Mechanisms of Swelling of the Super Water-Absorbents Derived from Cellulose Graft Copolymers

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Chapter 6

Morphologies of Hydrogels of Cellulose Graft Copolymers

6.1 Introduction

The hydrogel of the synthesized cellulose graft copolymer showed an unique swelling behavior with the change in the swelling condition. The swelling ratio largely varied with the change in the swelling condition, and the porous structure and the dynamic viscoelasticity also changed with the voluminal change.

The structures of various gels have been investigated by using of the diffraction or scattering technique by X-ray, neutron, or lasers, but the theories and experimental operations of them have not been established yet [176].

The morphological studies for various gels have been also reported [202, 210, 248, 264-278]. The structures of the gels have been observed by use of an optical microscope, a scanning electron microscope(SEM), and a transmission electron microscope [202, 210, 248, 264-278]. However, it is impossible to observe directly the the original gels, and some opperations such as dyeing, fixation, 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 hydrogels [176]. It is described by Kimura 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 a SEM with cryogenic apparatuses on cryogenic state [279].

The morphologies of the hydrogels of the super absorbent polymers have not been studied in detail. However, it is interested in the relationships between the absorbencies of the super absorbent polymers and the morphologies of their hydrogels and in the chages in the morphologies with the voluminal change due to the change in the swelling condition. Therefore, the morphological study of the hydrogels of the cellulose graft copolymers was carried out by the observation using a cryogenic scanning electron microscope(CRYO-SEM) on cryogenic state.

6.2 Experimental

6.2.1 Samples

The partially hydrolyzed graft copolymers of crosslinked polyacrylamide(PAM) on cellulosics such as a bleached kraft pulp from softwood being in powdery form(P/PULP), a cellulosic film that was extracted with water and ethanol to remove flexibilizer(FILM), and a nonwoven fabric from regenerated cellulose(NWF) were used as the sample in this chapter, which were syntesized as described in Chapters 1 and 2. The PAM and partially hydrolyzed PAM(PAM-Hyd) and a commercial super absorbent polymer from starch polymer(COMMERCIAL-1) were also used. Table 6.1 shows the characteristics of the samples used in this chapter.

6.2.2 CRYO-SEM Observation

The hydrogels of the cellulose graft copolymers and other samples were completely swollen at 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 on cryogenic state by use of a CRYO-SEM(JSM-5400/CRU, JEOL Ltd.), operated at accelerating voltages of 5 or 10 kV.

Table 6.1 Characteristics of Cellulose Graft Copolymers and Commercial Super Absorbent Polymer Used in This Chapter

Sample	Graft Copolymer	Amount of MBAA[A] (wt% of AM)	D G[B] (%)	D H[C] (%)	WRV[D] (g/g)
A	P/PULP-AM[E]	0.60	294.2	——	44.8
B	P/PULP-AM-Hyd[F]	0.60	294.2	70.7	1772.8
C	P/PULP-AM-Hyd	0.90	440.7	69.6	756.7
D	P/PULP-AM-Hyd	0.10	338.7	63.2	2635.2
E	P/PULP-AM-Hyd	0.00	86.9	76.6	117.8
F	FILM-AM-Hyd[G]	0.00	401.3	64.8	151.5
G	NWF-AM-Hyd[H]	0.00	330.1	62.8	76.8
H	PAM[I]	1.00	19.0[J]	——	19.1
I	PAM-Hyd[K]	1.00	8.3[J]	56.5	634.7
J	COMMERCIAL-1[L]	——	——	——	987.8

Conditions of graft copolymerization and post-hydrolysis were described in Chapters 1 and 2.

A) Amount of the addition of *N,N'*-methylenebisacrylamide(MBAA) as a crosslinker.
B) Degree of grafting.
C) Degree of hydrolysis.
D) Water retention value.
E) Graft copolymer of PAM on P/PULP.
F) Partially hydrolyzed graft copolymer of PAM on P/PULP.
G) Partially hydrolyzed graft copolymer of PAM on FILM.
H) Partially hydrolyzed graft copolymer of PAM on NWF.
I) Crosslinked polyacrylamide(see Chapter 2).
J) Nitrogen content of polymer.
K) Partially hydrolyzed crosslinked polyacrylamide(see Chapter 2).
L) Commercial super absorbent polymer of the partially hydrolyzed graft copolymer of crosslinked polyacrylonitrile on starch (see Table 1.5 in Chapter 1).

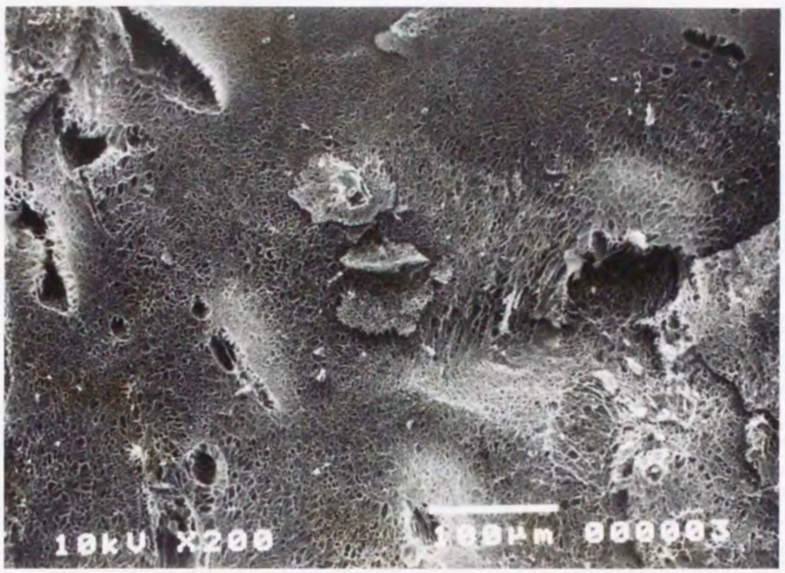
6.3 Results and Discussion

The P/PULP trunk polymer was hydrophilized by the graft copolymerization of acrylamide. However, the P/PULP-AM(Sample A) graft copolymer could only slightly swell, and its water retention value(WRV) was 44.8 g/g. Fig. 6.1 shows the CRYO-SEM photograph representing a surface view of the swollen P/PULP-AM. The structure of the hydrogel was sponge-like 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 P/PULP-AM-Hyd(Sample B) reached 1772.8 g/g. Fig. 6.2 shows the CRYO-SEM image of the hydrogel of P/PULP-AM-Hyd. A honeycomb-like structure was observed. The membraneous walls were continuous, and the pores were separated by them. The membraneous walls were very thin and the thickness was less than 0.1 μm. The pores were polygonal and were surrounded by three to nine membraneous walls. The pore size was not uniform being 10-100 μm in diagonal and was extremely larger than that of the hydrogel of P/PULP-AM.

