50	85·7	48·9	883000	99·58	22
7	Gelatinized	100	89·5	48·5	1267000	99·68	25
8	Gelatinized	200	87·4	47·0	1629000	99·88	12
9	Gelatinized	400	79·7	46·8	2066000	99·96	6

[a] Polymerization was obtained using 10 g starch (db), 127 ml water and 10 g acrylonitrile.
[b] Obtained by hydrolysis of the corresponding SPAN in 1 N HCl under reflux for 2 h.
[c] Calculated from % PAN by Kjeldahl analysis.
[d] Calculated from intrinsic viscosity in DMF at 30°C.

grafted PAN for granular starch was one tenth of that for the gelatinized starch. The molecular weight of the PAN increased with increase in AGU/Ce^{4+} for gelatinized starch as reported in an earlier work (Fanta *et al.*, 1982*a*, 1983). The LSPAN samples, which were obtained by hydrolysis in 1 N HCl for 2 h under reflux, are considered to have short chain oligo-saccharides (*DP* 5–34 as end groups, judging from their nitrogen contents. The LSPAN samples were saponified, neutralized and cast into films and the water absorbencies of the resulting HLSPAN films were determined (see Fig. 5).

Two HLSPAN samples made from SPAN with low *DP* of PAN gave very weak gels. It was difficult to determine the absorbency because the gel tended to pass through and clog the sieve. The absorbency was not determined exactly but was estimated to be not very high for these samples. An HLSPAN made from SPAN with molecular weight of PAN of 1×10^6 showed a high absorbency (4000 g g^{-1}), and HLSPAN made from SPAN with molecular weight of PAN of $1{\cdot}3 \times 10^6$ showed the highest absorbency of 6000 g g^{-1}. Thereafter, the water absorbency of HLSPAN decreased with increasing *DP* of PAN.

The effect of heating on the absorbency of HLSPAN was also studied. Similar tendencies to those for HSPAN were observed when the samples were heated at 100 and 135°C. However, the HLSPAN heated at 170°C

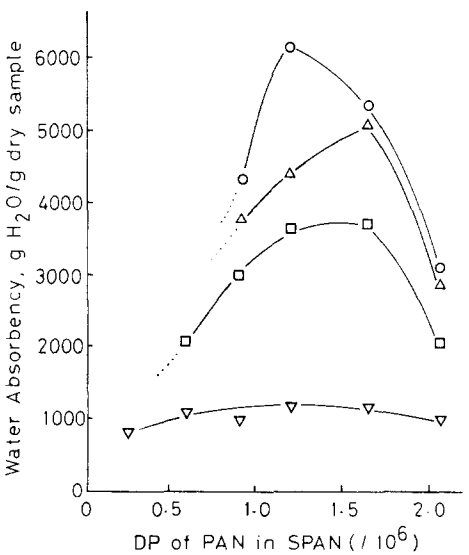

Fig. 5. Water absorbency versus *DP* of PAN in SPAN for HLSPAN made by acid hydrolysis in 1 N HCl for 2 h followed by saponification: ○, as dried at 35°C; △, heated at 100°C for 1 h; □, heated at 135°C; ▽, heated at 170°C.

showed that the effect of the molecular weight of PAN is less significant. Even the HLSPAN made from SPAN with the lowest *DP* of PAN showed water absorbency of 800 g g^{-1}. All six samples absorbed about the same amount (*c.* 1000 g g^{-1}) of water.

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