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Super Absorbent Polymers from Mixtures of Polyacrylonitrile and Saccharides

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ABSTRACT

Super absorbent polymer (HMPAN) films were prepared from alkali-treated mixtures of polyacrylonitrile (PAN) with various starches, maize flour, maize meal, mono- and oligosaccharides, and polyhydric alcohols by casting at 35°C. Water absorbencies of the as-cast HMPAN films ranged from 4650 g H_2O *(g dry sample)*$^{-1}$ *for HMPAN from galactitol to 574 gg*$^{-1}$ *for HMPAN from short chain amylose. Some HMPAN films such as those made from high amylose maize starch and diols formed very weak swollen gel films when placed in water, so that their absorbencies could not be determined; however, after heating at 170°C for 1 h, they yielded swollen gels in water which were strong enough for absorbency measurements. The absorbencies of the HMPAN films differed, but all samples showed lower absorbencies after heating. Different crosslinking reactions took place during heating. HMPAN films made from PAN and monohydric alcohols such as cyclohexanols also showed absorbent properties. It was suggested that different crosslinking mechanisms took place in these materials.*

INTRODUCTION

Polyacrylonitrile (PAN) moieties of starch–PAN graft copolymers (SPAN) are converted in hot aqueous alkali into copolymers of metal

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acrylate and acrylamide. The first super absorbent polymer (Super Slurper), which could rapidly absorb large quantities of water and retain it even under pressure in the form of a highly swollen gel, was prepared from SPAN by saponification, followed by neutralization and drying (Taylor & Bagley, 1974). Later work (Fanta *et al.*, 1978) showed that absorbent materials could also be produced directly from maize flour and maize meal by similar chemical modifications. The high absorbency observed was considered to result from the very lightly crosslinked polyelectrolyte structure.

Recently, Fanta *et al.* (1982) indicated by a solubility test that crosslinks were formed during graft copolymerization, by coupling of the two growing PAN radicals, and during saponification, by the attack of starch alkoxide ions on the nitrile groups as the initiation reaction of nitrile polymerization in the early stages of saponification. The formation of a conjugated polyimine structure by nitrile polymerization is easily shown by the development of a red–orange color in the early stages of the reaction. The polyimine bonds are cleaved in later stages of the reaction to give poly(acrylate–co–acrylamide) as shown by the fading of the color to light yellow. The initially formed oxygen-carbon bonds between the starch hydroxyls and nitrile groups of the PAN chains remain as crosslinking sites. Saponified SPAN (HSPAN) existed largely as swollen gel particles which coalesce into films during drying at ambient temperature when cast (Taylor & Bagley, 1974). Fanta *et al.* considered that interdiffusion of polymer chain ends on the surfaces of individual gel particles, and formation of hydrogen bonds between these polymer chains make the films resistant to redispersion into gel particles when placed in water.

If crosslinks could really be formed between the alkoxide ions of starch and the nitrile groups of PAN, crosslinked absorbent polymers should also be obtained by treating PAN homopolymers with starch in hot aqueous alkali. Fanta *et al.* (1982) demonstrated that PAN saponified in aqueous alkali in the presence of starch became partially insoluble. Preparation of absorbent polymers by saponification of PAN in the presence of polyhydroxy polymers such as starch and poly(vinyl alcohol) followed by neutralization and casting (and aging, if necessary) was reported in a US Patent (Fanta & Doane, 1978).

In a previous paper (Yamaguchi *et al.*, 1987), it was reported that when SPAN was partially hydrolyzed under acidic conditions before saponification, the resulting saponified polymers, containing very short starch moieties, showed much higher absorbency than that of the regular saponified HSPAN. These results are consistent with the proposal that the starch hydroxyls are involved in the crosslinking. In this paper, the absorbent properties of the saponified mixtures (HMPAN) from the mixture of PAN with various starches, maize flour and maize meal is reported. HMPAN films from mixtures of PAN with low molecular weight saccharides such as glucose, polyhydric alcohols such as alditols, and monohydric alcohols such as cyclohexanols were also studied.

