

Morphological Study of Hydrogels of Cellulosic Super Water Absorbents by CRYO-SEM Observation

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SYNOPSIS

The structures of the hydrogels of the partially hydrolyzed cellulose-*graft*-polyacrylamide copolymers as super water absorbents were examined by use of a cryogenic scanning electron microscope. The hydrogel of the wood pulp graft copolymer that had been not hydrolyzed (P/PULP-AM) formed a spongelike structure with numerous circular micropores. The highly swollen hydrogel of the partially hydrolyzed wood pulp graft copolymer (P/PULP-AM-Hyd), on the other hand, formed a honeycomblike structure with polygonal pores surrounded with membraneous walls. A hydrogel of a crosslinked polyacrylamide (PAM) formed a similar structure to that of P/PULP-AM, but the honeycomblike structure shown in P/PULP-AM-Hyd was not observed in the partially hydrolyzed PAM. The pore size of the honeycomblike structure of the hydrogel of P/PULP-AM-Hyd decreased with an increase in the amount of the crosslinker added at graft copolymerization. For the hydrogel of the P/PULP-AM-Hyd with less addition of the crosslinker, however, the honeycomblike structure had been broken. The hydrogel of the P/PULP-AM-Hyd without the addition of the crosslinker did not show a honeycomblike structure. In spite of no addition of the crosslinker, the cellulosic film and nonwoven fabric graft copolymers formed honeycomblike structures. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Super water absorbents can be swollen in water and demonstrate high water absorbencies. Many kinds have been prepared from synthetic and natural polymers by graft copolymerization, crosslinking polymerization, and other hydrophilization and water insolubilization. Some of them are currently commercialized and used in various fields.

We synthesized cellulosic super water absorbents in fibrous and sheet forms by graft copolymerization of acrylamide and acrylic acid onto several kinds of cellulose such as wood pulps, a film, and a nonwoven fabric and by posthydrolysis.¹ The cellulose graft copolymers could absorb more water than the commercial absorbents did. The type of cellulosic substrate and the composition, crosslinking density, and

amount of the grafted branch polymer affected not only the absorbency of the graft copolymer but the rheological properties of the hydrogel and dispersion such as viscosity and dynamic viscoelasticity and the porous structure examined by the solute exclusion technique of the hydrogel.² The hydrogel of the cellulose graft copolymer showed a unique swelling behavior with changes in the swelling condition, and this swelling behavior was investigated by the examination of the solution absorbency, the distribution of pores, and the dynamic viscoelasticity.³

The morphology of the hydrogel of the cellulose graft copolymer would be affected by the type of cellulosic substrate and the composition, crosslinking density, and amount of the grafted branch polymer and would change with the voluminal change. However, the morphologies of the hydrogels of the super water absorbents has not been studied in detail.

On the other hand, the morphological studies for many kinds of gels from synthetic and natural polymers have been reported.⁴⁻¹⁰ The structures of the

gels have been observed by use of an optical microscope, a scanning electron microscope (SEM), and a transmission electron microscope. However, it is impossible to observe the original gels directly, and some operations such as dyeing, fixing, drying, and embedding of the gels must be carried out for the observations. Therefore, there is no assurance that the observed images indicate the essential structures of the gels. Kimura describes that some artifacts have been developed on the SEM images of the gels that were freeze dried or critical point dried, and that the most essential structures of the gels can be shown in the SEM images by use of an SEM with cryogenic apparatuses on cryogenic state.¹¹

In this report, therefore, the morphological study of the hydrogels of the highly water absorptive cellulose graft copolymers was carried out by observation using a cryogenic scanning electron microscope (CRYO-SEM) on cryogenic state to investigate the effects of the chemical composition and crosslinking density of the graft copolymer on the structure of the hydrogel.

