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아크릴계 水溶性高分子의 合成과 그 吸水機能

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Synthesis of Acrylic Water-Soluble Polymer and its hygroscopicity

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Abstract: As a hygroscopic polymer, acrylic water-soluble polymers were prepared by suspension polymerization and were saponified with aqueous NaOH and purified by washing with methanol to remove all traces of excess NaOH. The compositions of Poly(MA-co-VAc) was verified by elemental analysis, IR, NMR spectroscopy and Poly (MA-co-VAc-co-MMA) was by IR and NMR spectroscopy. Hygroscopic capacity of these polymers was measured on aqueous NaOH solution and increased with the order of Poly (MA-co-VAc-co-MMA) < Poly sodium acrylate < Poly (MA-co-VAc). In these cases, hygroscopic value of Poly (MA-co-VAc) was 540 g/g. In the case of Poly (MA-co-VAc), hygroscopic capacity was increased with the increase of water content in the aqueous solution of nonelectrolytes and decreased with the increase of ion concentration in that of electrolytes. While the swelling remained constantly high in the pH range of 5-9, it dropped drastically when pH was lowered further. Hygroscopic capacity of polymer was not affected largely with the variance of temperature, and decreased with the increase of drying temperature.

1. INTRODUCTION

Generally, pulp, cotton and sponze are used as water absorbent materials. But they have not only limited water absorption capacities but also poor water preservations[1]. Particularly, paper-products are made of fibrinous materials and water is absorbed through the capillaries between fibers.

Chemical modifications of water-soluble polymers have attracted a considerable attention to improve the properties of water absorption and preservation. Hygroscopic polymers have the advantages of superior water absorption and excellent water preservation properties[2].

On the other hand, hygroscopic polymers containing ionic groups are called the poly-

electrolytes which are slightly crosslinked by irradation, crosslinking agent[3] or heat-treatment[4]. They have two main groups, which can be distinguished by those that swell in water but do not dissolve completely due to the presence of either covalent crosslinks or strong ionic group and those that dissolve in water, like the ionic homopolymers[5], for example, poly (sodium acrylate) or poly (sodium phosphate).

Hygroscopic mechanism of polyelectrolytes can be explained by the theory of ion network[6]. Schematic diagram of hydrogel ion network is represented in Fig. 1. In this case, it is observed that the concentration of mobile ions in the gel will be greater than that of the outside, in qualitative terms, because of the attracting force of the fixed charges. Consequently, the osmotic pressure of the inside gel will exceed that of the external solution. The swelling force may be brought about by osmotic pressure difference between the gel and solution[7]. And the factor which restricts water absorption capacity is the rubber elasticity of polyelectrolyte. Therefore water absorption capacity is determined by the above two factors.

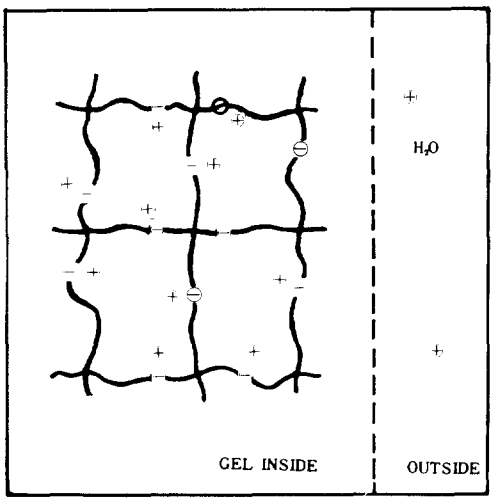
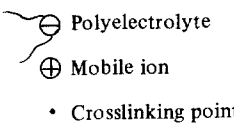


Fig. 1. Schematic diagram of hydrogel ion network.