MATERIALS AND METHODS

The maize starch, waxy maize starch, oxidized maize starch (highly oxidized by sodium hypochlorite), short chain amylose, glucose, maltose, maltotriose, cyclodextrins and maize meal used were obtained from Nihon Shokuhin Kako (Japan Maize Products). Maize flour was obtained from Sunny Maize Co., Tokyo, Japan. Galactitol, glucitol, mannitol, inositol, glyceraldehyde, cyclohexanediols, hexanol and cyclohexanol were guaranteed reagent grade of Koso Chemical, Tokyo, Japan. Acrylonitrile (chemical reagent grade of Yoneyama Chemical Ind., Oosaka, Japan) was distilled at atmospheric pressure and stored at 5°C before use. PAN (Mv, 533000) used in this work was prepared by radical polymerization of acrylonitrile with a redox initiator system.

Polymerization of acrylonitrile

Into water (200 ml) purged with nitrogen was added 22 g purified acrylonitrile and a 50 ml aqueous solution containing 0·3 g potassium persulfate and 0·15 g sodium bisulfate. The mixture was allowed to react at 40°C for 3 h with stirring under a nitrogen atmosphere. The precipitates were collected by filtration, washed with acetone and dried under vacuum at room temperature, yielding polyacrylonitrile (PAN) in 75% yield. The viscosity-average molecular weight of PAN was calculated from the intrinsic viscosity measured in dimethylformamide at 30°C according to Shibukawa *et al.* (1968).

Saponification of polyacrylonitrile in the presence of various saccharides or alcohols

Mixtures (1:1 wt/wt) of PAN with various starches, oxidized maize starch, maize flour, maize meal and short chain amylose (D.S., 23) were treated with sodium hydroxide at 100–105°C. The saponified product (HMPAN) in the reaction mixture was neutralized to pH 6–7 and poured into a large volume of methanol. The precipitate was collected, dried and dissolved (or more correctly, dispersed) in water and cast into film on a Teflon plate. The as-cast HMPAN film could no longer be redispersed in water. The absorbency of the film was determined in distilled water before and after heating. A typical example is given below.

A suspension of 0·5 g maize starch and 0·5 g PAN in 0·7 N NaOH (20 ml) was heated on a steam-bath until the mixture became red–orange, and then heated in an oven at 100–105°C for 2 h. The reaction mixture was then neutralized with glacial acetic acid to pH 6–7 and poured into methanol (300 ml) and kept stirring for 30 s. The precipitate was collected and dried under vacuum at room temperature. The product was added to water (400 ml) with stirring. The resulting dispersion was filtered through a G-1 sintered glass filter. The filtrate was cast on a Teflon plate and dried in a forced-air oven at 35°C.

About 0·1 g of the polymer film was heated in a vacuum oven at 135 or 170°C for 1 h.

Absorbency measurement

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

RESULTS AND DISCUSSION

The swollen gel of HMPAN made from waxy maize starch was very weak and the accurate absorbency could not be determined, since the gel film was broken into small pieces which passed through the sieve when separation of the gel was intended for the determination of absorbency. In such a case, the absorbency must be very high. The water absorbency of the as-cast HMPAN films made from starch varieties increase in the order: high amylose maize starch < maize starch < waxy maize starch. This order is the same as that observed previously with super absorbent HMPAN polymers made from graft copolymers of PAN onto starch varieties (Yamaguchi *et al.*, 1987).

HMPAN made from a mixture of PAN and oxidized maize starch, made by the reaction of sodium hypochlorite, also gave a very weak gel when placed in water and its absorbency could not be determined. HMPAN made from a mixture of PAN and maize flour gave a very high absorbency comparable to those noted for the super absorbent materials made from graft copolymers of PAN onto maize flour and maize meal

(Fanta *et al.*, 1978). HMPAN made with maize meal gave a gel too weak for the determination of the absorbency.

For comparison, PAN was saponified alone and the product (HPAN) was cast into film. The as-cast HPAN film was completely soluble in water. However, the film became insoluble after heat treatment and could absorb 1765 g H_2O (g dry sample)$^{-1}$. Table 1 shows the absorbency values for the polysaccharide HMPAN films determined after heating at 170°C. The absorbency decreased substantially on heat treatment by an amount that varied from sample to sample. For example, the absorbency of HMPAN made from PAN and maize starch decreased after heat treatment to 1/20 of the absorbency before heat treatment, while the absorbency of HMPAN made from high amylose maize starch decreased to 1/6 on heat treatment. Therefore, the order of the absorbency of the HMPAN films made from the starches after heat treatment is opposite to the order before heat treatment. The absorbency of the heat treated samples increased in the order: waxy maize starch < maize starch < high amylose maize starch. All the as-cast HMPAN films, for which absorbencies could not be determined, gave stronger gels when heated and placed in water.