EXPERIMENTAL

Preparation of Samples

The graft copolymerization of acrylamide (AM) with *N,N'*-methylenebisacrylamide (MBAA) as a crosslinker onto cellulose by ceric ion initiation was carried out according to a procedure previously described.¹ The celluloses used for the trunk polymers were a NBKP (bleached kraft pulp from softwood)

in a powdered form (P/PULP), a cellulosic film (FILM), and a nonwoven fabric of regenerated cellulose (NWF). After the graft copolymerization, amide groups in the graft copolymers were converted into carboxyl groups by alkaline hydrolysis as described in a previous study.¹ Table I shows the characteristics of the cellulose graft copolymers used in this study.

The structures of the hydrogels of the graft copolymers were compared with those of the concentrated solution of hydroxyethyl cellulose (HEC) and the hydrogel of a crosslinked polyacrylamide (PAM). HEC was of reagent grade (Wako Pure Chemical Industries, Ltd., the intrinsic viscosity in water at 30°C was 7.64). PAM was synthesized from AM and MBAA by initiation of the redox system as follows: 10 g of AM and 30 mg of potassium persulfate were dissolved in 40 mL of water. Separate from this solution, 100 mg of MBAA and 30 mg of iron (II) sulfate were dissolved in 50 mL of water. The two solutions were mixed and allowed to polymerize for 1 h at 20°C. After polymerization, the polymer was washed with water to remove any residual impurities. Partially hydrolyzed PAM (PAM-Hyd) was prepared by the following procedure: 1 g of PAM was added to 50 g of 0.5*N* aqueous sodium hydroxide solution and allowed to stand for 48 h at 20°C. Then, the hydrogel was washed with water to remove the alkali. Table II shows the characteristics of PAM and PAM-Hyd used in this study.

Water absorbency was measured by the screening method and expressed as a water retention value (WRV) calculated in grams of water per gram of dry polymer.¹

Table I Super Water Absorbents of Cellulose Graft Copolymers

Sample	Graft Copolymer	Addition of MBAA ^a (wt %)	Degree of Grafting ^b (%)	Degree of Hydrolysis ^c (%)	WRV (g/g)
A	P/PULP-AM ^d	0.6	294.2	—	44.8
B	P/PULP-AM-Hyd ^e	0.6	294.2	70.7	1772.8
C	P/PULP-AM-Hyd	0.9	440.7	69.6	756.7
D	P/PULP-AM-Hyd	0.1	338.7	63.2	2635.2
E	P/PULP-AM-Hyd	0	86.9	76.6	117.8
F	FILM-AM-Hyd ^f	0	401.3	64.8	151.5
G	NWF-AM-Hyd ^g	0	330.1	62.8	76.8

^a Weight ratio of MBAA for AM on copolymerization.

^b Weight ratio of the polyacrylamide for the cellulose in the graft copolymer.

^c Extent of the conversion of the amide groups into the carboxyl groups in the graft copolymer by alkaline hydrolysis.

^d Graft copolymer of polyacrylamide onto P/PULP.

^e Partially hydrolyzed P/PULP-AM.

^f Partially hydrolyzed graft copolymer of polyacrylamide onto FILM.

^g Partially hydrolyzed graft copolymer of polyacrylamide onto NWF.

Table II Crosslinked Polyacrylamide Gel and Partially Hydrolyzed Gel

Sample	Gel	Content of Nitrogen ^a (%)	Degree of Hydrolysis (%)	WRV (g/g)
H	PAM	19.0	—	19.1
I	PAM-Hyd	8.3	56.5	634.7

^a The nitrogen content in the polymer was determined by the Kjeldahl method.

Observation of Structures

The hydrogels of the cellulose graft copolymers and other samples were completely swollen to equilibrium. They were rapidly frozen in liquid nitrogen and then cut with an installed cold knife and sputtered with gold in the cryogenic apparatuses. The sputtered specimens were observed by use of a CRYO-SEM (JSM-5400/CRU, JEOL Ltd., Japan) on cryogenic state, operated at accelerating voltages of 5 or 10 kV.

