

Preparation of a Crosslinked Poly(acrylic acid) Based New Dehydrating Agent by Using the Taguchi Method

Jun-Kyu Kim and Yang-Kyoo Han*

Department of Chemistry, Hanyang University, Seoul 133-791, Korea

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Abstract: A new crosslinked, poly(acrylic acid)-based, dehydrating agent was synthesized through solution polymerization. The Taguchi method, a robust experimental design, was adopted to optimize the synthetic conditions based on the moisture and water absorbing capacities of the dehydrating agent. The method applied for the experiment was a standard L27 (3^8) orthogonal array with eight parameters and three levels. By analyzing the variance of the test results, the most effective parameters to control the moisture absorbing capacity (MAC) and its rate were the kind of alkaline base (LiOH, NaOH, or KOH) used as a neutralizing agent of the acrylic acid monomer and the degree of neutralization: The maximum MAC of 40% was achieved at only 2 h at 32 °C and 50% RH when KOH was used as a base and the degree of neutralization was 90%, respectively. However, the water absorbing capacity (WAC) of the resulting dehydrating agent was very low at 158 g/g, indicating that WAC is unaffected by MAC and its rate in this system. The surface morphologies of the agents were examined using scanning electron microscopy (SEM).

Keywords: novel dehydrating agent, Taguchi method, crosslinked poly(acrylic acid) metal salt, moisture absorbing capacity, water absorbency.

Introduction

So far, diverse materials such as silica gel, zeolite, and alkaline halides (calcium chloride, magnesium chloride, lithium chloride) have been widely used as desiccants or dehumidifying agents to remove moisture in air. Among them, alkaline halides exhibit the highest moisture absorbing capacity (MAC) as well as fast absorbing rates, but they tend to liquefy after absorbing moisture. Such tendency limits their applications as a dehydrating agent for preserving foods, electrical cables, and electronic assemblies from the moisture. Thus silica gel and zeolite are still being utilized as desiccants to store them for a long term even though they have inherent demerits such as lower MAC and slower absorbing rate than calcium chloride, difficulty in reuse, and fast aging in highly humid condition. Therefore, a new class of dehydrating agents is needed. Recently, superabsorbent is reported as one of the most promising advanced materials.¹

Superabsorbent is a crosslinked network of hydrophilic polymers that can absorb and retain aqueous fluids up to thousands times of their own weight, and absorbed water is hardly removable even under pressure. Because of its excellent water absorption properties relative to traditional absorbing materials such as polyurethane sponge, natural cotton and pulp, etc., superabsorbent has raised considerable inter-

est in many fields such as hygienic products, horticulture, gel actuators, drug delivery systems, water-blocking tapes, food packaging, and coal dewatering.¹⁻⁵

In addition to its liquid-water absorption characteristic, superabsorbent polymers can also absorb water from the vapor state and can be used to control humidity.¹ Superabsorbent can absorb and release more moisture per mass from air than does silica gel, and its moisture absorbing capacity depends on the relative humidity of the atmosphere.^{1,9}

Among recently developed superabsorbents, acrylic acid based superabsorbents, have been extensively studied because of their availability, low price, and facile polymerization to generate high molecular weight polymers.⁶⁻⁸ Modified acrylic acid based superabsorbents have been prepared to enhance absorbency,⁸ and to prepare composites with other materials.^{5,10,11} Studies on fast-swelling superabsorbent,¹² and swelling kinetics have been performed thoroughly¹³ but more studies on high MAC and a moisture absorbing rate at low humidity are needed. One of the suggestions to improve the MAC was to modify dried superabsorbents by adding a salt solution which has the 5~15 wt% of concentration.¹⁴

In this study, to enhance the MAC, acrylic acid based superabsorbents were prepared by a solution polymerization technique in an industrial point of view. These materials are applicable as dehydrating agents for not only foods and electronic assemblies packaging but also high efficiency regenerative evaporative cooler system (HERECS).^{14,15} Gener-

*Corresponding Author. E-mail: ykhan@hanyang.ac.kr

ally, "one-parameter-at-a-time" experiments have been conducted in most of the previous studies to determine the optimum condition. This method often overlooks interactive effects of different parameters on results even in simple cases. However, fractional factorial design based on a Taguchi's orthogonal array (OA) can be a very effective methodology to investigate the effects of multiple parameters, as well as potential interactions among these factors in time- and cost-effective manners.^{11,16} Eight important parameters were selected with three different levels to elucidate the correlations between the parameters and absorbing characters. An L27 (3⁸) orthogonal array to optimize the test parameters for the absorbing capacity was adopted. The surface morphology was also investigated.

