

Properties of Highly Water-Absorptive Hydroxyethylcellulose Graft Copolymers: Viscoelasticity and Moisture Sorption

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SYNOPSIS

The viscoelasticity of the hydrogels, the moisture sorption, and the characteristics of the sorbed water of highly water-absorptive hydroxyethylcellulose (HEC) graft copolymers [e.g., HEC graft copolymers containing partially hydrolyzed polyacrylamide (HEC-P-Hyd-PAM), etc.] were investigated in comparison with commercial absorbents. The viscosity (η) and the rigidity (G) of the dispersions of their hydrogels were, respectively, proportional to the second to the sixth powers and the fifth to the seventh powers of their concentrations ($\eta = KC^{2-6}$ and $G = K'C^{5-7}$). With respect to the characteristics of the sorbed water, the conductivity of 0.1 N KCl in the hydrogels of the HEC water absorbents was about 11.8 mS/cm, which was almost the same as that of 0.1 N KCl in pure water, and the water absorbency of dry matter (soybean seeds) in their hydrogels was almost the same as that in pure water. These results suggest that most of the sorbed water in the HEC super water absorbents behaves like free water. The maximum volume of sorbed moisture in a monolayer fashion (V_m) of HEC-P-Hyd-PAM analyzed using the Brunauer–Emmett–Teller equation was about 0.21 g/g (1.2 mol water/polymer repeat unit), and there was no cluster water at 92% relative humidity or below as a result of applying the cluster function concept. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, there has been a great demand for super water absorbents as sanitary materials and as agricultural and gardening agents. Therefore, an understanding of the fundamental properties of super water absorbents is of great value for their practical application.

In previous articles,¹⁻³ we reported the synthesis and some properties of the graft copolymers of highly water-absorbent hydroxycellulose (HEC), other polysaccharides (e.g., mannan, alginic acid, agar, pectin, starch, etc.), and lignosulfonate samples as super water absorbents. In addition it was found that HEC-P-Hyd-PAM could absorb large amounts of water, namely 3000 g water/g absorbent.

There have also been studies⁴ about the rheological properties such as viscoelasticity and rigidity of the hydrogels of super water absorbents of hydrolyzed starch-polyacrylonitrile graft copolymers. However, there are few reports concerning these same properties and the moisture sorption of cellulosic super water absorbents except for the study of highly water-absorptive cellulose graft copolymers by Yoshinobu and coworkers.⁵

The purpose of this study was to investigate the fundamental properties of the HEC super water absorbents such as the viscoelasticity of the hydrogels, the state of sorbed water in the super water absorbents, and moisture sorption compared with those of some commercial super water absorbents. The investigated HEC super water absorbents were HEC graft copolymers containing partially hydrolyzed polyacrylamide (HEC-P-Hyd-PAM), partially hydrolyzed polymethacrylate (HEC-P-Hyd-PMA), sodium polyacrylate (HEC-PAANa), and polydimethylaminopropyl acrylamide (HEC-PDMAP).

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EXPERIMENTAL

Materials

Reagent grade dimethylaminopropyl acrylamide and HEC were obtained from Kojin Co., Ltd. and Tokyo Chemical Industry Co., Ltd., Japan, respectively. The former was purified by a conventional method. Commercial super water absorbents; Sanwet-IM 1000 [starch cross-linked sodium polyacrylate (St-PAA-Coml. Abs.)]; GP-03 [polyvinyl alcohol maleic acid ester (PVA-Coml. Abs.)]; aqualic CA [cross-linked sodium polyacrylate (PAA-Coml. Abs.)]; and cross-linked carboxymethyl cellulose (CMC-Coml. Abs.) were obtained from Sanyo Chemical Industries, Ltd., the Nippon Synthetic Chemical Industry Co., Ltd., Nippon Catalytic Chemical Industry Co., Ltd., and Daicel Chemical Industries, Ltd., Japan, respectively, and used without further purification. HEC-P-Hyd-PAM, HEC-P-Hyd-PMA, HEC-PAANa, and HEC-PDMAP as super water absorbents were synthesized as described in previous articles.¹⁻³

The synthesized HEC super water absorbents are shown in Table I.

Measurement of Viscoelasticity and Viscosity

The viscoelasticity and the viscosity of the hydrogels and their dispersions of the HEC super water absorbents were measured using a rotating cylinder rheometer with free damped oscillation (Torsion Pendulum rheometer, Rhesca Co., Tokyo Ltd., Japan) and a rotating viscometer (Tokyo Keiki Co., Ltd., Japan) at various temperatures, respectively. The super water absorbent was slowly added to pure water that was being constantly stirred, which was continued until the solution became a hydrogel or a dispersion.