Fig. 6.3 shows the CRYO-SEM image of the hydrogel of COMMERCIAL-1. A continuous membranous structure was observed. Nevertheless both of COMMERCIAL-1 and P/PULP-AM-Hyd were the partially hydrolyzed graft copolymers, the structure of COMMERCIAL-1 was different from that of P/PULP-

(A)



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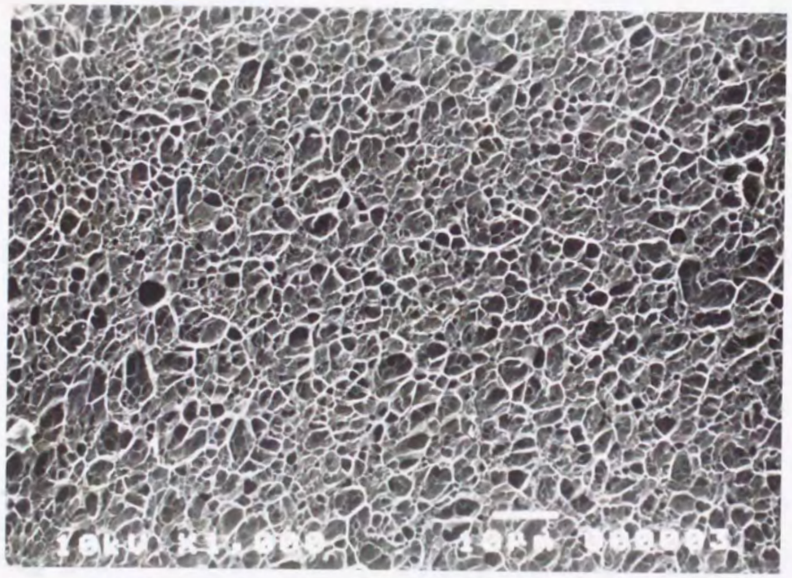
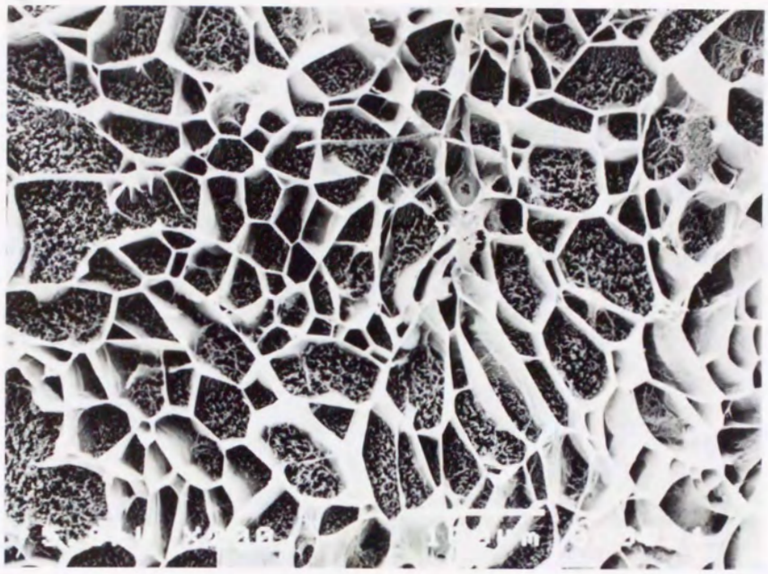


Fig. 6.1 CRYO-SEM photographs of hydrogel of P/PULP-AM(Sample A). Scale bars represent 100 μm in (A) and 10 μm in (B).

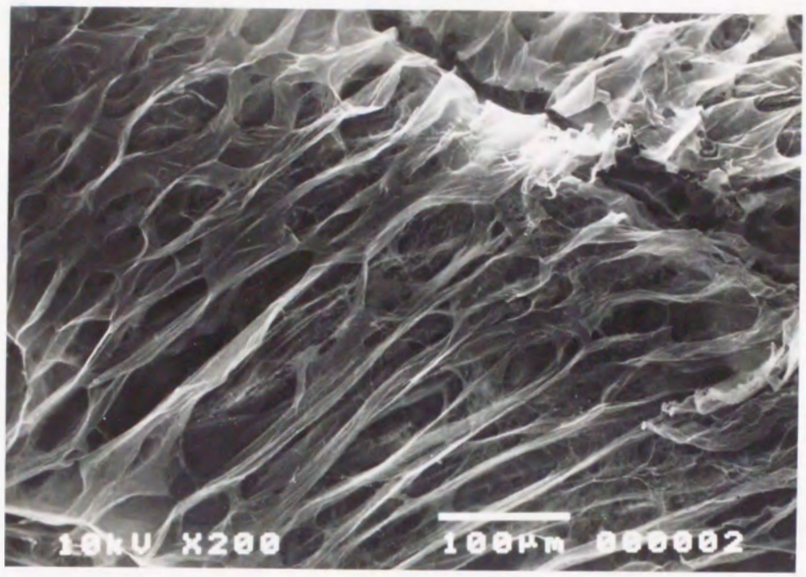
(A)



(B)

Fig. 6.2 CRYO-SEM photographs of hydrogel of P/PULP-AM-Hyd(Sample B). Scale bars represent 100 μm in (A) and 10 μm in (B).

(A)



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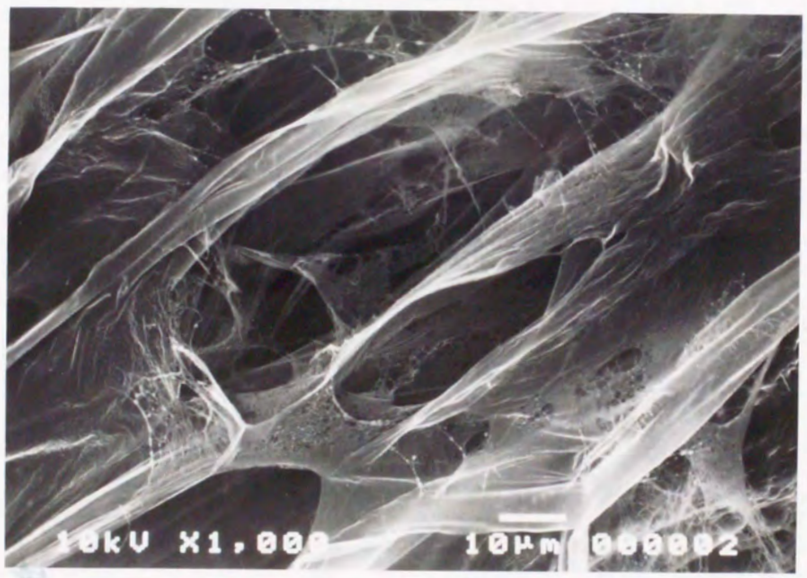


Fig. 6.3 CRYO-SEM photographs of hydrogel of COMMERCIAL-1(Sample J). Scale bars represent 100 μm in (A) and 10 μm in (B).

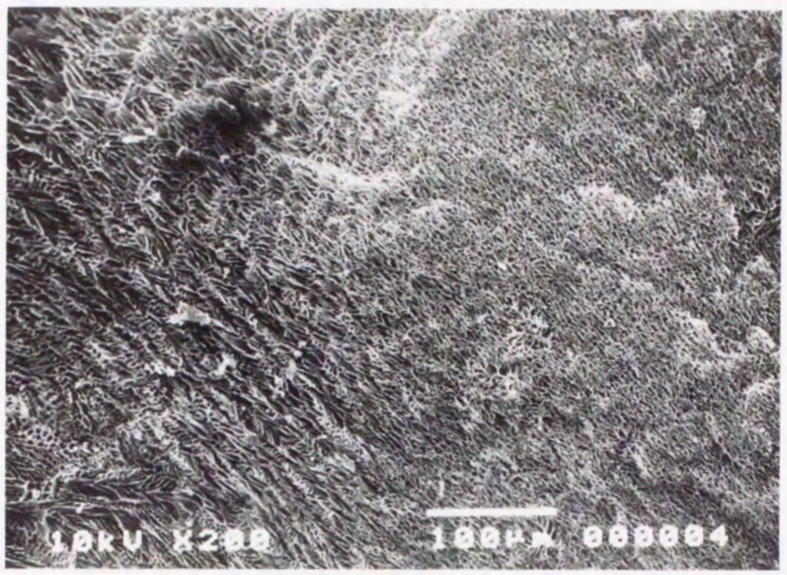
AM-Hyd.