RESULTS

The P/PULP graft copolymer (P/PULP-AM) was hydrophilic but could only slightly swell. Its WRV was 44.8 g/g. Figure 1 shows a CRYO-SEM photograph representing a surface view of the swollen P/PULP-AM. The structure of the hydrogel was spongelike and had numerous circular micropores of uniform size. The pore size was 2–5 μm in diameter.

By alkaline hydrolysis, the graft copolymer demonstrated high water absorbency. The WRV of the

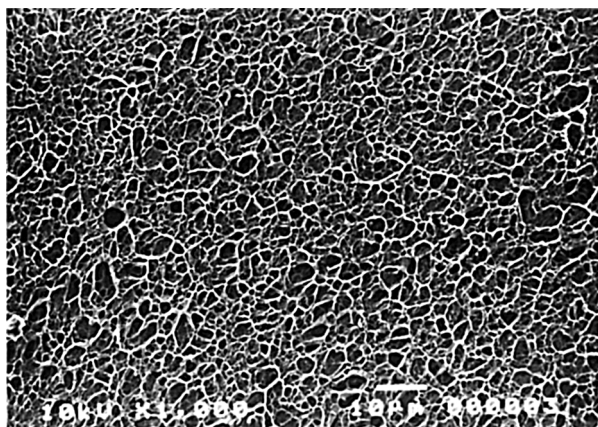


Figure 1 CRYO-SEM photograph of hydrogel of P/PULP-AM. Scale bar represents 10 μm .

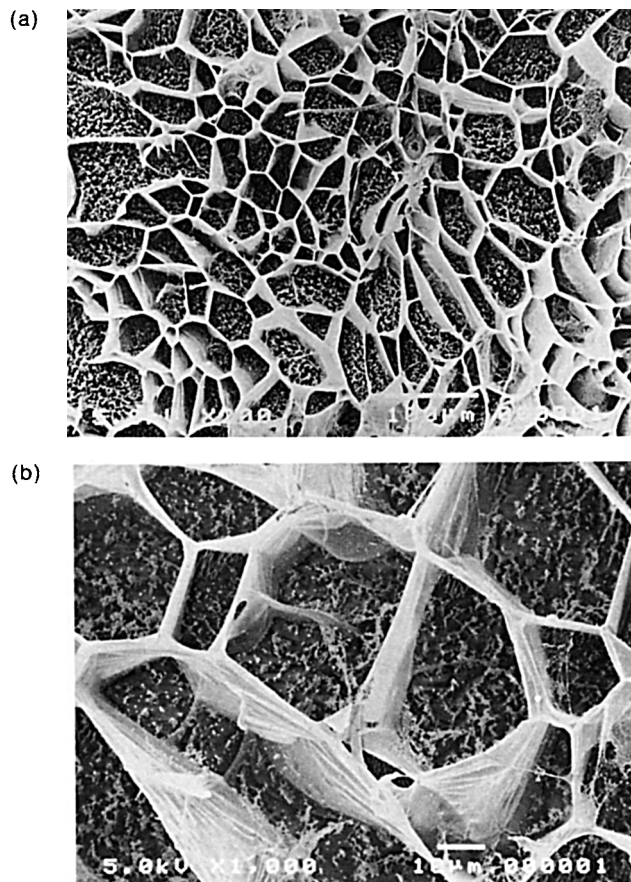


Figure 2 CRYO-SEM photographs of hydrogel of P/PULP-AM-Hyd. Scale bars represent (a) 100 μm and (b) 10 μm .

partially hydrolyzed P/PULP-AM (P/PULP-AM-Hyd) reached 1772.8 g/g. Figure 2 shows an image of the hydrogel of P/PULP-AM-Hyd. A honeycomblike structure was observed. The membranous walls were continuous, and the pores were separated by them. The membranous walls were very thin and the thickness was less than 0.1 μm . The pores were polygonal and were surrounded by three to nine membranous walls. The pore size was not uniform being 10–100 μm in diagonal and was much larger than that of the hydrogel of P/PULP-AM.

