

Porous Structure and Rheological Properties of Hydrogels of Highly Water-Absorptive Cellulose Graft Copolymers

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SYNOPSIS

The porous structures of the highly swollen hydrogels of cellulose-acrylamide graft copolymers were studied by the solute exclusion technique. For these hydrogels, the cumulative volume of pores up to 560 Å in pore width was between 450 and 850 mL/g, and was between 20 and 30% of the total pore volume. With an increasing in the amount of crosslinker added in the grafting procedure, the cumulative pore volume up to 560 Å decreased. Furthermore, larger pores shrunk preferentially. In the range of concentration from 0.003 to 0.3%, the viscosity of the hydrogels increased remarkably with an increase in concentration. The concentration dependence of the viscosity showed a transition at about 0.03%, which corresponded to the reciprocal of the water retention values for each copolymer. At concentrations over 3%, fluidity of the hydrogels was lost and the water swollen copolymers became viscoelastic. This dynamic viscoelasticity remained essentially unchanged in the temperature range of 20 to 80°C. The dynamic viscoelasticity was dependent on the concentration, but the concentration dependence was smaller than that of the viscosity. The larger the amount of the crosslinker added, the larger the value of dynamic modulus became.

INTRODUCTION

In our previous article,¹ it was shown that acrylamide graft copolymers onto cellulose such as wood pulps, a nonwoven fabric, and a cellulosic film demonstrated high water-absorbency. Grafted pulps were fibrous or powdered absorbents and the graft copolymers onto nonwoven fabrics and films were sheet form absorbents. The grafted pulps had especially high water-absorbency, with water retention value (WRV) of up to about 3000 g of water per g of dry copolymer. Their WRVs were influenced by the proportion of acrylamide in the graft copolymer and the amount of crosslinker added.

Super water-absorbents are rapidly swollen to hydrogels when contacted with water. The swollen hydrogels can demonstrate fluidity, and, on drying, shrink and may become viscoelastic.

The porous structure of gels from synthetic or natural polymers has been studied by microscopic and rheological methods.²⁻¹⁵ For example, Taylor

and Bagley have studied rheological properties for the hydrogels and dispersions of the starchy absorbents.¹⁶⁻²⁰

Super water-absorbents have been applied increasingly in many fields. It seemed of interest to relate the rheological properties of these hydrogels with their porous structure. Accordingly, in this study, the porous structures of the highly swollen hydrogels of the grafted pulps were studied by the solute exclusion technique, and the rheological properties, such as viscosity or dynamic viscoelasticity, of the hydrogels and their dispersions were also investigated.

EXPERIMENTAL

Preparation of Samples

Preparation of the absorbent (pulp-AM-Hyd) was carried out according to the procedure described previously.¹ Wood pulps for the trunk polymer used in this study were the following: a bleached kraft pulp from softwood (NBKP), a commercial NBKP in a powdered form (P/PULP), and a water-soluble

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Table I Highly Water-Absorptive Cellulose-Acrylamide Graft Copolymers

Sample	Graft Copolymer	MBAA (%)	Degree of Grafting (%)	Degree of Hydrolysis (%)	WRV (g/g)
A	NBKP-AM-Hyd	0.30	140	54.8	1927
B	NBKP-AM-Hyd	0.30	218	63.0	2693
C	CE/NBKP-AM-Hyd	0.30	112	64.1	2818
D	CE/NBKP-AM-Hyd	0.30	150	72.8	2710
E	P/PULP-AM-Hyd	0.10	334	63.2	2635
F	P/PULP-AM-Hyd	0.30	315	65.4	3010
G	P/PULP-AM-Hyd	0.60	294	70.7	1773
H	P/PULP-AM-Hyd	0.90	441	69.6	757

sample (CE/PULP) made by slight cyanoethylation of NBKP. Acrylamide was grafted onto the wood pulps by ceric ion initiation using *N,N'*-methylenebisacrylamide (MBAA) as a crosslinker. Amide groups in the graft copolymer (pulp-AM) were converted to carboxyl groups by alkaline hydrolysis. Water retention value (WRV) of the pulp-AM-Hyd was measured by screening through an 80 mesh sieve and was calculated in grams of solution per gram of absorbent. The degree of grafting, the degree of hydrolysis, and the WRVs of the graft copolymers are shown in Table I.