Determination of Sorbed Water Properties

The conductivity of 0.1 N KCl in the hydrogels of the HEC water absorbents was measured with a conductivity meter (Toa Dempa Co., Ltd., Japan) at 20°C.

The degree of swelling (water absorbency) of dry materials (soybean seeds) in both water and the hydrogels of the water absorbents was determined as follows. Ten dry soybean seeds were added to water or their hydrogels, and after they were allowed to stand for 24 h at 65% relative humidity (RH) and 20°C, the swollen soybean seeds were taken out of the water or hydrogels. They were then weighed, and the degree of swelling was calculated as grams of water per gram of dry soybean seed (g/g).

Moisture Sorption

The measurement of water vapor sorption isotherms was carried out at 20°C. The water absorbents were completely dried over P₂O₅ in a vacuum dryer at 40°C for a week, and then a weighing bottle containing about 500–800 mg of the dry samples was kept in a desiccator in order to maintain a certain RH adjusted by using an aqueous solution of sulfuric acid at a given concentration. Usually it took more than 2 months of water sorption equilibrium to be attained.

RESULTS AND DISCUSSION

Viscoelasticity, Viscosity, and Rigidity

Figures 1 and 2 show the apparent viscosity curves of the dispersions of the swollen hydrogels of the HEC super water absorbents, commercial water absorbents, and an aqueous HEC solution. The ap-

Table I Highly Water-Absorptive HEC Graft Copolymers

Sample	Cross-linking Agent Conc. (%)	Degree of Grafting (%)	Degree of Hydrolysis (%)	Water Absorbency (g/g)
HEC-P-Hyd-PAM 1	0.3	162.0	62.0	1249.0
HEC-P-Hyd-PAM 2	0.3	315.0	58.1	2200.0
HEC-P-Hyd-PAM 3	0.3	397.0	59.5	1786.0
HEC-P-Hyd-PAM 4	0.1	464.3	55.7	755.3
HEC-P-Hyd-PAM 5	1.5	590.0	58.4	1026.7
HEC-P-Hyd-PAM 6	0.3	1816.7	59.2	616.0
HEC-P-Hyd-PMA	—	—	—	1884.0
HEC-PAANa	0.3	—	—	1000.0
HEC-PDMAP	0.3	5.2	—	85.0

parent viscosity curves of the hydrogel dispersions of the HEC super water absorbents and commercial products showed thixotropy and gave a non-Newtonian viscosity, that is to say, the apparent viscosity decreased as the shear rate increased. However, as shown in Figure 1, with an increase in temperature and with a decrease in their concentration, those of HEC-P-Hyd-PAM approached a Newtonian viscosity analogous to the apparent viscosity curves of linear polymer solutions. Also, Figure 1 shows that the apparent viscosity of the hydrogel dispersions of HEC-P-Hyd-PAM decreased as the temperature increased, which is similar to the typical temperature dependences of the linear polymer solutions. The apparent activation energy (E) of this viscosity of the hydrogels of HEC-P-Hyd-PAM was about 19.6 kJ/mol using from the following equation:⁶

$$\eta = B \exp(E/RT) \quad (1)$$

where B is a constant, R is the gas constant, T is the absolute temperature, and that value ($E = 19.6$ kJ/mol) is similar to that of the polymer melt.

Figure 2 shows that the order of viscosity was HEC-P-Hyd-PAM > St-PAA-Coml. Abs. > PVA-Coml. Abs. > HEC-P-Hyd-PMA > HEC. Moreover, the water absorbency and the viscosity of the dispersions of the hydrogel of HEC-P-Hyd-PAM were

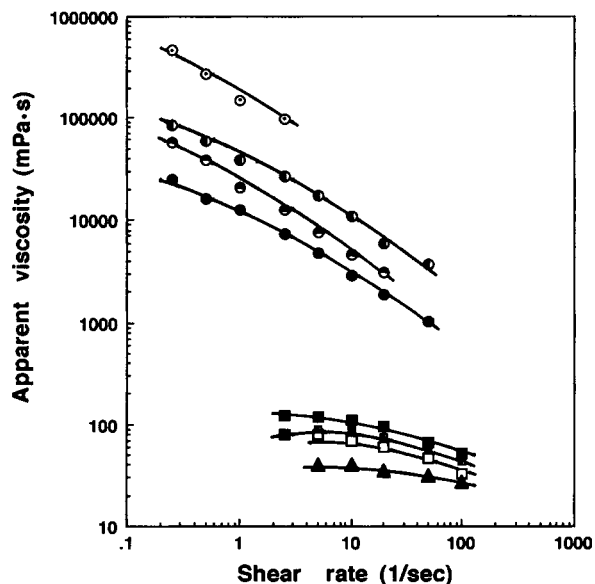


Figure 1 Apparent viscosity curves of the dispersions of the hydrogels of HEC-P-Hyd-PAM 5. Temperature: (■) 10°C; (●, ○, ⊙, ⊞) 20°C; (□) 35°C; (▲) 50°C. Concentration: (■, ⊞, □, ▲) 0.03%; (●) 0.047%; (○) 0.06%; (⊙) 0.1%; (⊞) 0.3%.