A 10 wt % aqueous solution of HEC had a high viscosity, so it was possible to observe it by the CRYO-SEM using the same technique as the other hydrogels. The result in Figure 3 indicated that the HEC solution formed a filmlike structure with small holes. The holes observed in Figure 3 were apparently distinct from the pores observed in Figures 1 and 2.

Figure 4 shows the image of the hydrogel of PAM. The spongelike structure similar to that of the hy-

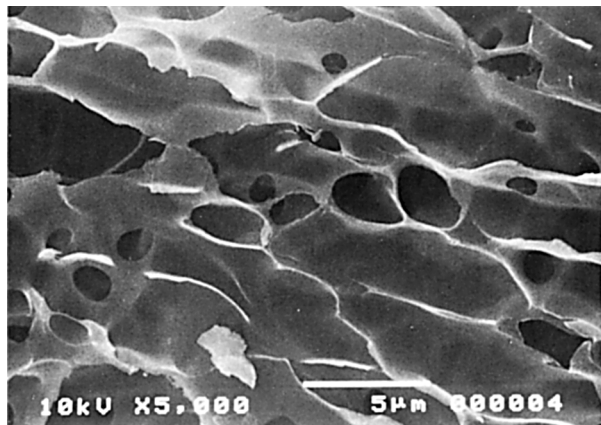


Figure 3 CRYO-SEM photograph of 10 wt % aqueous HEC solution. Scale bar represents 5 μm .

drogel of P/PULP-AM was observed. The pore size was 5–10 μm in diameter. The WRV of PAM was lower than that of P/PULP-AM as shown in Tables I and II, and so the hydrogel of PAM had larger pores than that of P/PULP-AM did in spite of its lower swelling. On the other hand, the hydrogel of PAM-Hyd highly swelled and its WRV was 634.7 g/g. However, the hydrogel of PAM-Hyd did not show a honeycomblike structure that was shown in the hydrogel of P/PULP-AM-Hyd. The hydrogel of PAM-Hyd randomly aggregated and exhibited a granular structure as shown in Figure 5.

The effect of the amount of the crosslinker added at graft copolymerization on the structure of the hydrogel of P/PULP-AM-Hyd is shown in Figure 6. The WRV of the graft copolymer was affected by the amounts of the crosslinker as shown in Table I.

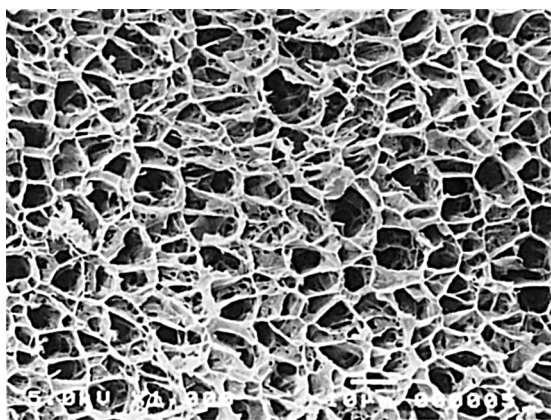


Figure 4 CRYO-SEM photograph of hydrogel of PAM. Scale bar represents 10 μm .

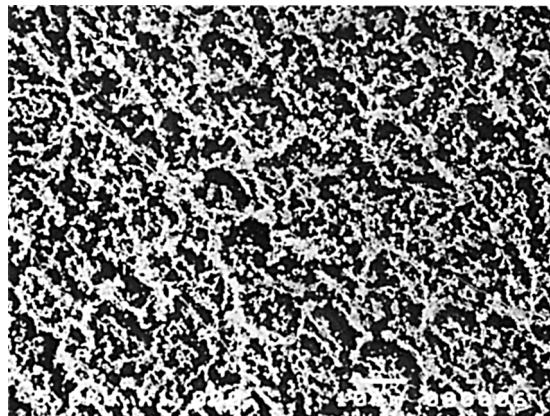


Figure 5 CRYO-SEM photograph of hydrogel of PAM-Hyd. Scale bar represents 10 μm .