Solute Exclusion Technique

The porous structures of the hydrogels were examined by the solute exclusion technique, according to the method of Stone et al.²¹⁻²³ The solute molecules used were a series of dextran fractions obtained

Table II Molecular Weights and Hydrodynamic Diameters of the Solute Molecules Used in This Experiment

Solute Molecule	Molecular Weight	Molecular Diameter in Solution (Å)
Glucose	180.16	8 ^a
Maltose	360.31	10 ^a
Raffinose	594.51	12 ^a
Dextran T10	11,200	51 ^b
Dextran T40	39,800	90 ^b
Dextran T70	70,000	118 ^b
Dextran T500	420,000	270 ^b
Dextran T2000	2,000,000	560 ^b

^a The diameter was found by interpolation of the diffusion data given by Longworth.²⁴

^b The diameter was found by interpolation of the diffusion data given by Granath.²⁵

from Pharmacia Ltd., together with a few simple sugars (glucose, maltose, and raffinose) obtained from Wako Pure Chemical Industries, Ltd. Their molecular weights and hydrodynamic diameters are listed in Table II.

The procedure was as follows: a 10 mg sample of the dried graft copolymer was weighed into an Erlenmeyer flask. To this was added about 30 g of water. The mixture was allowed to stand for 60 h in order to swell the graft copolymer completely. Then, about 30 g of a 1% stock solution of a solute molecule was added to the gel dispersion in the flask. The flask was then tightly stoppered and shaken for 60 h. After this time, the gel dispersion was filtered through a glass filter. The concentration of the filtrate was compared with that of the original stock solution of dextran using the Knauer Differential-Refractionmeter (Type 98.00). The amount of water inaccessible to the solute molecule, which corresponded to the cumulative pore volume in the gel, was calculated according to,²¹⁻²³

$$\delta = \frac{w + q}{p} \times \left(1 - \frac{w}{w + q} \times \frac{c_i}{c_f} \right) \quad (1)$$

where δ = Inaccessible water in grams per gram of dry copolymer, p = Dry weight of sample, q = Weight of water in sample, w = Weight of solution of solute molecules, c_i = Initial concentration of solution of solute molecules, and c_f = Final concentration of solution after addition of swollen copolymer.

Viscosity Measurement

Because a slip occurs between the hydrogel particles in the dispersion, and the hydrogel is destroyed locally during measuring, it is difficult to measure the viscosity of the hydrogel and its dispersion correctly

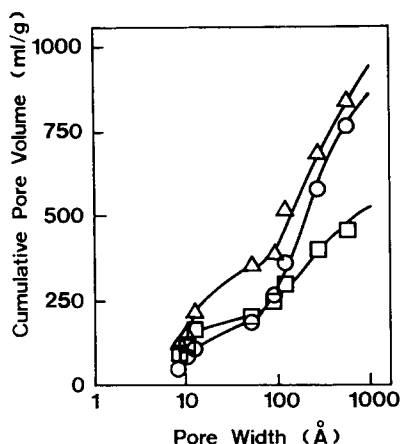


Figure 1 Accessibility curves of hydrogels of pulp-AM-Hyds. Plots: (□) NBKP-AM-Hyd (Sample A), (Δ) CE/PULP-AM-Hyd (Sample C), and (○) P/PULP-AM-Hyd (Sample F).

by the conventional dynamical viscometers. So, a viscometer, Rheo Catch SVM-100 (Snow Brand Milk Products Co., Ltd., Japan), based on the principle of the heat conduction through the hydrogel, was used in this study.²⁶⁻²⁸

The hydrogel and their dispersions were prepared as follows: the graft copolymer was placed in the glass tube, together with 110 mL of deaerated water, to obtain the required concentration of the polymer. This glass tube was put into a thermostated bath controlled at 30°C and the polymer was swollen completely. The viscosities of the hydrogels were measured by the viscometer at different concentrations.