These materials, which have many applications, can be used as soil modifier, oil-water separator, carrier for the aromatic fume, and sanitation material[8]. The objective of the present investigation is to study the hygroscopic polymer with high-rigidity and excellent water absorption. For the purpose of improving the hydrogel, acrylic water-soluble polymers were synthesized with various conditions and hygroscopic capacities of these hydrogels were measured on several conditions.

2. EXPERIMENTAL

2-1. Materials and Method

Methyl acrylate (MA), methyl methacrylate (MMA) and vinyl acetate (VAc) were freshly distilled. Benzoyl peroxide (BPO) and 2,2′-azo bisisobutyronitrile (AIBN) were purified via recrystallization. Extra pure grade of reagents were used for crosslinking agents and other reagents without further purification.

The Schimadzu DT-200 Thermal Analyzer was used for the differential thermal analysis. Its operation was carried out under nitrogen atmosphere with heating rate of 10°C/min. Elemental analysis was carried out with YANACO MT-2 type CHN CORDER. Infrared spectra were obtained with a JASCO DS-701G Infrared Spectrophotometer. (JEOL JIN-MH-100) was used for the NMR analysis. $CDCl_3$ was used as a solvent. Rigaku X-Ray diffractometer 2037 was operated at 30 KV and 15 mA with a scintillation counter detector and molibdene source. A diffraction pattern from 18° to 4°, 2θ was obtained at the rate of 4° 2θ/min.

2-2. Syntheses of hygroscopic polymers

Copolymer of methyl acrylate with vinyl acetate was prepared by the suspension polymerization. A 500ml four-necked reaction kettle was equipped with a stirrer, a reflux condenser,

a thermometer, a nitrogen-inlet tube and distilled water, polyvinyl alcohol (DP, 1,400), AIBN with monomer were charged into the kettle and flushed out with a slow stream of nitrogen. After six hours of polymerization at 65°C, the product was filtered and washed with water and dried in vacuum oven at 40°C for two days.

Polysodium acrylate was prepared by the reverse-suspension polymerization. Hexane as a solvent, potassium persulfate with monomer, N,N -methylene bisacrylamide as a crosslinking agent were charged into the kettle and flushed out with nitrogen. After three hours of polymerization at 60°C, polymerization was terminated and the product was dried in vacuo at 40°C for two days.

Poly (MA-co-VAc-co-MMA) terpolymer was also prepared by the suspension polymerization. Polymerization was carried out at 65°C and the product was filtered and washed with water and dried in vacuo at 40°C by the similar method when the preparation of Poly (MA-co-VAc) mentioned above.

By using benzene as a solvent, viscosity was measured at 30±0.1°C with Ostwald viscometer. Intrinsic viscosities are shown in Table 1. Polymers were saponified by using 5N NaOH solution in methanol. This reaction was continued for five hours at 65°C. The product was washed with methanol to remove all traces of excess NaOH and by - products. After washing, it should be dried in vacuo at 60°C for two days[9,10].

2-3. Measurement of hygroscopic capacity

Dried hydrogel was swelled with distilled water at 20°C for one hour and separated with 60 mesh sieve. After allowing swelled hydrogels to stand for 10 minutes, measured its weights. The value of hygroscopic capacity was obtained as follows.

$$\text{Hygroscopic capacity} = \frac{\text{Sample weight after swelling}}{\text{Weight of the dried sample}}$$

3. RESULTS AND DISCUSSION

3-1. Identification and thermal analysis of polymers

Reaction conditions and characterizations for the hygroscopic polymers are summarized in Table 1.

Poly (MA-co-VAc) copolymer was identified by elemental analysis, IR and NMR spectroscopy.

In elemental analysis, its results were shown as C, 54.89 : H, 7.17 : O, 37.94 as percentage ratios. That result was in line with that of theoretical calculations. Theoretical calculation result of copolymer, as $C_4H_6O_2$, was C, 55.81 : H, 6.98 : O, 37.21 as percentage ratios.