To compare the structures of the hydrogels with one another, therefore, the hydrogels were to swell to an approximately equal ratio except for that of the P/PULP-AM-Hyd without the addition of the crosslinker. The honeycomblike structures with polygonal pores were observed in the hydrogels of the P/PULP-AM-Hyd with 0.9 and 0.6 wt % addition of MBAA. As shown in Figures 6(a) and 6(b), the pore sizes of the honeycomblike structure of the hydrogels of the P/PULP-AM-Hyds with 0.9 and 0.6 wt % addition of MBAA were 10–30 μm and 20–50 μm in diagonal, respectively. The pore size decreased with an increase in the amount of the crosslinker.

On the other hand, as shown in Figure 6(c), the honeycomblike structure would have been formed in the hydrogel of the P/PULP-AM-Hyd with 0.1 wt % addition of MBAA but had been broken during observation. Furthermore, the hydrogels of the P/PULP-AM-Hyd without the addition of the crosslinker, as shown in Figure 6(d), did not form a honeycomblike structure but formed a laminated structure.

Figures 7 and 8 show the images of the hydrogels of the graft copolymers in sheet forms. Although the crosslinker had not been added at graft copolymerization, the hydrogels of FILM-AM-Hyd and NWF-AM-Hyd partly formed honeycomblike structures. The pore sizes of the honeycomblike structures of the hydrogels of FILM-AM-Hyd and NWF-AM-Hyd were 2–10 and 3–15 μm in diagonal, respectively, and these sizes were smaller and more uniform than those of P/PULP-AM-Hyds. The pore size of NWF-AM-Hyd was larger than that of FILM-AM-Hyd, though FILM-AM-Hyd was swelled more highly than NWF-AM-Hyd was.