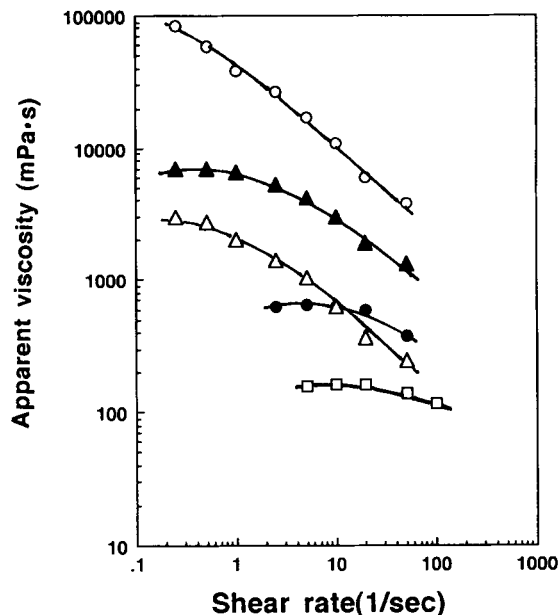


Figure 2 Apparent viscosity curves of the dispersions of the hydrogels of some super water absorbents and an aqueous HEC solution at 20°C. Concentration: (○) HEC-P-Hyd-PAM 5 (0.1%); (●) HEC-P-Hyd-PMA (0.1%); (▲) St-PAA-Coml. Abs. (0.1%); (△) PVA-Coml. Abs. (0.1%); (□) HEC (1.0%).

larger than those of St-PAA-Coml. Abs. and PVA-Coml. Abs. These results suggest that the molecular weight of HEC-P-Hyd-PAM is larger than that of the commercial materials. This is one of the reasons why HEC-P-Hyd-PAM is able to absorb a larger amount of water than commercial absorbents.

As shown in Figure 3, the zero shear viscosity of the dispersions of the hydrogels of the HEC water absorbents, commercial products, and an aqueous HEC solution increased as the concentrations increased, and the viscosity of these hydrogels of the HEC water absorbents (HEC-P-Hyd-PAM and HEC-PAANa) was proportional to the sixth to seventh powers of the concentration ($\eta_0 = KC^{6-7}$) until a fixed concentration was reached.

In general, the zero shear viscosity of very highly concentrated solutions of linear polymers and polymer melts are proportional to the fifth or the sixth powers of the concentration.⁷ Therefore, the concentration dependence of the zero shear viscosity of the dispersions of the hydrogels of the HEC super water absorbents was similar or slightly larger than that of highly concentrated solutions of linear polymers and polymer melts.

The zero shear viscosity of the dispersions of the hydrogels of the commercial water absorbents (St-PAA-Coml. Abs. and PVA-Coml. Abs.) was propor-

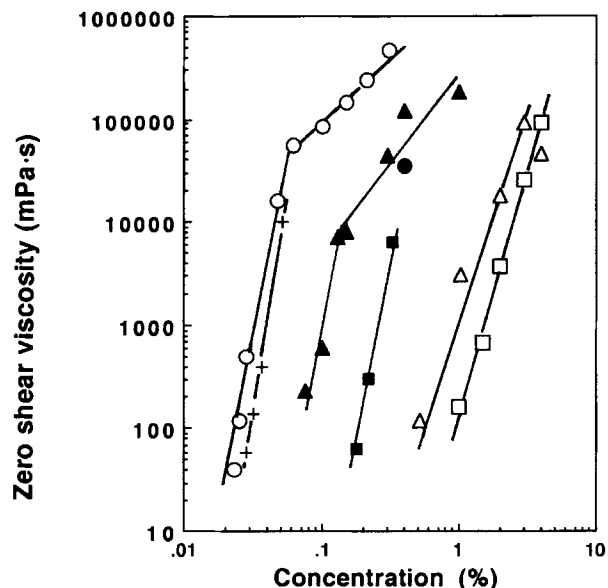


Figure 3 Zero shear viscosity of the dispersions of the hydrogels of the HEC water absorbents, commercial absorbents, and an aqueous HEC solution at 20°C. (■) HEC-PAANa; (+) HEC-P-Hyd-PAM 6. The other symbols are the same as shown in Figure 2.

tional to the sixth and the fourth powers of the concentration, respectively ($\eta_0 = KC^6$ and $\eta_0 = KC^4$). Their exponent values are similar to those of highly concentrated linear polymer solutions and polymer melts.