IR spectrum of the copolymer is given in Fig. 2(a). For poly (methyl acrylate)[11], C=O and C-O stretching vibration bands at 1733 cm^{-1}

Table 1. Syntheses of Hygroscopic Polymer

Polymer	Initiator	Dispersant	Reaction Temperature (℃)	Reaction Time (hour)	Intrinsic Viscosity	Crosslinking Agent	Hygroscopic Capacity (g/g)
Poly (MA-co-VAc)	AIBN	H_2O	65	6	2.55	–	540
Polysodium acrylate	Potassium Persulfate	Hexane	60	3	–	N, N'-methylene bisacrylamide	410
Poly (MA-co-VAc-co-MMA)	AIBN	H_2O	65	6	0.84	–	390

and 1160 cm^{-1} appear strongly and aliphatic CH_2- stretching vibration has a band at 2924 cm^{-1}. For poly (vinyl acetate)[12], C-O stretching band at 1240 cm^{-1}, acetoxyl methyl symmetric bending at 1378 cm^{-1} and C=O stretching vibration at 1738 cm^{-1} appear separately.

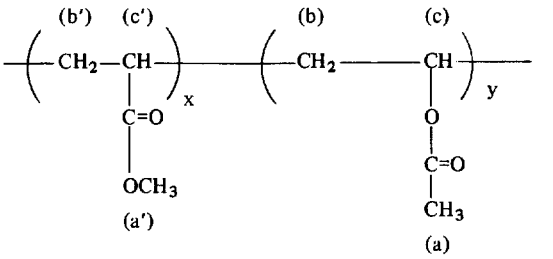
In Fig. 2(a), copolymer has both characteristic bands of poly (methyl acrylate) and poly (vinyl acetate) so it is identified as poly (MA-co-VAc).

In Fig. 2(b), COO^--strong band at 1560 cm^{-1} newly appears as a result of saponification reaction.

In Fig. 2(c), C=O and C-O stretching vibration bands at 1745 cm^{-1} and 1160 cm^{-1} appear respectively C—O—C stretching band and acetoxyl methyl symmetric bending at 1240 cm^{-1} and 1378 cm^{-1} appear. Aliphatic CH_2- stretching vibration band appear at 2960 cm^{-1}.

In Fig. 3 to 4, NMR spectra[13] of poly (methyl acrylate), poly (vinyl acetate) and copolymers are shown.

The general structure of the copolymer from methyl acrylate and vinyl acetate can be written as follows.



Each 100 MHz NMR spectra of Poly (MA),

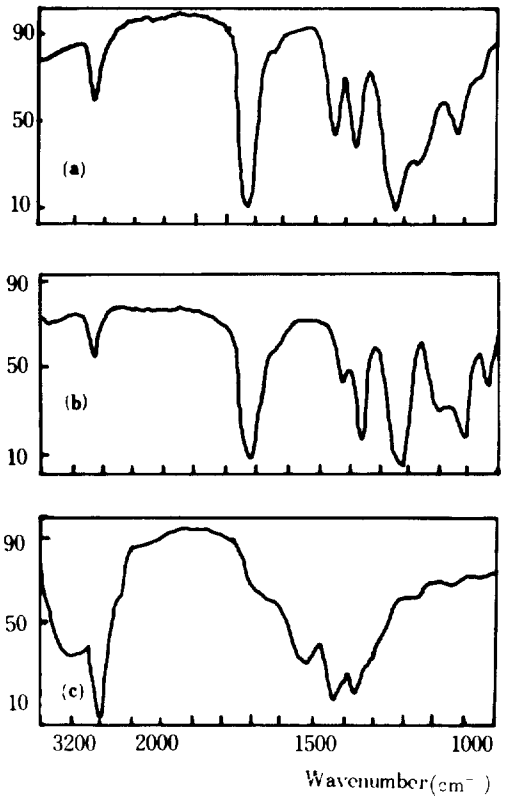


Fig. 2. IR spectra of polymers
(a) Poly(MA-co-VAc)
(b) Polysodium acrylate
(c) Poly (MA-co-VAc-co-MMA)