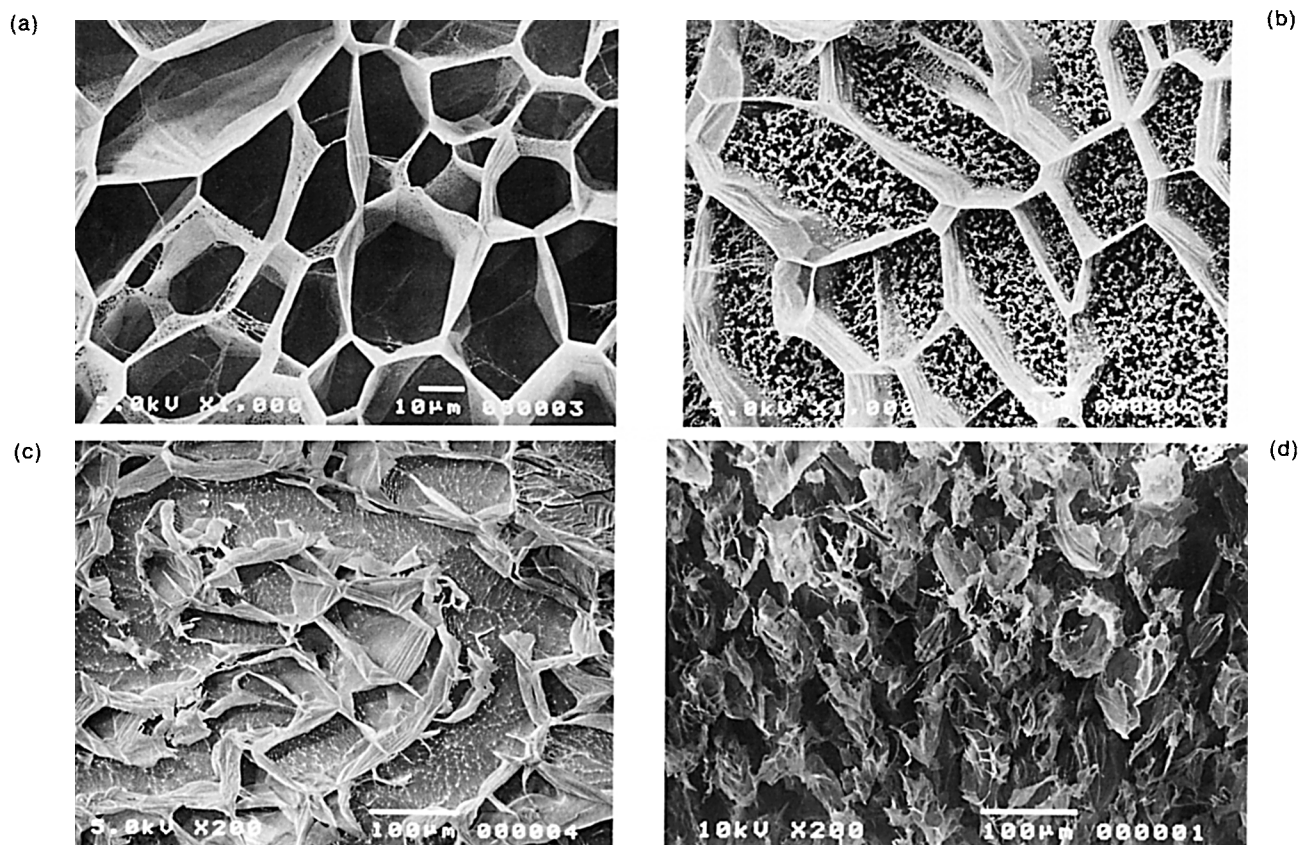


Figure 6 CRYO-SEM photographs of hydrogels of P/PULP-AM-Hyds: (a) with 0.9 wt % addition of MBAA; (b) with 0.6 wt % addition of MBAA; (c) with 0.1 wt % addition of MBAA; (d) without addition of MBAA. WRVs equal (a) 756.7 g/g, (b) 775.4 g/g, (c) 863.9 g/g, and (d) 117.8 g/g. Scale bars represent 10 μm in (a) and (b) and 100 μm in (c) and (d).

DISCUSSION

The results of the morphological study of the hydrogels by observation using a CRYO-SEM are summarized in Table III. Honeycomblike structures with pores separated by membraneous walls were observed in the hydrogels of the P/PULP-AM-Hyds with the addition of the crosslinker and the FILM-AM-Hyd and NWF-AM-Hyd in sheet forms. The absorbency and dynamic viscoelasticity of the hydrogel of the cellulose graft copolymer changed by freezing-melting operation, and the honeycomblike structure was surely formed by the growing of ice crystals in the hydrogel during the freezing process and the aggregation of the polymer.^{11,12} On the other hand, it is known that the growing of ice crystals in a gel can be minimized by the freeze-etching of the gel swollen with aqueous solution of cryoprotectants such as dimethyl sulfoxide, glycerol, and sucrose, but this method could not be applicable to the ob-

servation using the CRYO-SEM because of the slow sublimation of these cryoprotectants and the occurrence of the residues of them on the surface of the sample after sublimation.

While both hydrogels of the P/PULP-AM-Hyd with the addition of the crosslinker and PAM-Hyd had significantly swollen in water, the former formed a honeycomblike structure, but the latter randomly aggregated and exhibited a granular structure. We assume that this result is due to the differences in the expansion of the polymer network in the hydrogel and in the magnitude of the affinity of the polymer network for water. P/PULP-AM-Hyd synthesized from a water-insoluble cellulosic substrate is composed of two components with different magnitudes of affinity for water. One is an ionic network of partially hydrolyzed polyacrylamide branch polymer, which homogeneously expands in the hydrogel and is a component with a stronger affinity for water. The other is a nonionic linear polymer of cellulose