A ten wt% aqueous solution of hydroxyethylcellulose (HEC, the intrinsic viscosity in water at 30 °C was 7.64) had a high viscosity as shown in Fig. 5.3 in Chapter 5, so it was possible to observe it by the CRYO-SEM using the same technique as the other hydrogels. The result in Fig. 6.4 indicated that the HEC solution formed a film-like structure with small holes. The holes observed in Fig. 6.4 were apparently distinct from the pores observed in Figs. 6.1 and 6.2.

Fig. 6.5 shows the CRYO-SEM image of the hydrogel of PAM. The sponge-like structure similar to that of the hydrogel of P/PULP-AM was observed. The pore size was 5-10 μm in diameter. Although the WRV of PAM(Sample H) was lower than that of P/PULP-AM(Sample A) as shown in Table 6.1, the hydrogel of PAM had larger pores than that of P/PULP-AM 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(Sample I) did not show a honeycomb-like structure that was shown in the hydrogel of P/PULP-AM-Hyd(Sample B). The hydrogel of PAM-Hyd randomly aggregated and exhibited a granular structure as shown in Fig. 6.6.

The effect of the amount of the crosslinker(*N,N'*-methylenebisacrylamide, MBAA) added at the graft

(A)



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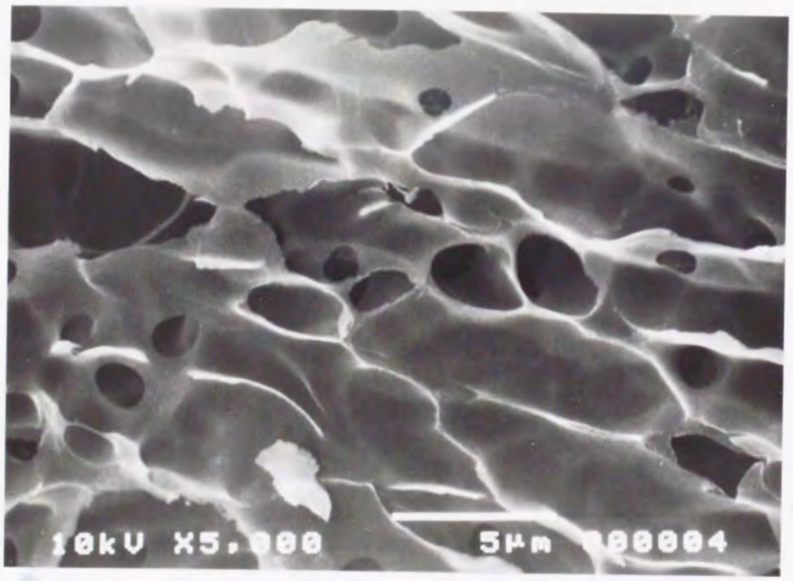
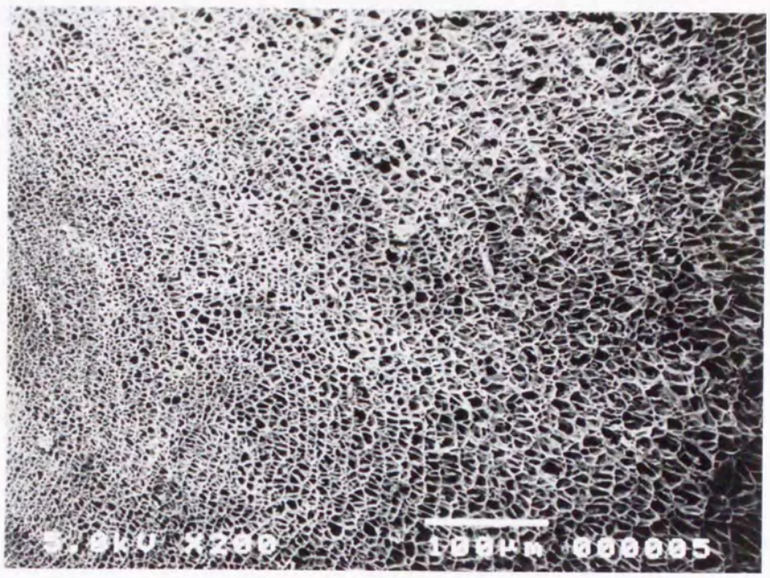


Fig. 6.4 CRYO-SEM photographs of 10 wt% aqueous solution of HEC. Scale bars represent 100 μm in (A) and 5 μm in (B).

(A)



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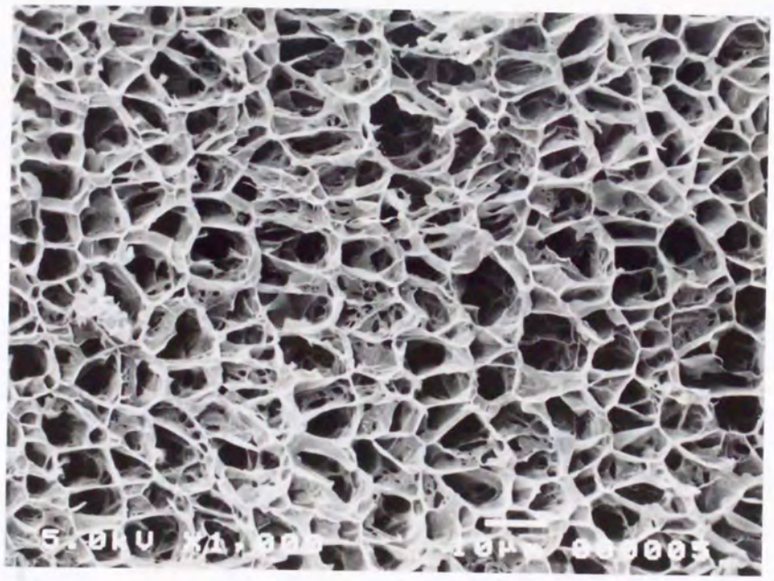
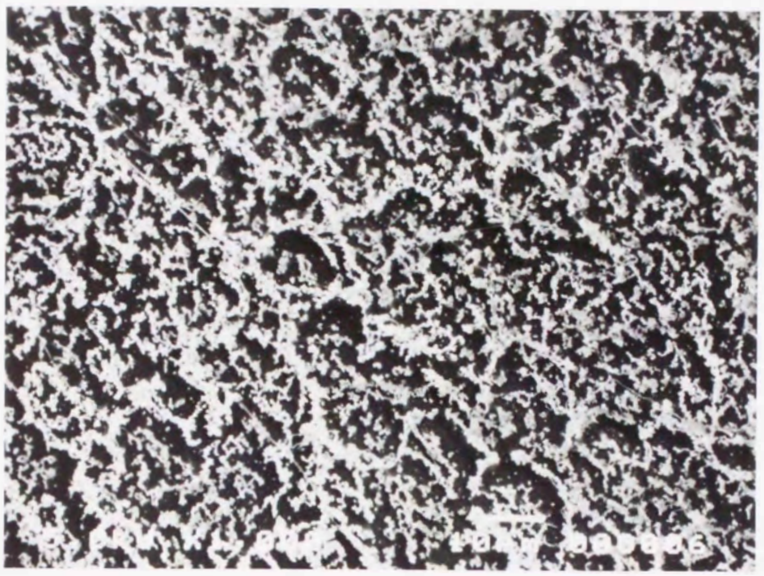


Fig. 6.5 CRYO-SEM photographs of hydrogel of PAM(Sample H). Scale bars represent 100 μm in (A) and 10 μm in (B).