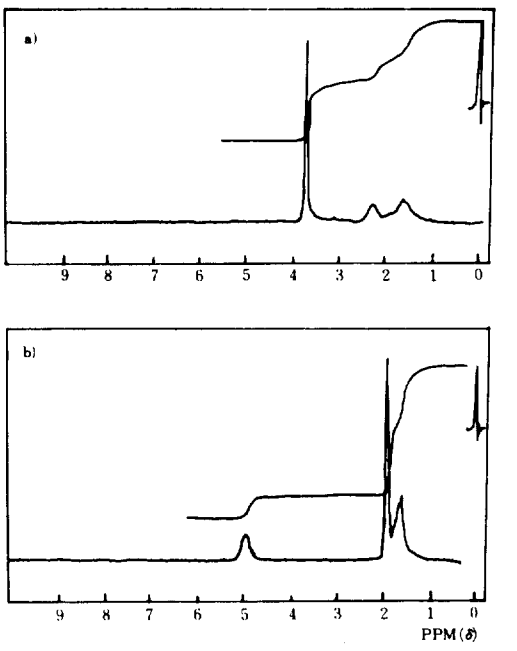


Fig. 3. NMR spectra of polymethyl acrylate and polyvinyl acetate.
(a) Polymethyl. acrylate
(b) Polyvinyl. acetate

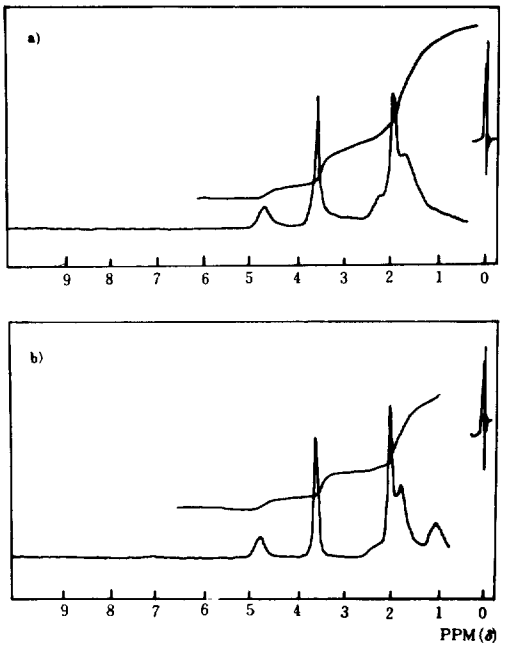


Fig. 4. NMR spectra of copolymers.
(a) Poly (MA-co-VAc)
(b) Poly (MA-co-VAc-co-MMA)

Table 2. Copolymer Composition

Run No.	Feed Composition (mol %)		Copolymer Composition (mol %) *	
	MA	VAc	MA	VAc
1	100	0	100	0
2	80	20	83	17
3	60	40	67	33
4	40	60	55	45
5	20	80	33	67
6	0	100	0	100

* Calculated from Kulkarni's equation by NMR method.

Poly (VAc), and Poly (MA-co-VAc) was shown in Fig. 3(a), Fig. 3(b) and Fig. 4(a). In Fig. 4(a), the peak at δ 0.00 is the peak of internal reference T.M.S. The peak at δ 2.0 is the methyl group of Poly (VAc) and that at δ 3.7 is the methyl group of Poly (MA), and both methylene groups of Poly (MA), Poly (VAc) have same shift position, δ 1.7 and the peak at δ 4.9 is the