Dynamic Viscoelasticity Measurement

Hydrogels used for the measurement of viscoelasticity were formed into a cylindrical shape. A fixed weight of dry polymer was shaped into a tablet with a mold and a manual press. The tablet was placed in a tube that was greased on its inside surface with silicone grease. Then deaerated water was added to the tube. When the polymer had swollen completely, it was removed from the tube. The radius and height of the hydrogel were both 1 cm.

Measurement of the viscoelasticity of the hydrogel was performed using a compressible oscillating plate/plate rheometer (Rheograph-Gel, Toyoseki Co., Ltd., Japan). The complex elastic modulus, E^* , was obtained from

$$E^* = E' + iE'' \quad (2)$$

in which E' is the real component and E'' is the imaginary component.

RESULTS AND DISCUSSIONS

Porous Structures of Hydrogels

Typical plots of cumulative pore volume vs. pore width are given for hydrogels of the graft copolymers in Figure 1. The hydrolyzed copolymers were very porous. Stone and Scallan^{22,23} found that the total pore volume of water swollen pulps were from 0.8 to 2.0 mL/g. They also found the cumulative pore volume increased proportionally with an increase in average width of the pore and that the maximum pore width varied from 90 to 560 Å. However, as shown in Figure 1, the cumulative pore volumes up to 560 Å for the water swollen graft copolymers were from 400 to 900 mL/g and they increased rapidly at about 100 Å. The volume corresponding to each pore size for the hydrogels was about 100 times those expected for nongrafted pulps. Table I shows that the total pore volume, as measured by the WRV, was considerably larger than the cumulative pore volume up to 560 Å, as measured by solute exclusion. For example, in the hydrogel of NBKP-AM-Hyd, only about 24% of the WRV was occupied by pores up to 560 Å. Thus, pores larger than 560 Å comprised over 70% of the total pore volume. The results in Figure 1 show that the cumulative pore volume, up to 560 Å of CE/PULP-AM-Hyd, was larger than those of other graft copolymers. Furthermore, the pore volume for all pore sizes in CE/PULP-AM-Hyd was larger than those of the others. It is interesting to note that in spite of the greater swelling of CE/PULP-AM-Hyd for pore sizes up to 560 Å, P/PULP-AM-Hyd and CE/PULP-AM-Hyd showed similar WRVs at values greater than 2500 g/g. This behavior may have been due to the more homogeneous distribution of polyacrylamide chains in the water-soluble CE/PULP. Also, the pores formed by the dehydration-aggregation in the recovery process may be larger for the graft copolymer from the water-soluble CE/PULP.

Figure 2 shows the accessibility curves of P/PULP-AM-Hyds prepared with different amounts of MBAA as a crosslinker. The WRVs of the copolymers differed considerably (Table I) and, therefore, for the comparison in Figure 2, the cumulative pore volume is expressed as a percentage of the WRV (relative cumulative pore volume). The relative cumulative pore volumes up to 560 Å for P/PULP-AM-Hyds, prepared with 0.10% or 0.30%

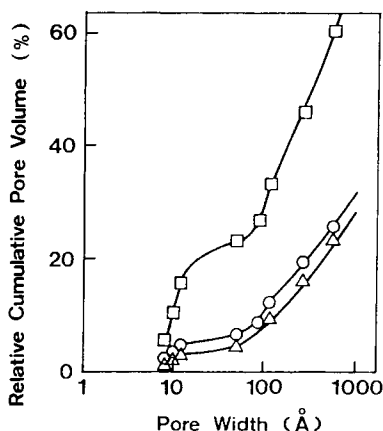


Figure 2 Effect of the percent addition of crosslinker on the porous structure of P/PULP-AM-Hyds. Plots: (Δ) 0.1% addition of MBAA onto P/PULP-AM-Hyd (Sample E), (\circ) 0.3% addition (Sample F), and (\square) 0.9% addition (Sample H).