Experimental

Materials. Acrylic acid (AA, LG Chemical) was distilled under reduced pressure. *N,N'*-Methylene bisacrylamide (MBA) was obtained from Aldrich and used as received. 1,6-Hexandiol diacrylate (HDDA) and triethyleneglycol diacrylate (TEGDA) were received from Miwon Commercial and used without further purification. Potassium persulfate (KPS), sodium metabisulfite (SMBS), lithium hydroxide monohydrate, sodium hydroxide, potassium hydroxide, and calcium chloride dihydrate all were used as received from Aldrich. Silica gel was obtained from Merck and dried at 105 °C for 1 h. A commercial poly(acrylic acid) base superabsorbent was supplied from Kolon Industries and screened by 30–50 mesh, and dried at 105 °C for 1 h.

Selection of Parameters and Levels for Experimental Design. Eight parameters including the type of crosslinker (X) and its concentration (C_x), the type of neutralization agent (NA) and its dilution concentration (C_{NA}), degree of neutralization (DN), initiator concentration (C_{INI}), polymerization temperature (T_{PZN}), drying temperature (T_{DRY}) were selected in this study. These parameters, which affect the final absorbing properties of the prepared samples, were selected on the basis of authors' past experiences for the conventional superabsorbent hydrogels being used for infant diapers and sanitary napkins. On the basis of literatures and our preliminary experiments, novel dehydrating agents were prepared with three different levels. The eight parameters and the varied levels are summarized in Table I.

Selection of OA and Assignment of Parameters. Standard tables known as an OA are used to design the experiments in the Taguchi method. An OA with three levels and eight parameters with the symbol of L27 (3⁸) OA are shown in Table II. Each row in the array represents a trial condition with the parameter levels. The columns correspond to the parameters specified in this study. The results were analyzed statistically, and main effect plot was obtained by using MINITAB 14 program.¹⁷

Preparation of Crosslinked Poly(acrylic acid) Based

Table I. Experimental Parameters and Their Levels

Parameters	Level-1	Level-2	Level-3
Crosslinker (X)	MBA	HDDA	TEGDA
C_x (mol/L)	3.2×10^{-3}	9.6×10^{-3}	2.9×10^{-2}
NA	LiOH	NaOH	KOH
C_{NA} (%)	18	22	26
DN (%)	50	70	90
C_{INI} (mol/L)	5.5×10^{-3}	1.1×10^{-2}	1.7×10^{-2}
T_{PZN} (°C)	40	50	60
T_{DRY} (°C)	65	85	105

Table II. Experimental Layout of an L27 (3⁸) Orthogonal Array by the Taguchi Method

Trial Number	Parameters and Their Levels							
	X	C_x	C_{NA}	NA	DN	C_{INI}	T_{PZN}	T_{DRY}
1	1	1	1	1	1	1	1	1
2	1	1	1	1	2	2	2	2
3	1	1	1	1	3	3	3	3
4	1	2	2	2	1	1	1	2
5	1	2	2	2	2	2	2	3
6	1	2	2	2	3	3	3	1
7	1	3	3	3	1	1	1	3
8	1	3	3	3	2	2	2	1
9	1	3	3	3	3	3	3	2
10	2	1	2	3	1	2	3	1
11	2	1	2	3	2	3	1	2
12	2	1	2	3	3	1	2	3
13	2	2	3	1	1	2	3	2
14	2	2	3	1	2	3	1	3
15	2	2	3	1	3	1	2	1
16	2	3	1	2	1	2	3	3
17	2	3	1	2	2	3	1	1
18	2	3	1	2	3	1	2	2
19	3	1	3	2	1	3	2	1
20	3	1	3	2	2	1	3	2
21	3	1	3	2	3	2	1	3
22	3	2	1	3	1	3	2	2
23	3	2	1	3	2	1	3	3
24	3	2	1	3	3	2	1	1
25	3	3	2	1	1	3	2	3
26	3	3	2	1	2	1	3	1
27	3	3	2	1	3	2	1	2