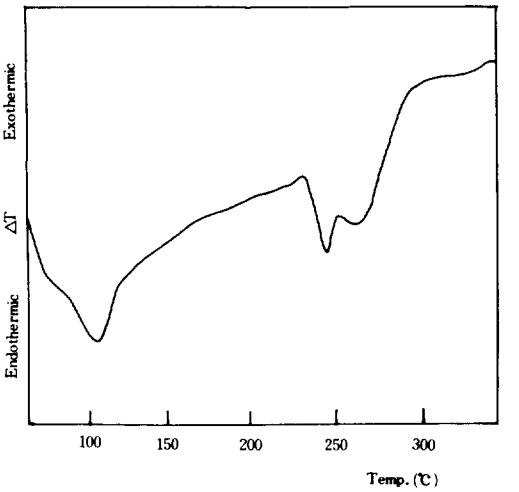


Fig. 5. Schematic differential thermal analysis diagram of hydrogel sample weight, 4.0mg; heating rate, 10°C/min; atomosphere, N_2.

methine group of Poly (VAc) and that at δ 2.3 is that of Poly (MA).

N.G. Kulkarni et al.[14] reported that the unit ratio of the two monomer can be calculated by the following equation.

$$\frac{m_1}{m_2} = \frac{5\,Sa'}{3(Sabb'c\text{-}Sa')}$$

$\frac{m_1}{m_2}$: The ratio of the two monomer units in the resulting copolymer

S : The peak area of the signal

The peak area of the signal was obtained by the height of relative integrating curve and above equation provides a determination of polymer composition. In Table 2, the compositions of copolymer are shown. As the content of vinyl acetate was increased in the monomer feed, the content of methyl acrylate in copolymer was much higher than that of monomer mixture.

(reactivity ratio : $r_{MA} = 3 \pm 0.3$, $r_{VAC} = 0.5 \pm 0.06$ at 60°C)[15]

Identification of Poly (MA-co-VAc-co-MMA) was carried out by the IR and NMR spectroscopy. Those spectra were shown at Fig. 2(c) and Fig. 4(b), respectively. For terpoly-

mer, C=O and C-O stretching vibration bands were shown at 1745 cm^{-1} and 1160 cm^{-1}, C-O-C stretching vibration band at 1240 cm^{-1}, and symmetric bending of the acetoxyl methyl was shown at 1378 cm^{-1} and aliphatic CH_2 stretching vibration was at 2960 cm^{-1}.

In the NMR spectrum, α-methyl proton peak of methyl methacrylate was shown at δ 1.0.

Polymer sample was subjected to differential thermal analysis(DTA) and the DTA thermogram of the sample are shown in Fig. 5. Deflection occuring at about 110°C is the result of changes in interplanar distances of the PVA crystallite[16]. Previous works have reported that discontinuous heat expansion of the lattice spacing was found by the X-ray diffraction studies. And thermal melting curve overlaps with the decomposition deflection indicating that melting occurs with decomposition.

3-2. Hygroscopic capacity

Hygroscopic samples were dried in a vacuum oven at 50°C overnight. The dried samples were weighed immediately, and immersed in aqueous NaOH solution maintained at 20°C for one hour. Swelling polymer was separated by sieve for ten minutes.

Hygroscopic value was increased with the order of terpolymer < polysodium acrylate < copolymer. Comparison of hygroscopic capacity in above polymers is represented in Fig. 6. In this case, maximum hygroscopic capacity of

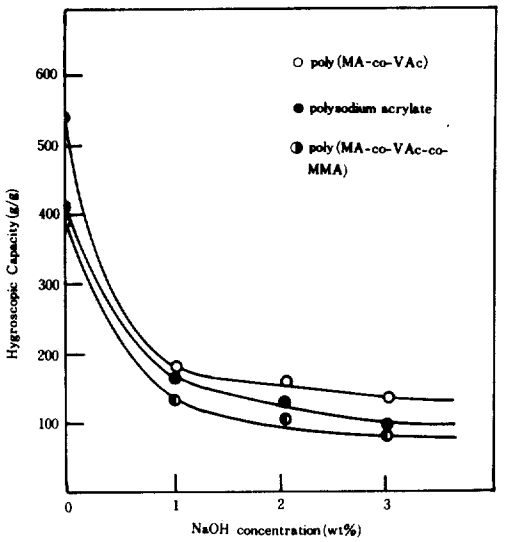


Fig. 6. Comparison of hygroscopic capacity in different hydrogel.