(A)



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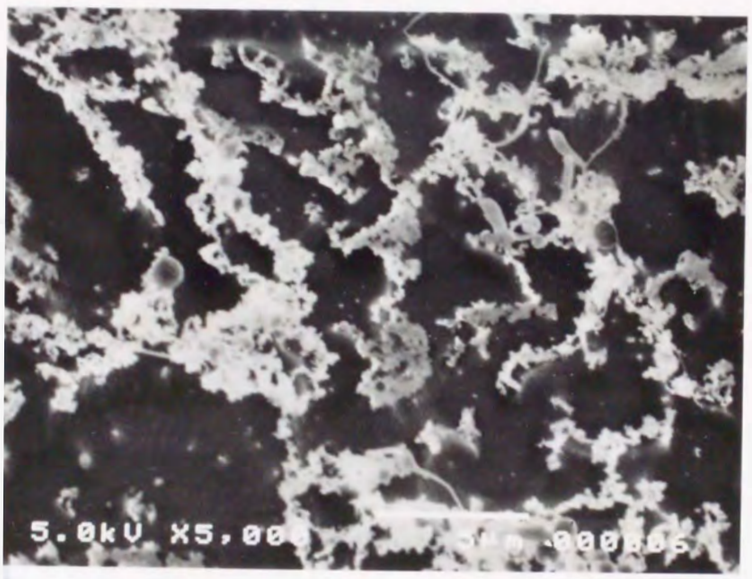


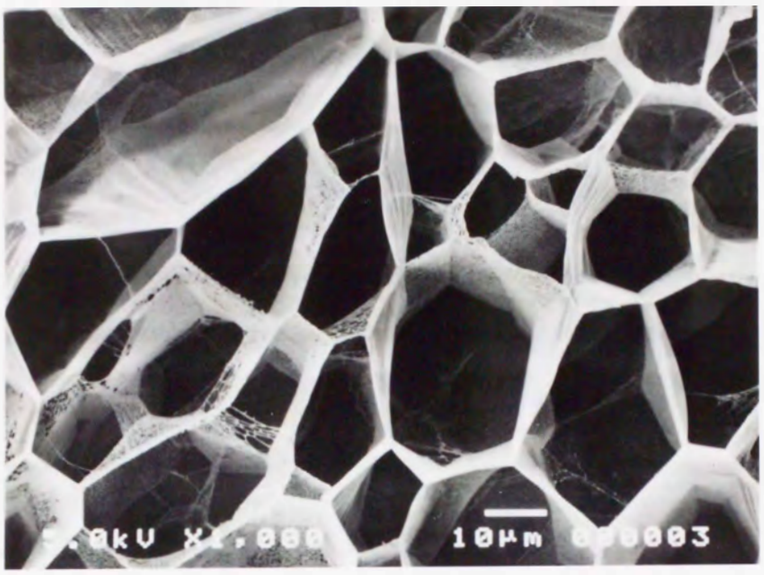
Fig. 6.6 CRYO-SEM photographs of hydrogel of PAM-Hyd(Sample I). Scale bars represent 10 μm in (A) and 5 μm in (B).

copolymerization on the structure of the hydrogel of P/PULP-AM-Hyd is shown in Fig. 6.7. The WRV of the graft copolymer was affected by the amount of the crosslinker as shown in Table 6.1. To compare the structures of the hydrogels with one another, therefore, the hydrogels were to swell to an approximately equal ratio in the visinity of 800 g/g except for that of the P/PULP-AM-Hyd without the addition of the crosslinker(Sample E). The honeycomb-like structures with polygonal pores were observed in the hydrogels of the P/PULP-AM-Hyds with 0.90 wt% and 0.60 wt% addition of MBAA(Samples C and B). As shown in Figs. 6.7(A) and 6.7(B), the pore sizes of the honeycomb-like structure of the hydrogels of the P/PULP-AM-Hyds with 0.90 wt% and 0.60 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 Fig. 6.7(C), the honeycomb-like structure would have been formed in the hydrogel of the P/PULP-AM-Hyd with 0.10 wt% addition of MBAA(Sample D) but had been broken. Furthermore, the hydrogels of the P/PULP-AM-Hyd without the addition of the crosslinker(Sample E), as shown in Fig. 6.7(D), did not form a honeycomb-like structure, but formed a laminated structure.

Figs. 6.8 and 6.9 show the CRYO-SEM images of the

(A)

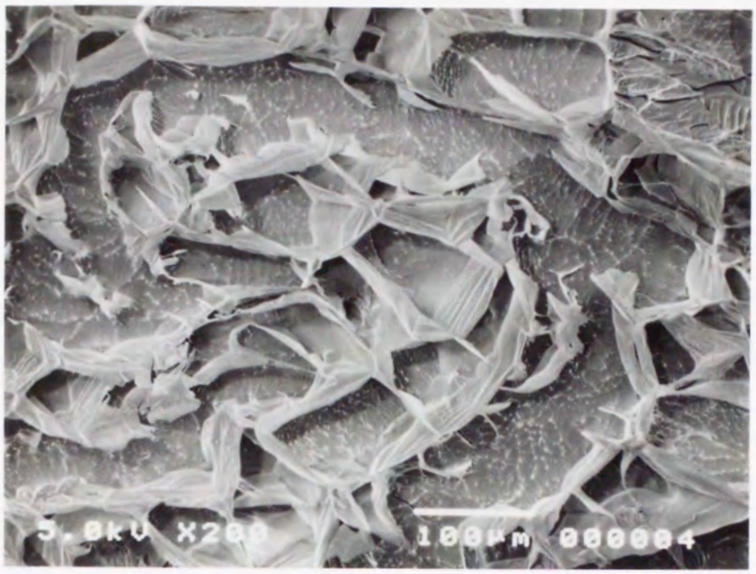


(B)

Fig. 6.7 CRYO-SEM photographs of hydrogels of P/PULP-AM-Hyds. Scale bars represent 10 μm.

Samples: (A), P/PULP-AM-Hyd with 0.90 wt% addition of MBAA(Sample C);
(B), P/PULP-AM-Hyd with 0.60 wt% addition of MBAA(Sample B).