New Dehydrating Agents. A series of the samples controlled by the eight different parameters were prepared by the following procedure: an appropriate amount of crosslinker was dissolved in 20.0 g of AA and added to a 250 mL four-neck flask equipped with a mechanical stirrer, a reflux condenser, a funnel, and a nitrogen inlet adapter. The reactor was immersed in a thermo-controlled water bath preset at 20 °C. Then, a given amount of neutralizing agent solution was added into the reactor slowly and temperature of the resulting solution was kept lower than 40 °C. After being purged with nitrogen for 30 min to remove oxy-

gen dissolved in the solution, the reactor was heated to 40 to 60 °C depending on the level of initiation temperature, and then the KPS and SMBS solutions were dropped into it with 2 min of interval. After stirring it for 3 to 5 min, when the solution became viscous, the viscous polymer solution was moved to a petri-dish (90 mm of diameter) and put into a convection oven maintained at the same temperature as initiation and kept for 3 h. The obtained hydrogels were cut into small pieces with a diameter of less than 5 mm and transferred to a 20-mesh screen and placed in a convection oven which is kept at 65 to 105 °C depending on the level of drying temperature for 12 to 24 h. The partially crosslinked poly(acrylic acid) based new dehydrating agents were milled and screened to obtain a particle size in the range of 30–50 mesh (300–600 μm), dried at 105 °C for 1 h, and finally stored away from moisture, heat, and light.

Measurement of Water Absorbing Capacity (WAC). In order to measure WAC, 0.05 g of each sample was immersed in 500 mL of distilled water at room temperature for 3 h to reach swelling equilibrium. The swollen gels were filtered through a 100-mesh screen under gravity for 1 h to remove unabsorbed water. The WAC is represented by the following equation: $WAC = M_2 - M_1 / M_1$, where M_1 and M_2 are weights of the dried samples and swollen gels, respectively. It was calculated as grams of the absorbed water per one gram of the sample.

Measurement of Water Absorbing Rate (WAR). A vortex disappearing time was measured to compare the absorbing rate of samples. 25 mL of distilled water was poured into a 50 mL of beaker and the water was stirred with a 20 mm octagonal magnetic bar at 600 rpm to make a vortex. 0.5 g of sample was dispersed into the vortex and then the time at which the vortex disappeared was recorded as WAR.

Measurement of Moisture Absorbing Capacity (MAC). 1.0 g of each sample was dispersed uniformly on a petri-dish (50 mm of diameter) and put into a humidity chamber preset at 32 °C and 50% RH (relative humidity). The change of weight of the sample was measured after 30 min, 1, 2, 3, 6, 12, and 24 h. The MAC is represented by the following equation: $MAC(\%) = M_2 - M_1 / S_1 \times 100$, where M_1 and M_2 are total weights of the petri-dish including the sample before and after the test, respectively, and S_1 is the sample weight before the test. It was calculated as weight percent (%) of the absorbed moisture per gram of the sample.

Characterization. Scanning electron microscopic (SEM) analysis of the samples was carried out on a Hitachi S-4800. The SEM samples were sputter-coated with platinum onto a silicon wafer.