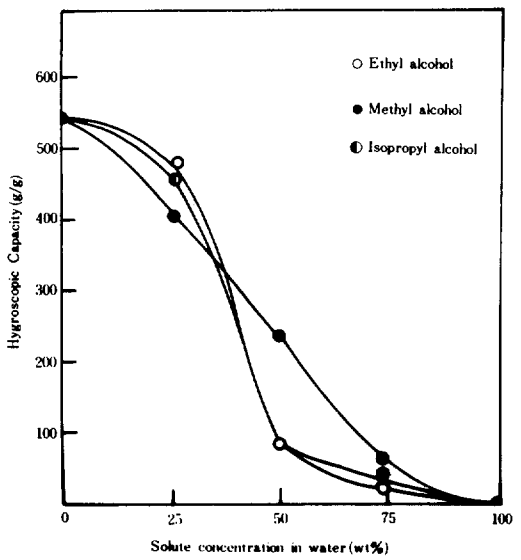


Fig. 7. Effect of non-electrolyte on hygroscopic capacity.

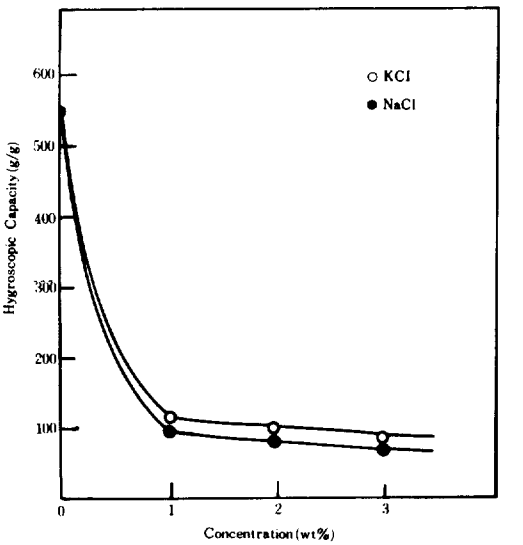


Fig. 8. Effect of electrolytes on hygroscopic capacity.

copolymer was 540 g/g. And so, as a superior hydrogel, copolymer, poly (MA-co-VAc) measured the hygroscopic capacity at the various conditions and discussed its hygroscopic mechanism.

3-3. Effect of non-electrolyte solutions

Fig. 7 shows the effect of non-electrolytes on hygroscopic capacity. In this figure, hygroscopic capacity was increased with the increase of water content in the aqueous solution of non-electrolytes. In non-electrolyte solution, hydrogel absorbed only the external water and this phenomenon explains the selective absorption behavior of hydrogel in non-electrolyte solution.

3-4. Effect of electrolyte solutions

As indicated in Fig. 8, hygroscopic capacity is rapidly decreased with the increase of mobile ion concentration[17]. While the concentration of external mobile ion is increased, osmotic pressure is decreased due to the decrease of the difference of mobile ion concentration. The swelling of gel was considered to be caused by an osmotic pressure differential resulting from a difference in concentration of mobile ions between the interior of the gel and the exterior solution.

3-5. Effect of different pH

The super absorbent samples were soaked at the solution of different pH which was adjusted with either sodium hydroxide or hydrochloric acid. Fig. 9 shows the swelling behavior of the samples as a function of pH.

Lindstrom and Carlsson showed clearly that the swelling of super absorbent pulp was maximum at about neutrality and was depressed at both low and high pH values[18]. It was coincident with the phenomenon that while the swelling remained constantly high in the pH range of 9-5, it dropped drastically when pH was lowered further.