MBAA, were less than 30%, while a 0.90% addition of MBAA gave a relative cumulative pore volume of up to 560 Å of 60%. Thus, the increased addition of crosslinker not only increased the total pore volume, but increased the percentages of pore volume in pores up to 560 Å in width. From the investigation by Takahashi et al.,²⁹ the amount of the crosslinker effective in creating branches was less than the amount of the crosslinker simply added onto the chain in the grafting procedure. Addition of MBAA to the chain without branching would increase the charge density and thus the volume of pores formed by dehydration-aggregation in the recovery process. The results in Figure 2 suggest that with a 0.90% addition of crosslinker, the chain addition is the predominant reaction of MBAA.

The effect of the degree of swelling on the porous structure was studied by experiments with one pulp copolymer in three different conditions. Sample P/PULP-AM was swollen in water. The graft copolymer was then hydrolyzed (P/PULP-AM-Hyd) and

was swollen in both water and 0.1% aqueous sodium chloride. In order to examine whether the hydrodynamic molecular diameter of the solute molecule differs in pure water from the diameter in the aqueous NaCl solution, we measured the viscosities of Dextran T2000 both in water and in the NaCl solution. The intrinsic viscosity values in the NaCl solution was almost same it was in water. Thus, it can be assumed that the diameter of the solute molecule in the NaCl solution was equal to the diameter in water. The results obtained are given in Table III and Figure 3. Hydrolysis greatly increased the swelling, as shown by the increase in WRV in Table III. However, in 0.1% NaCl solution, P/PULP-AM-Hyd did not swell as much as in pure water because of the decreased electrostatic repulsion of the chains at higher ionic strength. As shown in Table III, the relative cumulative pore volume up to 560 Å decreased with an increase in swelling. For swollen P/PULP-AM, the cumulative pore volumes below each size were from approximately 44 to 99%, and these values were larger than those for swollen P/PULP-AM-Hyd. This result explains that a large part of the pores in the original copolymer swollen in water was smaller than 560 Å, but the pores in the hydrolyzed copolymer, swollen in water, were largely over 560 Å. On the other hand, with determining the effect of the electrolyte in solution on the porous structure, the cumulative pore volumes in each size of the swollen copolymer in aqueous sodium chloride were larger than those in pure water. The pores up to 120 Å increased gradually, those over 120 Å increased rapidly. This result probably indicates that large pores over 560 Å shrink preferentially instead of the overall shrinkage of pores in each size. That is, larger pores seem to shrink more easily. This behavior is expected. The porous structure of the swollen copolymer must change with the changing of the swelling ratio, that is, the total pore volume. The volume of super water-absorbents changes greatly depending on swelling condition, for exam-

Table III Cumulative Pore Volumes to 560 Å in Pore Width of P/PULP-AM and P/PULP-AM-Hyd

Graft Copolymer	Swelling Liquid	WRV (g/g)	CPV ₅₆₀ ^a (mL/g)	RCPV ₅₆₀ ^b (%)
P/PULP-AM	Water	45	44.4	99.0
P/PULP-AM-Hyd	NaCl ^c	338	289.0	85.5
P/PULP-AM-Hyd	Water	1773	408.5	23.0

^a Cumulative pore volume up to 560 Å in pore width.

^b Relative cumulative pore volume up to 560 Å in pore width.

^c 0.1% aqueous sodium chloride.