However, Figure 3 shows that the zero shear viscosity of the dispersions of the hydrogels of HEC-P-Hyd-PAM and commercial absorbents (St-PAA-Coml. Abs.) was proportional to their concentration ($\eta_0 = KC$) at concentrations greater than 0.05 and 0.2%, respectively. The reciprocal of the concentration of each deflection point showed each water absorbency of the water absorbents, that is to say, the former is about 2000 g/g and the latter is about 500 g/g.

Figure 4 shows that the dynamic viscosity of the dispersions of the hydrogels of the HEC super water absorbents and a commercial absorbent (PVA-Coml. Abs.) was proportional to the sixth power of the concentration ($\eta = KC^6$), and that of commercial absorbents (St-PAA-Coml. Abs. and CMC-Coml. Abs.) and an aqueous HEC solution was proportional to the second power of the concentration ($\eta = KC^2$). However, that of HEC-P-Hyd-PAM and St-PAA-Coml. Abs. gave deflection points of which the reciprocal of the concentration approximately shows the water absorbency, which was analogous to the case of the zero shear viscosity.

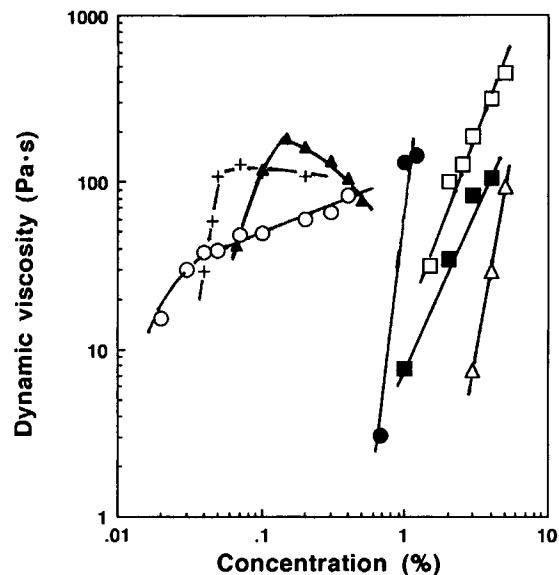


Figure 4 Dynamic viscosity of the dispersions of the hydrogels of the HEC super water absorbents and commercial ones and an aqueous HEC solution at 40°C. (+) HEC-P-Hyd-PAM 1; (○) HEC-P-Hyd-PAM 2; (●) HEC-P-Hyd-PMA; (■) CMC-Coml. Abs.; (▲) St-PAA-Coml. Abs.; (△) PVA-Coml. Abs.; (□) HEC.

Figure 5 shows that the dynamic rigidity of the dispersions of the hydrogels of the HEC super water absorbents and commercial absorbents and an aqueous HEC solution increased with an increase

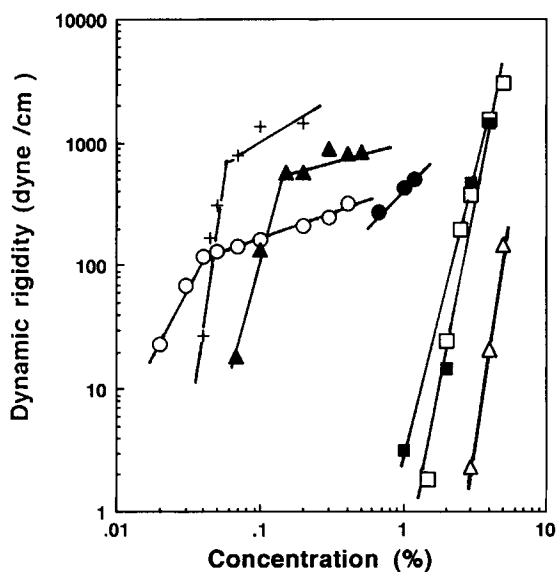


Figure 5 Dynamic rigidity of the dispersions of the hydrogels of the HEC super water absorbents and commercial ones and an aqueous HEC solution at 40°C. The symbols are the same as shown in Figure 4.