Table 1 also shows that short chain amylose gives super absorbent polymer when treated with PAN. The absorbency of the polymer after the heat treatment is the highest among those prepared from polysaccharides. During the course of the study (Yasuno *et al.*, 1985), it was

TABLE 1

Water Absorbency of HMPAN Films made from 1:1 wt/wt Mixtures of PAN and Polysaccharides

Polysaccharides used	*Absorbency (g H_2O g^{-1}) of HMPAN*		
	As-cast (A)	*Heated[a] (B)*	*B/A*
—[b]	Dissolved	1765	—
Maize starch	1398	69	0·05
Waxy maize starch	—[c]	33	—
High amylose maize starch	706	114	0·16
Oxidized maize starch	—[c]	131	—
Maize flour	2630	54	0·02
Maize meal	—[c]	125	—
Short chain amylose	574	335	0·58

[a] Heated at 170°C for 1 h.

[b] PAN was treated with aqueous alkali in the absence of polysaccharides.

[c] Swollen gels were too weak for absorbency determination.

TABLE 2
Water Absorbency of HMPAN Films made from 1:1 wt/wt Mixtures of PAN and Mono- and Oligosaccharides

Saccharides used	*Absorbency ($g\ H_2O\ g^{-1}$) of HMPAN*		
	As-cast (A)	*Heated[a] (B)*	*B/A*
Glucose	2309	262	0·11
Maltose	1237	175	0·14
Maltotriose	1219	551	0·45
Glyceraldehyde	1002	605	0·60
α-Cyclodextrin	—[b]	831	—
β-Cyclodextrin	3285	2978	0·90
γ-Cyclodextrin	—[b]	2475	—

[a] Heated at 170°C for 1 h.
[b] Swollen gels were too weak for absorbency determination.

found that PAN prepared in the presence of low molecular weight polysaccharides and ammonium ceric nitrate yielded super absorbent polymers after saponification, neutralization and casting.

In this work, the possibility of the formation of super absorbent polymers by the treatment of mixtures of PAN with various mono- and oligosaccharides in aqueous alkali was explored. Table 2 shows that glucose, maltose and maltotriose give super absorbent polymers which absorb more than 1000 g H_2O g^{-1}, and more than 150 gg^{-1} after heating. The color of the saponification mixtures turned black in these cases. Such browning phenomenon probably comes from the side reactions of the aldehyde forms of the saccharides.

Glyceraldehyde also gave super absorbent polymer by treatment with PAN in aqueous alkali. Again in this case, the color of the saponification mixture became black. Cyclodextrins, which do not have reducing groups, were also treated with PAN in aqueous alkali. The as-cast HMPAN film made from β-cyclodextrin showed a very high absorbency. Other cyclodextrin-based HMPAN films yielded gels too weak for the determination of the absorbencies when placed in water. All the three cyclodextrin HMPAN samples showed high absorbencies (>800 gg^{-1}) after the heat treatment. As expected, the absorbent polymers made from cylodextrins were not black, in contrast to those made from reducing saccharides.

The effect of the content of glucose in the mixtures with PAN on the absorbency of HMPAN films made from them was studied. Fig. 1 shows the water absorbency of the film before and after heat treatment (at 135

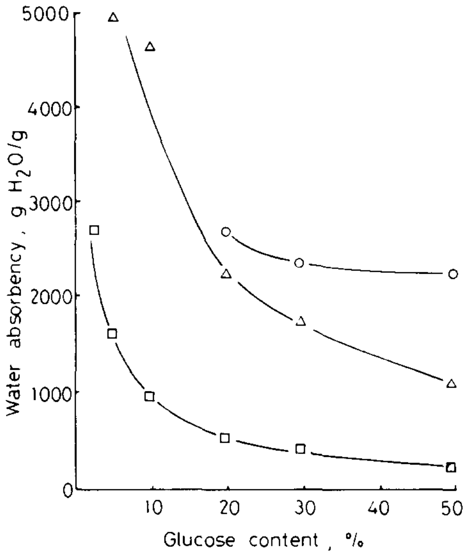

Fig. 1. Water absorbency of super absorbent polymers made from mixtures of PAN and glucose: ○, as dried at 35°C; △, heated at 135°C for 1 h; □, heated at 170°C for 1 h.

and 170°C for 1 h). The water absorbency of the as-cast film does not change greatly with the glucose content in the range between 20 and 50%. HMPAN films made with glucose contents below 20% gave only very weak gels when placed in water, but gave stronger gels after heat treatment at 135 or 170°C. The absorbency of the heated HMPAN films increases with a decrease in the glucose content as shown in Fig. 1. The highest absorbency observed is 5000 gg^{-1} for the film made from 5% content of glucose after heat treatment at 135°C.