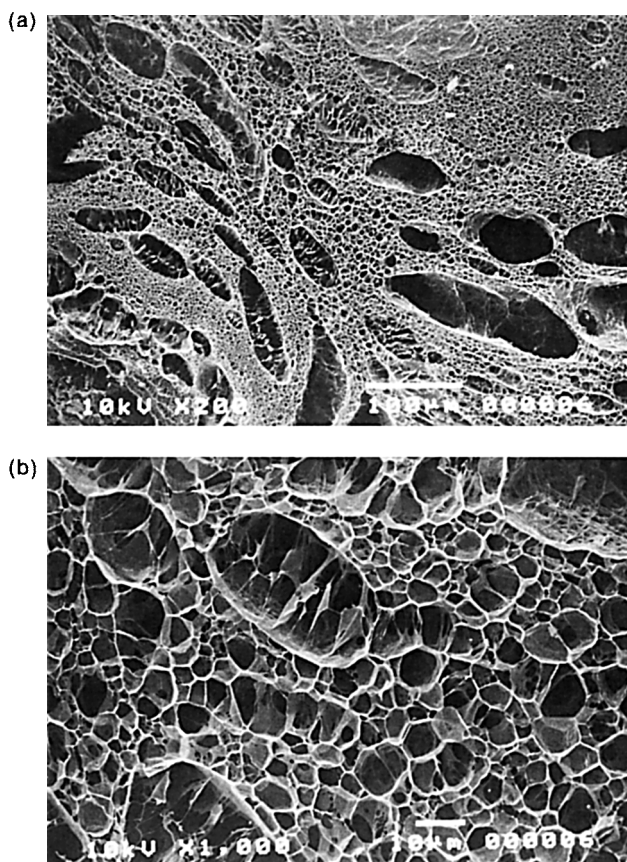


Figure 7 CRYO-SEM photographs of hydrogel of FILM-AM-Hyd. Scale bars represent (a) 100 μm and (b) 10 μm .

trunk polymer, which extends in the hydrogel but is a component with a weaker affinity for water. On the other hand, PAM-Hyd is composed only of the partially hydrolyzed polyacrylamide. And then, the polymer network of PAM-Hyd probably expands more homogeneously and has larger affinity for water than that of P/PULP-AM-Hyd dose. For P/PULP-AM-Hyd, moreover, the cellulose trunk polymer itself restrains the aggregation of the polymer network of the branch polymer. Consequently, we tentatively consider that the hydrogel of PAM-Hyd randomly aggregated but that of P/PULP-AM-Hyd formed the honeycomblike structure.

The hydrogels of P/PULP-AM and PAM, which had not been hydrolyzed, formed spongelike structures with micropores. Since both P/PULP-AM and PAM were nonionic polymers, their hydrogels contained a little amount of water and had high elasticities. Thus, their hydrogels did not randomly aggregated, but formed the spongelike structures. For the aqueous solution of HEC, in contrast to them, the molecules of HEC were completely soluble in

water, and a filmlike structure was formed. The holes of this structure seem to be due to the bubbles that were entrapped in the HEC solution because of its high viscosity.

The honeycomblike structure of the partially hydrolyzed graft copolymer was affected by the difference in the crosslinking density of the graft copolymer. The pore size of the honeycomblike structure decreased with an increase in the amount of the crosslinker added at graft copolymerization. In our previous study,² the elasticity of the hydrogel of the cellulose graft copolymer was shown to increase with an increase in the amount of crosslinker. The decrease in pore size would be attributed to the increase in the elasticity of the hydrogel. The honeycomblike structure of the hydrogel of the P/PULP-AM-Hyd with 0.1 wt % addition of the crosslinker had been broken during observation. This destruction is probably due to a low elasticity of that hydrogel. The hydrogel of the P/PULP-AM-Hyd without the addition of the crosslinker did not form a honeycomblike structure. Since the P/PULP-AM-Hyd