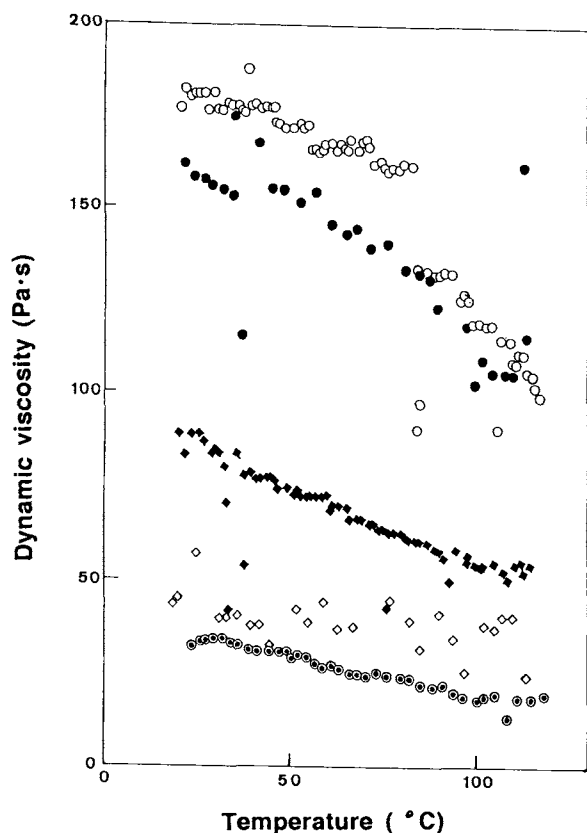


Figure 6 Relationship between the dynamic viscosity of the hydrogels of PVA-Coml. Abs. and temperature. Concentration: (●) 1%; (◇) 2%; (◆) 3%; (○) 4%; (●) 5%.

in the concentration, and their dynamic rigidity was proportional to the fifth to the seventh powers of the concentration ($G = K'C^{5-7}$) except for HEC-P-Hyd-PAM 1 ($\eta = K'C^2$). In general, dynamic rigidity of the natural polymer gels is proportional to the second or fourth powers of the concentration in the case of high or low solute concentrations, respectively. Therefore, the dynamic rigidity of almost all HEC and commercial water absorbents was larger than that of the natural polymer gels. Also, the dynamic rigidity of HEC-P-Hyd-PAM and St-PAA-Coml. Abs. gave deflection points and was proportional to 0.5 ($G = K'C^{0.5}$) at concentrations more than the deflection points as well as the case of the dynamic viscosity. The reciprocal of the concentration of each deflection point shows approximate water absorbency as well as the case of the zero shear and dynamic viscosities previously mentioned. This is due to a change in the structure of the water absorbent (HEC-P-Hyd-PAM or St-PAA-Coml. Abs.) systems at the deflection points.

Figures 6 and 7 show that the dynamic viscosity

and rigidity of the hydrogels of PVA-Coml. Abs. decreased with an increase in temperature as well as those of an aqueous linear polymer solution and polymer melts. The apparent activation energy of the hydrogels of PVA-Coml. Abs. was calculated using eq. (1), and its values were about 9.0 kJ/mol and 5.9 kJ/mol at 1 and 3% concentration, respectively.

The rheological behaviors of the dispersions of the hydrogels of the super water absorbents like HEC-P-Hyd-PAM seem to relatively resemble those of highly concentrated polymer solutions and polymer melts.

Moisture Sorption and State of Sorbed Water

In Figure 8, the moisture sorption isotherms of the HEC super water absorbents (HEC-P-Hyd-PAM and HEC-PDMAP), PAA-Coml. Abs., and HEC showed almost a sigmoid shape as well as most hydrophilic polymers. HEC-P-Hyd-PAM sorbed a large quantity of moisture [for example, 1.3 g/g (7.2 mol/polymer repeat unit) at 92.3% RH] in comparison with other HEC water absorbents and commercial ones, and its moisture regain was close to that of ionic water soluble polymers [for example, sodium polyacrylate, 1.7 g/g (8.7 mol/polymer repeat unit), polyvinyl amine, 0.8 g/g (1.9 mol/polymer repeat unit)].⁷