Results and Discussion

Polymerization. Partially crosslinked poly(acrylic acid)

Table III. Experimental Layout and Test Results of WAC, WAR, and MAC

Trial	X	C_X	C_{NA}	NA	DN	C_{INI}	T_{PZX}	T_{DRY}	WAC	WAR	MAC ^a
1	MBA	3.2×10^{-3}	18	LiOH	50	5.5×10^{-3}	40	65	198	45	0
2	MBA	3.2×10^{-3}	18	LiOH	70	1.1×10^{-2}	50	85	197	40	1
3	MBA	3.2×10^{-3}	18	LiOH	90	1.7×10^{-2}	60	105	625	38	0
4	MBA	9.6×10^{-3}	22	NaOH	50	5.5×10^{-3}	40	85	169	50	1
5	MBA	9.6×10^{-3}	22	NaOH	70	1.1×10^{-2}	50	105	165	48	5
6	MBA	9.6×10^{-3}	22	NaOH	90	1.7×10^{-2}	60	65	271	34	23
7	MBA	2.9×10^{-2}	26	KOH	50	5.5×10^{-3}	40	105	134	42	15
8	MBA	2.9×10^{-2}	26	KOH	70	1.1×10^{-2}	50	65	146	27	29
9	MBA	2.9×10^{-2}	26	KOH	90	1.7×10^{-2}	60	85	158	21	39
10	HDDA	3.2×10^{-3}	22	KOH	50	1.1×10^{-2}	60	65	262	24	14
11	HDDA	3.2×10^{-3}	22	KOH	70	1.7×10^{-2}	40	85	279	20	26
12	HDDA	3.2×10^{-3}	22	KOH	90	5.5×10^{-3}	50	105	380	18	36
13	HDDA	9.6×10^{-3}	26	LiOH	50	1.1×10^{-2}	60	85	175	43	0
14	HDDA	9.6×10^{-3}	26	LiOH	70	1.7×10^{-2}	40	105	170	47	0
15	HDDA	9.6×10^{-3}	26	LiOH	90	5.5×10^{-3}	50	65	289	41	2
16	HDDA	2.9×10^{-2}	18	NaOH	50	1.1×10^{-2}	60	105	144	55	2
17	HDDA	2.9×10^{-2}	18	NaOH	70	1.7×10^{-2}	40	65	186	38	9
18	HDDA	2.9×10^{-2}	18	NaOH	90	5.5×10^{-3}	50	85	271	25	22
19	TEGDA	3.2×10^{-3}	26	NaOH	50	1.7×10^{-2}	50	65	339	34	1
20	TEGDA	3.2×10^{-3}	26	NaOH	70	5.5×10^{-3}	60	85	280	32	9
21	TEGDA	3.2×10^{-3}	26	NaOH	90	1.1×10^{-2}	40	105	593	33	26
22	TEGDA	9.6×10^{-3}	18	KOH	50	1.7×10^{-2}	50	85	182	33	13
23	TEGDA	9.6×10^{-3}	18	KOH	70	5.5×10^{-3}	60	105	207	20	29
24	TEGDA	9.6×10^{-3}	18	KOH	90	1.1×10^{-2}	40	65	347	17	37
25	TEGDA	2.9×10^{-2}	22	LiOH	50	1.7×10^{-2}	50	105	120	62	0
26	TEGDA	2.9×10^{-2}	22	LiOH	70	5.5×10^{-3}	60	65	190	42	1
27	TEGDA	2.9×10^{-2}	22	LiOH	90	1.1×10^{-2}	40	85	255	43	0

^aMoisture absorbing capacity at 50%RH, after 2 h.

based new dehydrating agents were prepared by the solution polymerization procedure as described earlier. Three different crosslinkers with different concentrations were used. To