3-6. Effect of heat treatment

The annealing procedure following the drying stage is the one that introduces the crystallites in polymer and strengthens the material. Because only amorphous regions are swollen, the swelling ratio will be differed for

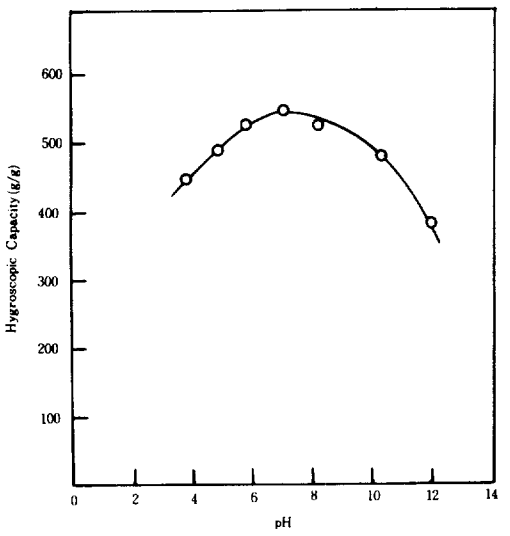


Fig. 9. Hygroscopic capacity at different pH.

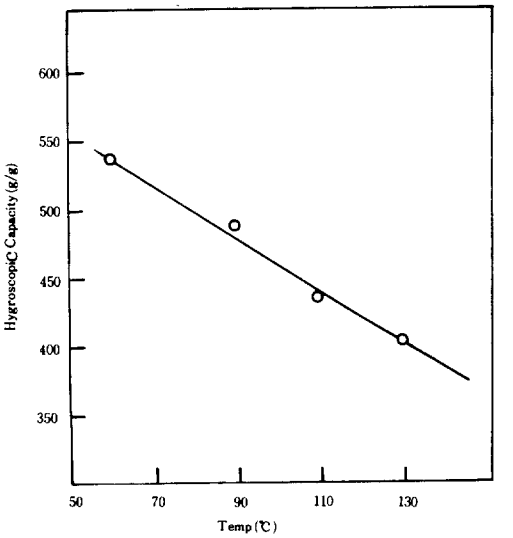


Fig. 10. Effect of drying temperature on hygroscopic capacity.

the different degrees of crystallinity.

Fig. 10 shows the hygroscopic capacity at various drying temperatures. The increase of drying temperature was accompanied by a smooth decrease in hygroscopic capacity up to 130°C. When sample was dried and heat-treated, crystallization was likewise induced and the microcrystalline portion was increased [19] In low temperature condition, the amorphous region of copolymer was dorminantly large. On the other hand, the crystalline region of copolymer was increased in high temperature annealing. And so, hygroscopic capacity was relatively decreased. Fig. 11 shows the effect of heat-treatment on the X-ray diffraction.

As shown in Fig. 11, diffraction intensities from copolymer increased with increasing drying temperature up to 130°C. It was evident that amorphous region of copolymer decreased with increasing drying temperature [20]

3-7. Effect of different mole ratio

Table 3 shows the effect of different mole ratio of copolymer on hygroscopic capacity. It was shown that hygroscopic capacity increased with increasing the component of methyl acrylate and maximum value was appeared at the vinyl alcohol mole ratio of 0.6 mole/mole. It seems, therefore swelling gel has poor water preservation in MA-rich region due to the weak rigidity after swelling. Because crystalline portion of vinyl alcohol is relatively decreased in this region, the reigidity after swelling is also decreased and the water which is absorbed in the exterior solution is partially extracted out. On the other hand, in VA-rich region, swelling gel doesn't show superabsorbing property excellently. In this region, hygroscopic capacity is also affected by the rigidity after swelling. High rigidity due to the increase of

Table 3. Effect of Mole Ratio on Hygroscopic capacity.