(C)



(D)

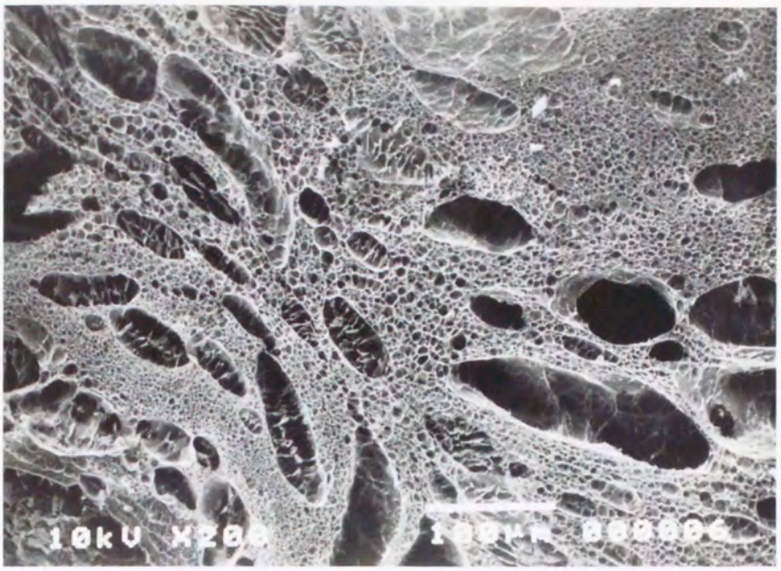
Fig. 6.7 CRYO-SEM photographs of hydrogels of P/PULP-AM-Hyds. Scale bars represent 100 μm.

Samples: (C), P/PULP-AM-Hyd with 0.10 wt% addition of MBAA(Sample D);
(D), P/PULP-AM-Hyd without addition of MBAA(Sample E).

hydrogels of the graft copolymers in sheet forms. Although the crosslinker had not been added at the graft copolymerization,, both hydrogels of FILM-AM-Hyd(Sample F) and NWF-AM-Hyd(Sample G) partly formed honeycomb-like structures. The pore sizes of the honeycomb-like structures of the hydrogels of FILM-AM-Hyd and NWF-AM-Hyd were 2-10 μm 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 the FILM-AM-Hyd swelled more highly than the NWF-AM-Hyd did.

The results of the morphological study of the hydrogels by the observation using a CRYO-SEM are summarized in Table 6.2. Honeycomb-like structures with pores separated by membraneous walls were observed in the hydrogels of the P/PULP-AM-Hyd 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 cellulose graft copolymer changed by freezing-melting operation, and the observed structures were surely formed by the growing of ice crystals in the hydrogel during the freezing process and the aggregation of the polymer [279, 280]. On the other hand, it is well-known that the growing of ice crystals in a gel can be minimized by the freeze-etching of the gel swollen with aqueous solutions of cryoprotectants such as dimethyl

(A)



(B)

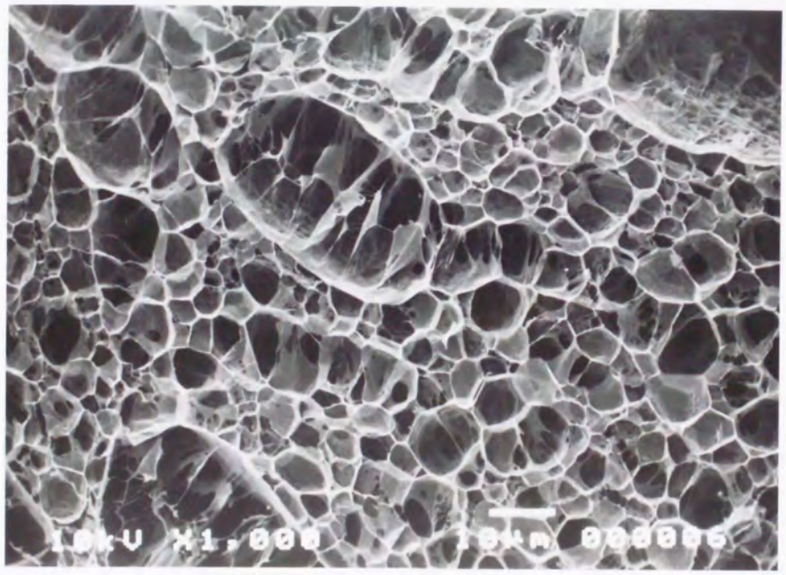
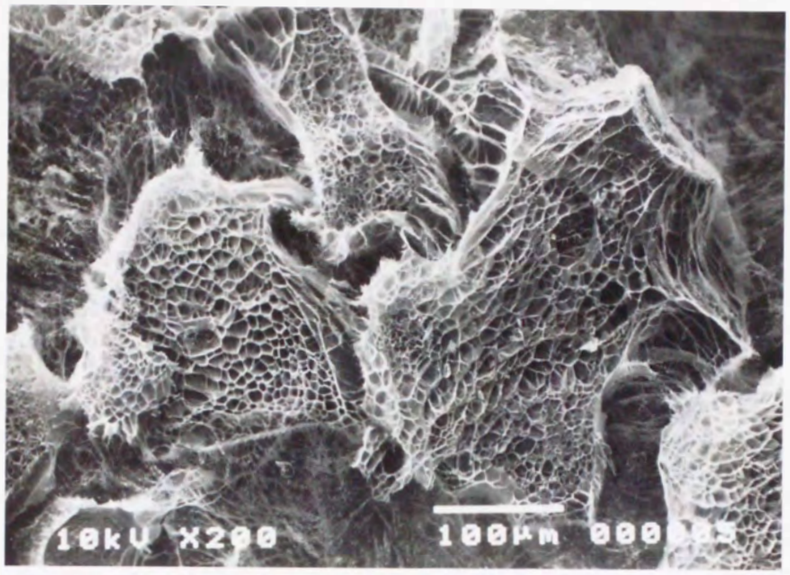


Fig. 6.8 CRYO-SEM photographs of hydrogel of FILM-AM-Hyd(Sample F). Scale bars represent 100 μm in (A) and 10 μm in (B).

(A)



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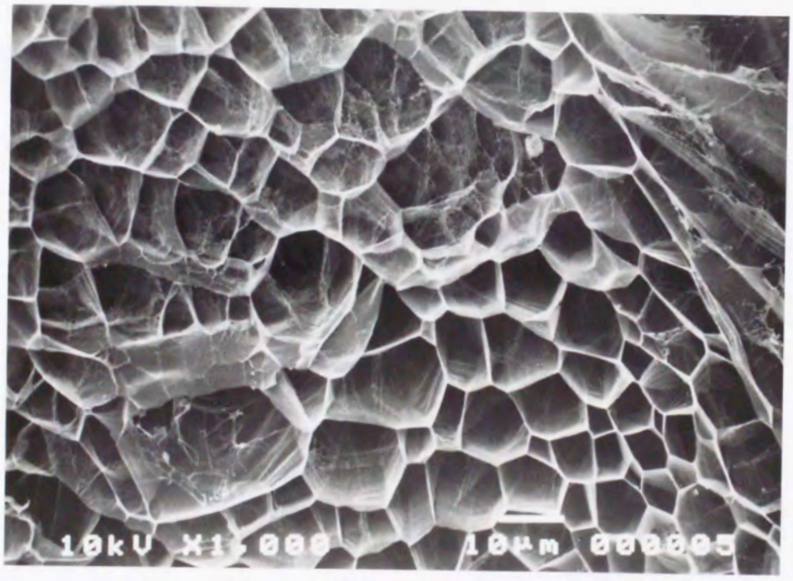

Fig. 6.9 CRYO-SEM photographs of hydrogel of NWF-AM-Hyd(Sample G). Scale bars represent 100 μm in (A) and 10 μm in (B).