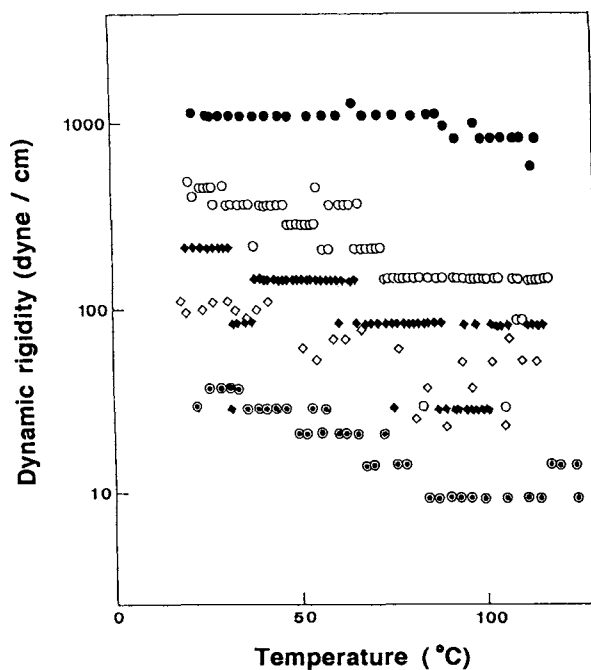


Figure 7 Relationship between the dynamic rigidity of the hydrogels of PVA-Coml. Abs. and temperature. The symbols are the same as shown in Figure 6.

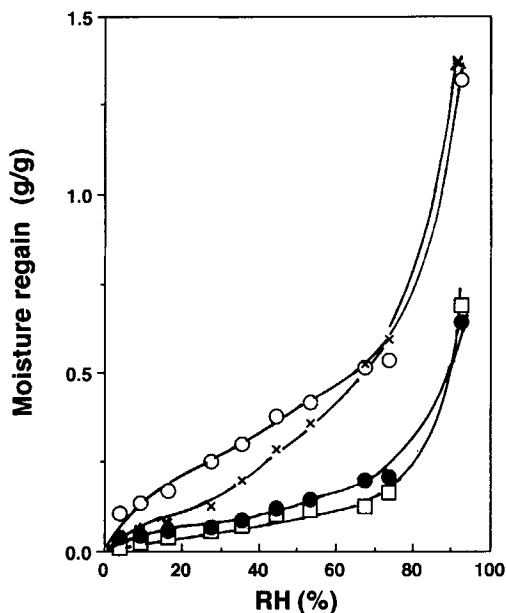


Figure 8 The moisture sorption isotherms of the HEC super water absorbents, commercial ones, and HEC at 20°C. (○) HEC-P-Hyd-PAM 4; (●) HEC-PDMAP; (×) PAA-Coml. Abs.; (□) HEC.

The moisture sorption isotherms were analyzed using the Brunauer–Emmett–Teller (BET) equation,⁸ which has been widely accepted for describing the sigmoidal shape for hydrophilic polymers. The BET equation is as follows:

$$x/V(1-x) = 1/V_m C + (C-1)x/V_m C \quad (2)$$

where V is the total value of adsorbed moisture in multilayer fashion, V_m is the maximum value of adsorbed moisture in monolayer fashion, C is the adsorptive energy factor, and x is the RH at 20°C.

In Figure 9, BET plots gave straight lines and therefore the values of V_m and C were determined from the slope and the intercept of the BET plots.

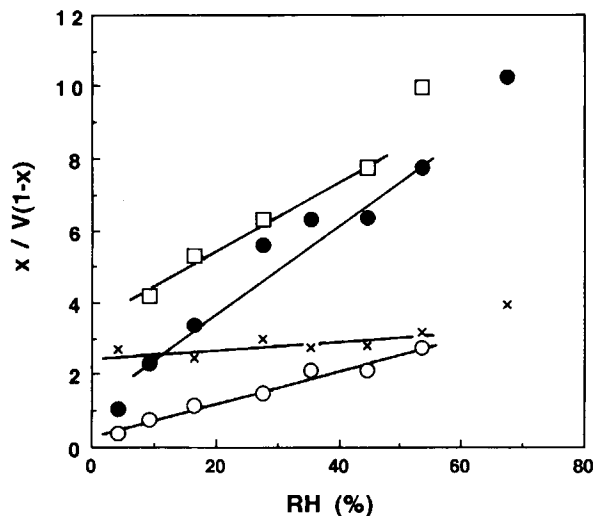


Figure 9 Relationship between the BET plots and the relative humidity at 20°C. The symbols are the same as shown in Figure 8.

The values of V_m and C of HEC-P-Hyd-PAM, HEC-PDMAP, commercial absorbents (PAA-Coml. Abs. and St-PAA-Coml. Abs.) and HEC are shown in Table II. It is evident that not only water absorbency but also the value of V_m of HEC-P-Hyd-PAM was higher than those of other HEC water absorbents and commercial absorbents.