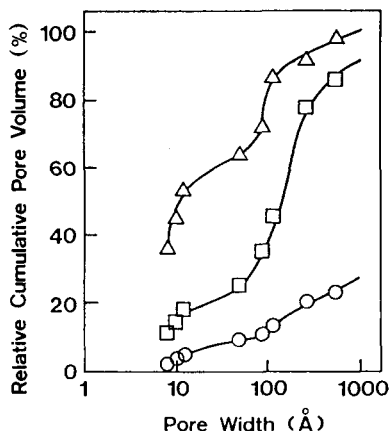


Figure 3 Effect of the swelling ratio on the porous structure of P/PULP-AM and P/PULP-AM-Hyd. Graft copolymer is "Sample G." Plots: (Δ) P/PULP-AM swollen in water, (\square) P/PULP-AM-Hyd swollen in 0.1% aqueous sodium chloride, and (\circ) P/PULP-AM-Hyd swollen in water.

ple, conditions such as the existence of the electrolyte in solution and the kind of solvent. The changes of the pore size and volume in the hydrogel are based on the voluminal change on the copolymer. The more highly swollen the sample, the smaller the proportion of pore volume occupied by smaller pores. More difficult to explain are the reflection points at a pore width of about 100 Å for all three curves in Figure 3. If swelling produced the same proportional increase at all pore widths, the reflection points would move to higher pore widths with greater swelling. This suggests that the distribution of pore sizes up to 560 Å did not change, even though the swelling of the hydrogel increases. Another possibility is that the reflection points in Figure 3 are artifacts produced by slight errors in the molecular diameters ascribed to the probes in Table II.

Viscosity of Hydrogel

The viscosity of the hydrogels and their dispersions are shown in Figure 4. As the concentration of the graft copolymers in the dispersions increased, the viscosity increased significantly. Each line in Figure 4 shows a change of slope at a particular concentration designated by arrows. These transition points coincide with the concentration corresponding to equilibrium swelling, that is, the reciprocal of the WRV. In Table IV, the slopes of the lines below and after their transitions are given. CE/PULP, which was water-soluble, was swollen in the hydrogel as well as the crosslinked branch polymers, so CE/

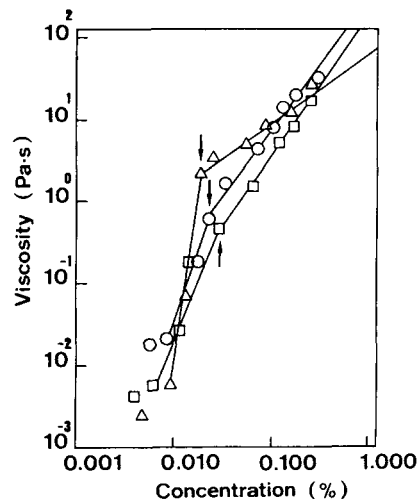


Figure 4 Concentration dependence of viscosity for hydrogels of pulp-AM-Hyds at 28°C. Plots: (\square) NBKP-AM-Hyd (Sample B), (Δ) CE/PULP-AM-Hyd (Sample C), and (\circ) P/PULP-AM-Hyd (Sample F).

PULP-AM-Hyd depended on the polymer concentration the most. The concentration dependence for the fibrous absorbents, NBKP-AM-Hyd, was larger than that for the powdered absorbents, P/PULP-AM-Hyd and CE/PULP-AM-Hyd. The adsorbent that used a insoluble cellulosic was more influenced by the concentration of the absorbent than the absorbent used a water-soluble cellulosic. The reason for this result may be that the insoluble cellulosic serves as a wick when the graft copolymer is swollen. Thus, the kind of the cellulosics used as the trunk polymer in the graft copolymers influenced the concentration dependence of the viscosity of the hydrogel dispersions.