Table 6.2 Morphologies of Hydrogels Observed by Use of CRYO-SEM

Figure	Sample	WRV at Observation (g/g)	Structure	Pore Size[A] (μm)
6.1	A	44.8	Sponge-like structure	Uniforem 2-5 μm
6.2	B	1772.8	Honeycomb-like structure	Not uniform 10-100 μm
6.3	J	987.8	Membranous structure	_____
6.4	10 wt% HEC solution	9.0	Film-like structure	_____
6.5	H	19.1	Sponge-like structure	Uniforem 3-8 μm
6.6	I	634.7	Granular structure	_____
6.7(A)	C	756.7	Honeycomb-like structure	Not uniform 5-40 μm
6.7(B)	B	775.4	Honeycomb-like structure	Not uniform 10-60 μm
6.7(C)	D	863.9	Broken honeycomb-like structure	_____
6.7(D)	E	117.8	Laminated structure	_____
6.8	F	151.5	Honeycomb-like structure	Uniforem 2-10 μm
6.9	G	76.8	Honeycomb-like structure	Uniforem 3-15 μm

A) The size of circular or polygonal pores in diameter or diagonally measured.

sulfoxide, glycerol, and sucrose, but this method could not be applicable to the observation using the CRYO-SEM because of the slow sublimation of these cryoprotectants and the occurrence of their residues on the surface of the sample after sublimation [279].

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 honeycomb-like structure, but the latter randomly aggregated and exhibited a granular structure. It is assumed that this result is due to the differences in the expansion of the polymer network in the hydrogel and in the magnitude of affinity of P/PULP-AM-Hyd and PAM-Hyd for water. P/PULP-AM-Hyd synthesized from a water-insoluble cellulose 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 trunk polymer, which also 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 does.

For P/PULP-AM-Hyd, moreover, the cellulose trunk polymer itself restrains the aggregation of the polymer network of the branch polymer. Consequently, it is tentatively considered that the hydrogel of PAM-Hyd randomly aggregated but that of P/PULP-AM-Hyd formed the honeycomb-like structure.

The hydrogels of P/PULP-AM and PAM, which had not been hydrolyzed, formed sponge-like structures with micropores. Since both of 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 aggregate, but formed the sponge-like structures. For the aqueous solution of HEC, in contrast to them, the molecules of HEC were completely soluble in water, and the film-like structure was formed. The holes of this structure would be due to the bubbles that were entrapped in the HEC solution because of its high viscosity.

The hydrogel of COMMERCIAL-1, which was the partially hydrolyzed graft copolymer of crosslinked polyacrylonitrile on starch, did not form a honeycomb-like structure but formed a membranous structure. As described in Chapter 3, the starch trunk polymer that consists of amylose and amylopectin has lower rigidity and less largely extends than the cellulose trunk polymer, and the expansion of the starch graft copolymer depends more largely on the expansion of the

branch polymer and less largely on the extention of the trunk polymer than the cellulose graft copolymer. Therefore, it is considered that the restraint of the polymer network of the branch polymer by the starch trunk polymer is smaller than that by the cellulose trunk polymer, and this is the reason why the starch graft copolymer did not form a honeycomb-like structure but formed the membranous structure.

The honeycomb-like 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 honeycomb-like structure decreased with an increase in the amount of the crosslinker added. As described in Chapter 5, the elasticity of the hydrogel of the cellulose graft copolymer was shown to increase with an increase in the amount of the crosslinker. The decrease in pore size would be attributed to the increase in the elasticity of the hydrogel. The honeycomb-like structure of the hydrogel of the P/PULP-AM-Hyd with 0.10 wt% addition of MBAA had been broken. The honeycomb-like structure of this hydrogel have probably broken during the growing of ice crystals because the polymer network of the P/PULP-AM-Hyd with 0.10 wt% addition of MBAA expanded largely but had a low elasticity. The hydrogel of the P/PULP-AM-Hyd without the addition of the crosslinker did not form a honeycomb-

like structure. Since the P/PULP-AM-Hyd without the addition of 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 crosslinker did not form a honeycomb-like structure, but formed the laminated structure.

Although both of 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 the graft copolymerization, the honeycomb-like 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 honeycomb-like structure of the hydrogel of NWF-AM-Hyd was larger than that of FILM-AM-Hyd. As compared with two types of cellulosic substrates, NWF had higher hydrophilicity and flexibility than FILM did. It is considered that this is one of the reasons why the hydrogel of NWF-AM-Hyd had larger pores than that of FILM-AM-Hyd did.

6.4 Conclusion

The morphologies of the hydrogels were examined by use of a CRYO-SEM. The hydrogel of P/PULP-AM that had been not hydrolyzed formed a sponge-like structure with numerous circular micropores of uniform size. The highly swollen hydrogel of P/PULP-AM-Hyd, on the other hand, formed a honeycomb-like structure with polygonal pores surrounded with membraneous walls. The hydrogel of COMMERCIAL-1, which was the partially hydrolyzed graft copolymer of crosslinked polyacrylonitrile on starch, formed a continuous membranous structure. A 10 wt% aqueous solution of HEC formed a film-like structure. The hydrogel of PAM as well as that of P/PULP-AM formed a sponge-like structure. However, the hydrogel of PAM-Hyd did not form a honeycomb-like structure and randomly aggregated. The morphology of the hydrogel of P/PULP-AM-Hyd was affected by the amount of the crosslinker added at the graft copolymerization. With a decrease in the amount of the crosslinker, the average pore size of the honeycomb-like structure increased. With a further decrease in the amount of the crosslinker, the honeycomb-like structure had been broken and ultimately had not been formed. Although the graft copolymers of FILM-AM-Hyd and NWF-AM-Hyd that had been shaped into the sheets were synthesized without the addtion of the crosslinker, their hydrogels formed honeycomb-like structures.

These structures were surely formed by the growing of ice crystals in the hydrogels during the freezing process. The difference in the structure of the hydrogel is considered to be due to the differences in the chemical composition of the polymer and in the crosslinking density of the polymer network. That is, it is considered that the growing of ice crystals in the hydrogel and the aggregation of the polymer are 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.

General Conclusion

The purpose of this research is to synthesize the super absorbent polymers derived from the cellulose graft copolymers, and to elucidate their swelling mechanisms. The partially hydrolyzed graft copolymers of crosslinked polyacrylamide(PAM) on various types of cellulosics and the graft copolymers of poly(acrylic acid)(PAA) on them were synthesized, and their absorbencies and hygroscopicies were measured in Chapter 1. The effects of the crosslinking density and the amount of the grafted branch polymer on the swelling behavior of the graft copolymer were examined in Chapter 2. In Chapter 3, the effect of the molecular chain length of the cellulose trunk polymer on the swelling behavior was examined. Furthermore, the changes in the porous structures, rheological properties, and morphologies of the hydrogels of the graft copolymers with their voluminal changes were examined. In Chapter 4, the porous structures were examined by using of the solute exclusion technique. In Chapter 5, the viscosities and dynamic viscoelasticities were examined. In Chapter 6, the morphological studies were carried out by the observation using a cryogenic scanning electron microscope(CRYO-SEM) on cryogenic state.