In order to elucidate the state of sorbed moisture in the super water absorbents, the cluster function (G_{11}/V_1) concept defined by Zimm–Lundberg⁹ was applied as follows:

$$G_{11}/V_1 = -\phi_2 \{ \delta, (x/\phi_1) / \delta x \}_{PT} - 1 \quad (3)$$

where ϕ_1 and ϕ_2 are the volume fraction of water and polymer, respectively; V_1 is the molecular volume of water; x is the RH, and G_{11} is the cluster integral. The values of G_{11}/V_1 are considered as a measure of water cluster tendency.⁹ When the clus-

Table II Values of V_m and C of Water Absorbents and HEC at 20°C

Sample	V_m (g/g)	V_m (mol/Polym. Repeat Unit)	C	r
HEC-P-Hyd-PAM 4	0.21	1.2	14.8	0.987
HEC-PDMAP	0.07	0.2	1.1	0.984
PAA-Coml. Abs.	0.24	1.2	2.3	0.842
St-PAA-Coml. Abs.	0.16	—	3.1	0.998
HEC	0.07	0.2	4.6	0.983

Values are in terms of the parameters of the BET equation.

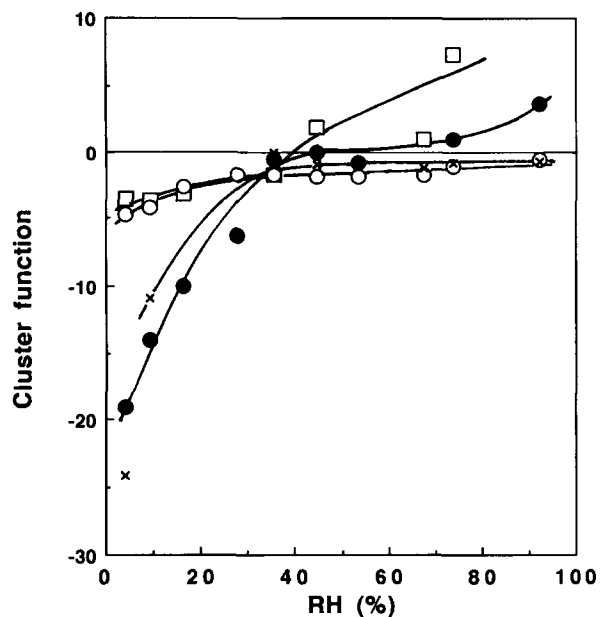


Figure 10 Relationship between the cluster function and the relative humidity. The symbols are the same as shown in Figure 8.

ter function⁹ is greater than -1 , molecules of sorbed water in polymers form a cluster. However, when it is lower than -1 , molecules of sorbed water strongly interact with polymer sites.

Figure 10 shows the cluster function of sorbed water of HEC-P-Hyd-PAM, HEC-PDMAP, HEC, and PAA-Coml. Abs. versus RH. In Figure 10, the cluster function of sorbed water in HEC-P-Hyd-PAM is lower than -1 at almost all RHs, therefore, it can be concluded that sorbed water in HEC-P-Hyd-PAM strongly interacts with carboxylic and hydroxyl groups in it, and does not form a cluster structure. However, the cluster functions of sorbed water in HEC-PDMAP and in HEC went through -1 at about 40% RH and continued to increase to large positive values at higher RHs. These results, therefore, suggest that the sorbed water of HEC-PDMAP and HEC forms cluster structures. In other words, five or six water molecules combine with each other by hydrogen bonding. Also, the cluster function of the sorbed water in PAA-Coml. Abs. went through -1 at 40% RH, and its values were slightly higher than -1 at the higher RH above 40%. This therefore suggests that the molecule of the sorbed water in PAA-Coml. Abs. does not form a cluster.

In conclusion, it is due to the specific water-polymer site interactions that HEC-P-Hyd-PAM and PAA-Coml. Abs. have no cluster water over the whole range of humidity in comparison with HEC-PDMAP and HEC.

Figure 11 shows the degree of swelling, namely water absorbency of dry matter (soybean seeds) in the hydrogels of the HEC water absorbents, commercial water absorbents (St-PAA-Coml. Abs., CMC-Coml. Abs., and PVA-Coml. Abs.), and water versus time of water sorption at 20°C. The degree of swelling of soybean seeds in the hydrogels of each water absorbent was almost the same as that of soybean seeds in water. This indicates that the sorbed water in the hydrogels of super water absorbents is composed of mostly free water.

In addition, the conductivity of 0.1 N KCl in the hydrogels of the HEC water absorbents and commercial ones was measured to examine the state of sorbed water in their hydrogels (Fig. 12). The conductivity of 0.1 N KCl in their hydrogels was about 11.8 mS/cm, which is almost the same value as that of 0.1 N KCl in pure water. However, the conductivity gradually deviated with an increase in the concentration of the super water absorbents. These results suggest that most of the water in the hydrogels of super water absorbents behave like free water.