Dynamic Viscoelasticity of Hydrogels

According to the studies by Nishinari et al.,^{9,10} the temperature dependence of the elastic modulus for

Table IV Viscosity Function for Hydrogels of Pulp-AM-Hyds

Graft Copolymer	Slope of Viscosity vs. Concentration	
	Hydrogel Dispersion	Swollen Hydrogel
NBKP-AM-Hyd	2.3	1.6
CE/PULP-AM-Hyd	6.7	0.7
P/PULP-AM-Hyd	2.8	1.4

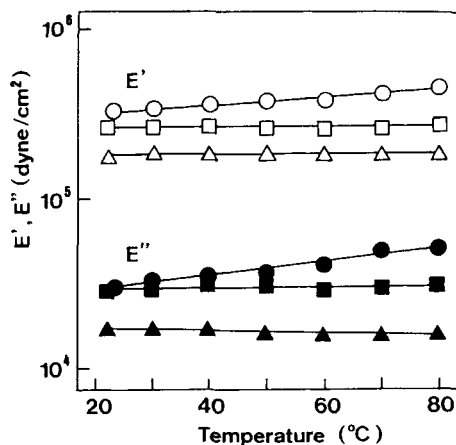


Figure 5 Temperature dependence of dynamic viscoelasticity for 6% hydrogels of pulp-AM-Hyds. Plots: (□) E' and (■) E'' for NBKP-AM-Hyd (Sample B), (△) E' and (▲) E'' for CE/PULP-AM-Hyd (Sample D), and (○) E' and (●) E'' for P/PULP-AM-Hyd (Sample F).

thermoreversible gels that are composed of cross-linking junction zones, connected with long flexible chains, seems to be governed mainly by the bonding energy required for a segment to be liberated from the junction zones and by the length of the flexible chains connecting these junction zones. For example, the elastic modulus increases with increasing temperature and then begins to decrease for some thermoreversible gels, such as agarose gels¹¹ or poly(vinyl alcohol) gels,¹² whose bonding energies of the crosslinking junction are moderate. In contrast, the elastic modulus decreases monotonically with increasing temperature for other gels, such as gelatin gels¹³ or carrageenan gels,¹⁴ whose bonding energies are small. As shown in Figure 5, the temperature dependencies of the dynamic viscoelasticity for the hydrogels of the grafted cellulose were different from those of the thermoreversible gels. For the hydrogels of CE/PULP-AM-Hyd and NBKP-AM-Hyd, the values of E' and E'' varied little with an increase in temperature. On the other hand, the values of E' and E'' of the hydrogel of P/PULP-AM-Hyd increased slightly with elevation of temperature. This temperature dependency was similar to that of polymer materials, which possess rubber-like elasticity.

The concentration dependencies of the dynamic viscoelasticity of hydrogels are shown in Figure 6. As did the viscosity (see Figure 4), the values of E' and E'' for the hydrogels increased with an increase in the concentration. As already described in Figure 3, the volume occupied by large pores in a hydrogel decreases with the shrinking of the hydrogel, that

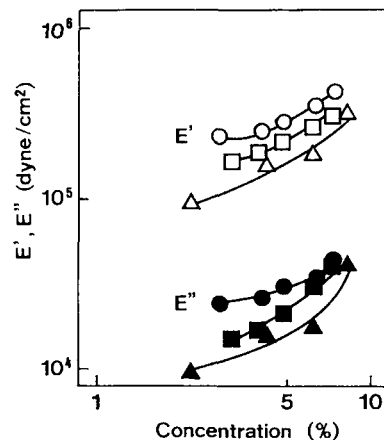


Figure 6 Concentration dependence of dynamic viscoelasticity for hydrogels of pulp-AM-Hyds at 30°C. Plots: (□) E' and (■) E'' for NBKP-AM-Hyd (Sample B), (△) E' and (▲) E'' for CE/PULP-AM-Hyd (Sample D), and (○) E' and (●) E'' for P/PULP-AM-Hyd (Sample F).

is, with a decrease in swelling ratio. For hydrogels at a constant volume, an increase in the concentration of graft copolymer corresponds to a decrease in the swelling ratio. Therefore, it is thought that the dynamic viscoelasticity for the hydrogel increased with shrinking of the hydrogel. However, the relationship between the dynamic viscoelasticity and the concentration was not linear and the concentration dependency of the dynamic viscoelasticity was smaller than that of viscosity. In the range of the concentration measured, the dynamic viscoelasticity, the hydrogels were swelling just a little less than a hundredth of the WRVs, and water was preferentially penetrating into smaller pores rather than