Conclusion

In Chapter 1, the graft copolymerization of acrylamide(AM) and acrylic acid(AA) with a crosslinker(*N,N'*-methylenebisacrylamide, MBAA) onto a bleached kraft pulp from softwood(NBKP), a NBKP being in powdery form(P/PULP), a water-solubilized NBKP modified by slight cyanoethylation (CE/PULP), a cellulosic film(FILM), and a nonwoven fabric from regenerated cellulose(NWF) was carried out by using of the ceric ion initiation method. The graft copolymers of PAM were partially hydrolyzed after the graft copolymerization. These graft copolymers were the super absorbent polymers in fibrous and sheet forms instead of the conventional ones in powdery and granular forms. The partially hydrolyzed graft copolymers of PAM on NBKP, P/PULP, and CE/PULP could absorb much water than the graft copolymers on starches and the commercial super absorbent polymers from starch and synthetic polymers did, and their water retention values(WRVs) reached about 2700-3000 g/g. The absorbency of the cellulose graft copolymer was affected by the degree of grafting and the amount of the crosslinker added at the graft copolymerization, *i.e.*, the amount and crosslinking density of the grafted branch polymer. Under a condition of a fixed amount of the crosslinker or a fixed degree of grafting, the WRVs of the graft copolymers showed the maximum values at about 200% grafting or at 0.30 wt% addition of MBAA. The WRVs of the graft copolymers on FILM

and on NWF increased with an increase in the DG and reached about 150 g/g and 250 g/g, respectively. The graft copolymers on NWF retained the sheet forms during swelling, but that on FILM were broken into gel particles. The graft copolymers on NWF had also high hygroscopicities and absorbed much moisture more rapidly than the original NWF did. The absorbency and hygroscopicity were affected by the species of the grafted branch polymers. The WRV and moisture gain decreased in the order of the amount of carboxyl groups in the graft copolymer.

In Chapter 2, to clarify the effects of the crosslinking density and amount of the branch polymer on the swelling behavior of the cellulose graft copolymer, the absorbencies for aqueous NaCl solutions of the graft copolymers with different crosslinking densities and amounts of the branch polymer were measured. The absorbency of the partially hydrolyzed graft copolymer of PAM on P/PULP(P/PULP-AM-Hyd), which had carboxyl groups in the branch polymer, decreased with an increase in the concentration of NaCl in external solution. This swelling phenomenon of the graft copolymer can be explained by Flory's theory of swelling as well as those of the polymer networks containing ionic groups. However, the swelling behavior of P/PULP-AM-Hyd did not quantitatively follow Flory's theory. The linear relationships between the

absorbencies for aqueous NaCl solutions and the logarithms of the concentrations of NaCl were obtained for the graft copolymers. The absorbency for water decreased with an increase in the crosslinking density of the branch polymer network. However, the P/PULP-AM-Hyd with higher crosslinking density of the branch polymer had higher absorbency for an aqueous NaCl solution and higher resistibility against the decrease in the absorbency with an increase in the concentration of NaCl than that with lower crosslinking density of the branch polymer did. The reason of these results is considered to be due to the higher elasticity of the P/PULP-AM-Hyd with higher crosslinking density of the branch polymer. P/PULP-AM-Hyd had the maximum absorbency for water with an increase in the amount of the branch polymer. With an increase in the amount of the branch polymer, however, the absorbency for an aqueous NaCl solution increased, but the resistibility against the decrease in the absorbency with an increase in the concentration of NaCl decreased. It is considered that the reason of these results is the increase in the amount of carboxyl groups that is depended on the expansion of the network of the graft copolymer and is affected by the neutral salt.

In Chapter 3, to clarify the action of the trunk polymer in the swelling of the graft copolymer, the effect

of the extension of the cellulose trunk polymer on the swelling behavior of the cellulose graft copolymer was discussed. The experiments were carried out by the use of the partially hydrolyzed graft copolymers of PAM on hydroxyethylcelluloses(HEC) with different molecular chain lengths(HEC-AM-Hyds), which were similar to one another in the crosslinking density, amount, and content of carboxyl groups of the grafted branch polymer. The absorbencies for water and aqueous NaCl solutions and the resistibility against the decrease in the absorbency with an increase in the concentration of NaCl increased with an increase in the molecular chain length of the HEC trunk polymer. Furthermore, the HEC graft copolymers had higher absorbencies for water and aqueous NaCl solutions and higher resistibility against the decrease in the absorbency with an increase in the concentration of NaCl than the amylose graft copolymer did. These results suggests that the extension of the trunk polymer affects in the swelling of the graft copolymer. It is known that the molecule of cellulose has higher rigidity and extends more largely in water than those of amylose and amylopectin or vinyl polymers, and that the molecular extension increases with an increase in the molecular chain length. Therefore, it is considered that the trunk polymer with higher rigidity and larger extension acts more effectively in the expansion of the network of the

graft copolymer. The reason of the absorbencies of the cellulose graft copolymers superior to those of the synthesized starch graft copolymers and the commercial absorbent polymers from starch and synthetic polymers would be also due to the higher rigidity and the larger extension of the cellulose trunk polymers.

In Chapter 4, the porous structures of the hydrogels of the cellulose graft copolymers were examined by using of the solute exclusion technique. The hydrogels of the hydrolyzed graft copolymers were extremely porous. The cumulative pore volumes up to 560 Å in pore width of them were went up to about 450-850 mL/g, but the relative cumulative pore volumes up to 560 Å to the total pore volume of them were only about 23-25%. The pores larger than 560 Å comprised over 70% of the total pore volume. On the other hand, the relative cumulative pore volume up to 560 Å of the hydrogel of the graft copolymer that had not been hydrolyzed reached 99%. Most of the total pore volume of the highly swollen hydrogel was occupied by the pores larger than 560 Å, and the relative pore volume in larger size than 560 Å increased with an increase in the total pore volume. To clarify the swelling behavior of the cellulose graft copolymer, the relationships between the changes in the porous structures and the swelling ratios with the change in the swelling condition were also examined. The total pore

volume decreased with an increase in the concentration of NaCl in solution. With a decrease in the total pore volume, the pore volume occupied by the pores larger than 560 Å in pore width steeply decreased with a decrease in the total pore volume, but that by the pores smaller than 560 Å slightly decreased. Therefore, the voluminal shrinkage of the hydrogel would be due to the preferential shrinkage of the pores larger than 560 Å rather than to the overall shrinkage of the pores in all sizes. Moreover, the relative pore volumes in each size up to 560 Å increased, but that in larger size than 560 Å decreased. The larger pore, which has lower crosslinking density than the smaller pore does, would more easily shrink than the smaller pore does. The WRV remarkably varied with pH, and a maximum WRV appeared at about pH 7. The porous structure also changed with a variation of the pH. The pore size distributions in the hydrogels swollen in alkaline solutions were different from those in the hydrogels swollen in acidic solutions but were similar to those in aqueous NaCl solutions. It is considered that the mechanism of the decrease in the absorbency, *i.e.*, the depression of the expansion of the polymer network in an alkaline solution was similar to that in an aqueous NaCl solution but was different from that in an acidic solution.