Samples	1	2	3	4	5
Mole Ratio (VAc/MA+VAc)	0.2	0.4	0.5	0.6	0.8
Hygroscopic Capacity (g/g)	395	420	480	540	390

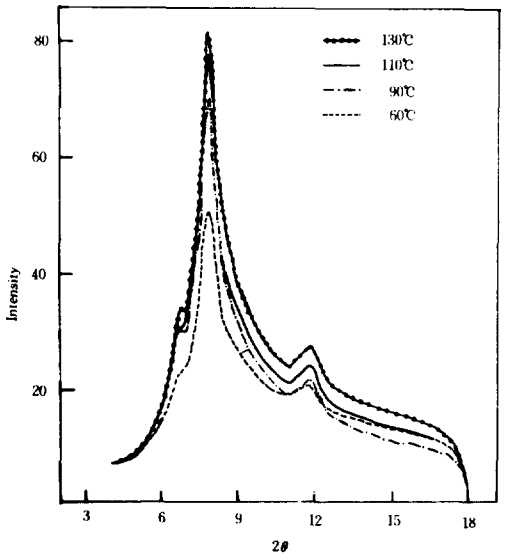


Fig. 11. Effect of heat treatment on the X-ray diffractogram of poly(vinyl alcohol-sodium acrylate).

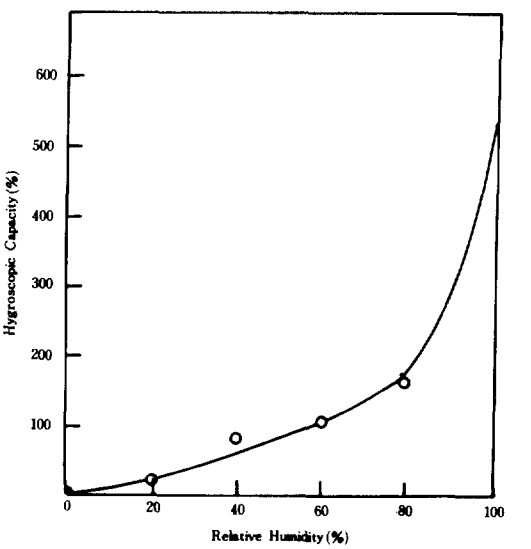


Fig. 12. Effect of relative humidity on hygroscopic capacity.

PVA crystalline portion dorminantly affects the decrease of hygroscopic capacity. And so, general hygroscopic capacity is determined by the concentration difference of mobile ion and the rigidity of hydrogel.

3-8. Effect of relative humidity

The sample was conditioned at the various relative humidities of 20°C for 72 hours and weighed. Fig. 12 shows that the hygroscopic capacity is increased with the relative humidity.

3-9. Effect of different solution temperature

As shown in Fig. 13, hygroscopic capacity of copolymer is almost independent on the temperature of solution. As the solution temperature was increased, hygroscopic capacity was slightly decreased. It is considered the water soluble portions in copolymer are gradually increased and dissolved in solution with the increase of solution temperature.

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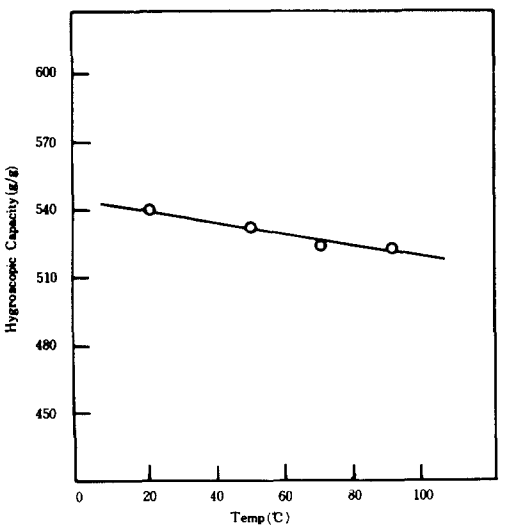

Fig. 13. Hygroscopic capacity at different temperatures.

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