The alkaline treatment of PAN with polyhydric alcohols other than saccharides was studied next. Mixtures (7:3 wt/wt) of PAN with alditols and inositol were treated with aqueous alkali. HMPAN films made from these absorb more than 2400 g H_2O g^{-1} before heat treatment and absorb more than 700 gg^{-1} after heat treatment at 170°C for 1 h (see Table 3). The color of the saponified mixture did not become black for these preparations. 1,6-Hexanediol and cyclohexanediols were also treated with PAN. The resulting HMPAN films gave very weak gels in water but showed very high absorbencies (700–4400 gg^{-1}) after heat treatment at 170°C. These polyhydric alcohols can work as the crosslinking agents during the alkaline treatment of PAN.

Unexpectedly, monohydric alcohols, hexanol and cyclohexanol, which cannot be crosslinking agents if only alkoxide groups are involved in crosslinking, were found to yield super absorbent polymers when

TABLE 3
Water Absorbency of HMPAN Films made from 7:3 wt/wt Mixtures of PAN and Poly- and Monohydric Alcohols

Alcohols used	*Absorbency ($g\,H_2O\,g^{-1}$) of HMPAN*		
	As-cast (A)	*Heated[a] (B)*	*B/A*
Galactitol	4650	705	0·15
Glucitol	2433	1402	0·58
Mannitol	2581	1608	0·62
Inisitol	2856	1802	0·63
1,6-Hexanediol	—[b]	3001	—
1,2-Cyclohexanediol	—[b]	4405	—
1,3-Cyclohexanediol	—[b]	1957	—
1,4-Cyclohexanediol	—[b]	700	—
n-Hexanol	—[b]	3805	—
Cyclohexanol	—[b]	2845	—

[a] Heated at 170°C for 1 h.
[b] Swollen gels were too weak for absorbency determination.

treated with PAN in aqueous alkali (see Table 3). The absorbencies of these products after heat treatment were above 2800 gg^{-1}.

All the heat-treated absorbent polymers made from mono- and oligosaccharides, polyhydric and monohydric alcohols show higher absorbencies than those of absorbent polymers made from starches, maize flour and maize meal. As mentioned earlier, PAN itself gave super absorbent polymer when saponified and heated at 170°C. HMPAN films made from β- and γ-cyclodextrins, 1,6-hexanediol, 1,2- and 1,3-cyclohexanediols, hexanol and cyclohexanol showed much higher absorbencies after heat treatment than that of the heated HMPAN film.

The ratio (B/A) of the absorbency determined after heating at 170°C (B) over that of the as-cast film (A) changes substantially with the raw materials of the absorbent polymers (see Tables 1–3). Most of the samples give ratios between 0·45 and 0·65. Maize flour and maize starch give very low ratios (0·02–0·05) while β-cyclodextrin gives a much higher ratio (0·9). In other words, maize flour- and maize starch-based HMPAN films were most susceptible to crosslinking during heating, while β-cyclodextrin-based HMPAN was the most resistant to crosslinking at elevated temperatures. During heat treatment, crosslinking should take place between poly(acrylate-co-acrylamide) chains since soluble poly(acrylate-co-acrylamide) made from PAN by saponification became insoluble on heat treatment. Additional crosslinking may take place between saccharides or polyhydric alcohols and poly(acrylate-co-acrylamide).

The present study showed that super absorbent polymers could be made by alkaline treatment of mixtures of PAN homopolymers with polysaccharides, mono- and oligosaccharides, and polyhydric alcohols. These can be explained by the earlier proposal (Fanta *et al.*, 1982) that crosslinking takes place between alkoxide ions from saccharides or polyhydric alcohols and nitrile groups of PAN chains. However, even monohydric alcohols, hexanol and cyclohexanol, were found to give super absorbent polymers by similar treatments. This fact cannot be explained by the proposed mechanism. It was known that when SPAN was saponified in ethanol-rich mixtures of ethanol and water, instead of aqueous alkali, crosslinks were formed between PAN chains (Fanta *et al.*, 1982). Further work is needed to clarify the mechanism of insolubilization during saponification in the presence of monofunctional alcohols.

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