In Chapter 5, the rheological properties such as

viscosities and dynamic viscoelasticities of the hydrogels and their dispersions of the cellulose graft copolymers were examined. The viscosities of the hydrogels of the graft copolymers were measured by use of a viscometer based on the heat transmission in the hydrogel. The concentration dependences for the hydrogels were differed from those for the solutions of linear polymers. The viscosities of the hydrogels steeply and linearly increased with an increase in the concentration, but each straight line for each hydrogel shows a change in slope at a particular concentration. These transition points coincided with the reciprocals of the WRVs. The dynamic viscoelasticities of the cylindrically moulded hydrogels of the cellulose graft copolymers were measured by use of a compressible oscillating plate/plate rheometer. The concentration dependences of the dynamic viscoelasticity for the hydrogels of the graft copolymers were different from those for the thermoreversible gels of agar and gelatin: The values of E' and E'' for the hydrogels of the graft copolymers nonlinearly increased with an increase in the concentration, although those for the thermoreversible gels linearly increased. The temperature dependences of the dynamic viscoelasticity for the hydrogels of the graft copolymers were different from those for the thermoreversible gels of agar and gelatin: With an increase in the temperature, the values of

E' and *E"* for the thermoreversible gels decreased, but those for the hydrogels of the cellulose graft copolymers scarcely varied or slightly increased. It is considered that these differences in the concentration and temperature dependence of the dynamic viscoelasticity between the hydrogels of the graft copolymers and the thermoreversible gels are due to the differences in the gelating process and in the bonding energy between them. To clarify the swelling behavior of the cellulose graft copolymer, the effect of the swelling condition on the dynamic viscoelasticity for the hydrogel of the cellulose graft copolymer was also examined. In spite of a fixed swelling ratio, *i.e.*, a fixed expansion of the network, the values of *E'* and *E"* for the hydrogel increased with an increase in the concentration of NaCl and also varied with the pH and their minimum values appeared at about pH 7. It is considered that these results were due to a change in the porous structure of the hydrogel.

In Chapter 6, the morphological study of the hydrogels of the cellulose graft copolymers was carried out by the observation using a cryogenic scanning electron microscope(CRYO-SEM) on cryogenic state. The hydrogel of the graft copolymer on P/PULP-AM and the crosslinked PAM that had been not hydrolyzed formed a sponge-like structure with numerous circular micropores of uniform size. On the other hand, the highly swollen hydrogel of P/PULP-AM-Hyd, on

the other hand, formed a honeycomb-like structure with polygonal pores surrounded with membraneous walls. However, the hydrogels of the commercial super absorbent polymer and the partially hydrolyzed crosslinked PAM did not form the honeycomb-like structure: The former formed a continuous membranous structure, and the latter randomly aggregated. The morphology of the hydrogel of P/PULP-AM-Hyd was affected by the amount of the crosslinker added at the graft copolymerization. With a decrease in the amount of the crosslinker, the average pore size of the honeycomb-like structure increased. With a further decrease in the amount of the crosslinker, the honeycomb-like structure had broken and ultimately had not been formed. Although the graft copolymers of FILM-AM-Hyd and NWF-AM-Hyd that had been shaped into the sheets were synthesized without addition of crosslinker, the hydrogels of them formed honeycomb-like structures. These structures were surely formed by the growing of ice crystals in the hydrogels during the freezing process. The difference in the structure of the hydrogel is considered to be due to the differences in the chemical composition of the polymer and in the crosslinking density of the polymer network. That is, it is considered that the growing of ice crystals in the hydrogel and the aggregation of the polymer are affected by the expansion of the polymer network in the hydrogel, the magnitude of the affinity of

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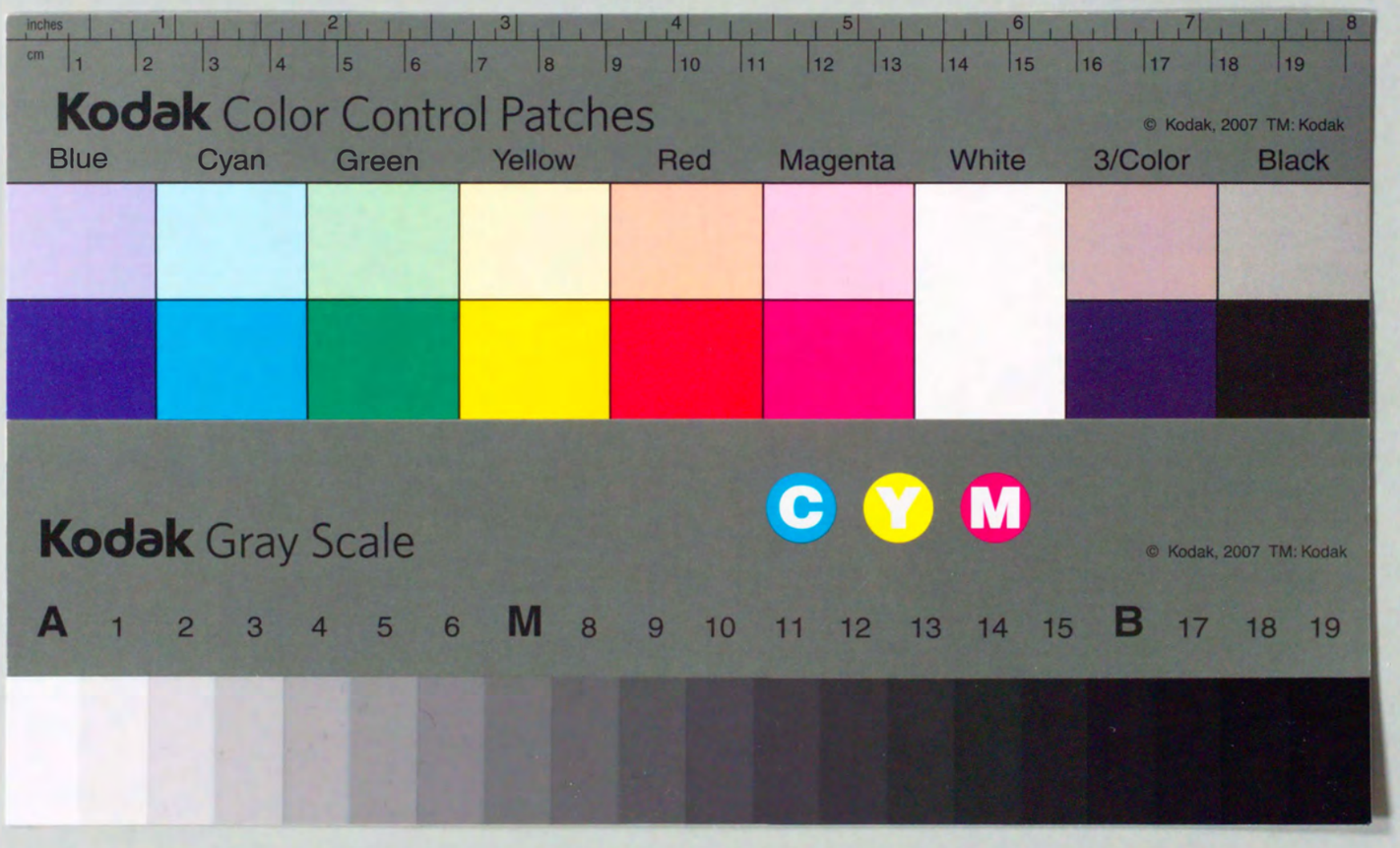
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