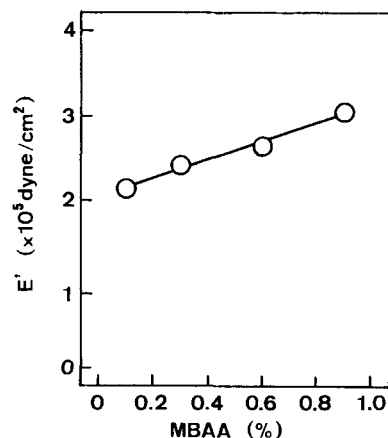


Figure 7 Effect of the percent addition of crosslinker on the value of E' for 4% hydrogels of P/PULP-AM-Hyds at 30°C.

larger ones. Thus, the hydrogels seem to be composed of very small pores and seem to be shrinking by degrees. Consequently, the values of E' and E'' for hydrogels increased gradually with increases in the concentration of graft copolymers.

The effect of the crosslinker on the dynamic viscoelasticity for hydrogels is shown in Figure 7. The values of E' increased with an increase in the percent addition of MBAA. We see in Figure 2 that the volume occupied by large pores in the hydrogels decreased and the volume occupied by small pores increased with an increase in the percent addition of MBAA. The dynamic viscoelasticity of hydrogels seems to increase with an increase in the percent addition of MBAA. Owing to the result described in Figure 2, however, the observed value of E' for P/PULP-AM-Hyd prepared with 0.9% addition of MBAA seems to be smaller than the value of E' expected. This situation is probably caused by the lower absorbency of this graft copolymer as compared with that of P/PULP-AM-Hyds with added 0.1% or 0.3% MBAA, that is, it is caused by the decrease of the WRV with an increase in the percent addition of MBAA. Further study on the porous structure and the rheological property for the super water-absorbents from cellulose will be discussed elsewhere.

CONCLUSION

The porous structures of the swollen hydrogels of hydrolyzed cellulose-acrylamide graft copolymers were studied by the solute exclusion technique. The cumulative pore volumes, up to 560 Å in pore width, were from 450 to 850 mL/g; this was from about 20 to 30% of the total pore volumes as measured by the water retention value. These results indicated that the absorbents were very porous and that a major part of the absorbed water existed in pores larger than 560 Å. The cumulative pore volume, up to 560 Å for the graft copolymer from a water-soluble CE/PULP, was larger than those of the grafted NBKP and the grafted P/PULP. With an increase in the amount of the crosslinker added in the grafting procedure, the cumulative pore volume up to 560 Å decreased. And the larger pores preferentially shrunk with the shrinking of the hydrogel, that is, with decrease of the amount of the absorbed water.

With an increase in the concentration of the graft copolymers in the range of concentration from 0.003 to 0.3%, the viscosity of the hydrogels and their dispersions increased rapidly. The concentration dependence of viscosity changed at concentrations of

about 0.03%, which corresponded to the reciprocals of the water retention values for each graft copolymer. Before changing, the slope of the viscosity function for the grafted CE/PULP was larger than those for the other grafted pulps. After changing, however, the magnitudes of these slopes decreased in the order NBKP-AM-Hyd > P/PULP-AM-Hyd > CE/PULP-AM-Hyd.

When the concentrations of the graft copolymers increased over 3%, the fluidity of the hydrogels was lost and they became viscoelastic. The dynamic viscoelasticity of the hydrogels depended on the concentration, but these concentration dependencies were smaller than those for viscosity. The dynamic viscoelasticity scarcely changed in the temperature range of 20 to 80°C. These temperature dependencies are different from those of the thermoreversible gels. The larger the amount of crosslinker added, the larger the viscoelasticity became.

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