CONCLUSIONS

The viscoelasticity of the dispersions of the hydrogels, the moisture sorption, and the characteristics of the sorbed water of the highly water-absorptive

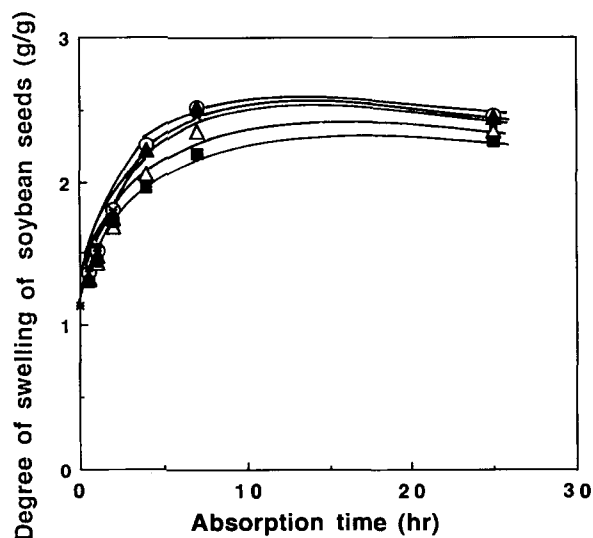


Figure 11 Relationship between the degree of swelling of soybean seeds in the hydrogels of the HEC water absorbents, commercial ones, and water and time of water sorption at 20°C. (○) HEC-P-Hyd-PAM 3; (▲) St-PAA-Coml. Abs.; (△) PVA-Coml. Abs.; (■) CMC-Coml. Abs.; (×) water.

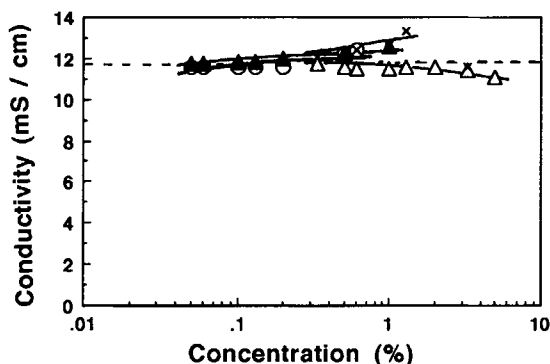


Figure 12 Relationship between the conductivity of 0.1 N KCl in the hydrogels of the HEC water absorbents and commercial ones and the concentration of the hydrogels. (○) HEC-P-hyd-PAM 3; (▲) St-PAA-Coml. Abs.; (△) PVA-Coml. Abs.; (×) PAA-Coml. Abs.

HEC graft copolymers containing partially hydrolyzed PAM, partially hydrolyzed PMA, PAANa, and PDMAP synthesized were investigated in comparison with commercial water absorbents, and the following results were obtained:

1. The apparent activation energy of the dispersions of the hydrogels of HEC-P-Hyd-PAM was about 19.6 kJ/mol, which is similar to that of the polymer melt.
2. The zero shear viscosity of the dispersions of the hydrogels of the HEC water absorbents and commercial ones was proportional to the fourth to seventh powers of the concentration ($\eta_0 = KC^{4-7}$).
3. The dynamic viscosity of the dispersions of the hydrogels of the HEC water absorbents and PVA-Coml. Abs. was proportional to the sixth power of the concentration ($\eta = KC^6$). However, that of commercial absorbents St-PAA-Coml. Abs. and CMC-Coml. Abs. was proportional to the second power of the concentration ($\eta = KC^2$). The dynamic rigidity of the dispersions of their hydrogels was proportional to the fifth to the seventh powers of the concentration ($G = K'C^{5-7}$). Also, the above viscosity and rigidity of HEC-P-Hyd-PAM and St-PAA-Coml. Abs. gave deflection points and the reciprocal of the concentration of each deflection point approximately

showed each water absorbency of the water absorbents.

4. The conductivity of 0.1 N KCl in the hydrogels of the HEC water absorbents was about 11.8 mS/cm, almost the same as that of 0.1 N KCl in pure water, and the water absorbency of dry matter (soybean seeds) in their hydrogels was almost the same as that in pure water. These results suggest that most of the sorbed water in the HEC super water absorbents behave like free water.
5. The maximum volume of sorbed moisture in a monolayer fashion (V_m) of HEC-P-Hyd-PAM analyzed using the BET equation was about 0.21 g/g (1.2 mol/polymer repeat unit), and it had no cluster water at 92% RH or below as a result of applying the cluster function concept.

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