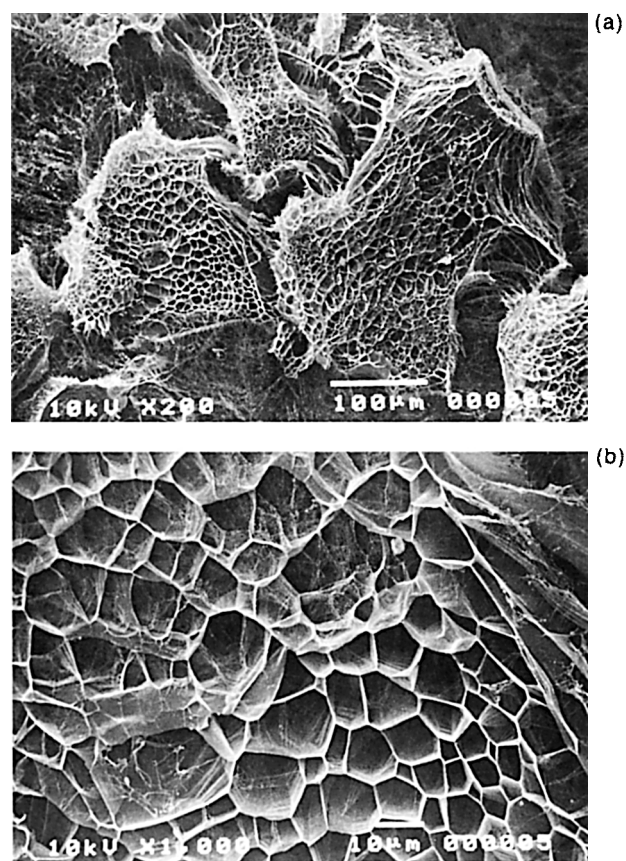


Figure 8 CRYO-SEM photographs of hydrogel of NWF-AM-Hyd. Scale bars represent (a) 100 μm and (b) 10 μm .

Table III Structures of Hydrogels Observed Using CRYO-SEM

Figure	Sample	WRV at Observation (g/g)	Structure	Pore Size ^a
1	A	44.8	Spongelike structure	Uniform 2–5 μm
2	B	1772.8	Honeycomblike structure	Not uniform 10–100 μm
3	10 wt % HEC solution	9.0	Filmlike structure	—
4	H	19.1	Spongelike structure	Uniform 3–8 μm
5	I	634.7	Granular structure	—
6(a)	C	756.7	Honeycomblike structure	Not uniform 5–40 μm
6(b)	B	775.4	Honeycomblike structure	Not uniform 10–60 μm
6(c)	D	863.9	Broken honeycomblike structure	—
6(d)	E	117.8	Laminated structure	—
7	F	151.5	Honeycomblike structure	Uniform 2–10 μm
8	G	76.8	Honeycomblike structure	Uniform 3–15 μm

^a The size of circular or polygonal pores in diameter or diagonally measured.

without the addition of the crosslinker had linear branches of partially hydrolyzed polyacrylamide, this graft copolymer was nearly water solubilized, and the elasticity of this hydrogel was extremely low. Accordingly, it is considered that the P/PULP-AM-Hyd without the addition of the crosslinker did not form a honeycomblike structure but formed a laminated structure.

Although FILM-AM-Hyd and NWF-AM-Hyd were synthesized without the addition of the crosslinker, the cellulosic substrates such as FILM and NWF were formed into sheets and prevented their graft copolymers from being water solubilized. Consequently, when the crosslinker was not added at graft copolymerization, the honeycomblike structure was not formed in the hydrogel of P/PULP-AM-Hyd but formed in those of FILM-AM-Hyd and NWF-AM-Hyd. The pore size in the honeycomblike structure of the hydrogel of NWF-AM-Hyd was larger than that of FILM-AM-Hyd. As compared with two kinds of cellulosic substrates, NWF had higher hydrophilicity and flexibility than FILM did. It is considered that this is one of the reasons the hydrogel of NWF-AM-Hyd had larger pores than did that of FILM-AM-Hyd.

In conclusion, the difference in the structure of the hydrogel observed by the CRYO-SEM was due to the differences in the chemical composition of the polymer and in the crosslinking density of the polymer network. That is, the growing of ice crystals in the hydrogel and the aggregation of the polymer were affected by the expansion of the polymer network in the hydrogel, the magnitude of the affinity of the polymer network for water, and the elasticity of the hydrogel.

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