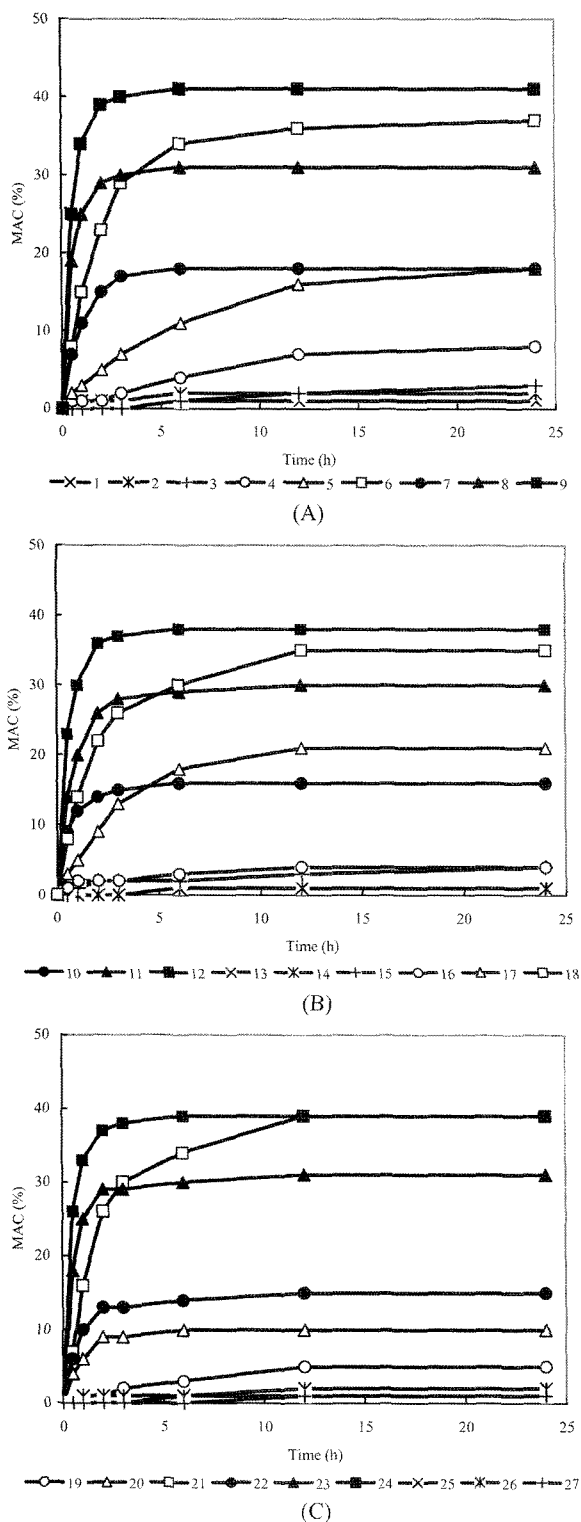


Figure 1. Moisture absorbing behaviors of the new dehydrating agents with time at 32 °C and 50% RH: (A) for trial # 1-9, (B) for trial # 10-18, and (C) for trial # 19-27.

initiate the polymerization at low temperature, potassium persulfate and sodium metabisulfite were used as a redox initiator system. The gelation time of the polymer solution during the polymerization became slow as the ionic metal size of alkaline base used as a neutralizing agent increases in order of $K^+ > Na^+ > Li^+$, the concentration of the initiators increases, and the temperature of the monomer solution increases. This indicates that these parameters greatly affect the rate of polymerization.

Water Absorbing Characteristics. The experimental layout and measured results are summarized in Table III. The highest WAC was shown at the trial #3 as 625 g, and lowest at the trial #25 as 120 g per a gram of the sample. WAR was in the range of 17 to 62 sec. In case of the conventional crosslinked poly(acrylic acid) based superabsorbents, their WACs are inversely proportional to their WARs. However, correlation between WAC and WAR was not found in this study.

Moisture Absorbing Characteristics. MAC (%) was plotted as a function of time, which is shown in Figure 1. The MAC was largely deviated from 0 to 39% at 2 h and from 1 to 41% at 24 h. The highest value was obtained at the trial #9, while the lowest was the trial # 1, 3, 13, 14, 25, and 27. All the samples, which LiOH was used as a neutralization agent, always exhibited the lowest MAC and slow WAR. On the contrary to these results, one interesting thing is that the samples, which KOH was used with high degree of neutralization, showed higher MAC and faster WAR even though they had a relatively low WAC. The samples treated with NaOH were in the middle. From these results, we can conclude that the ionization tendency and the size of the alkaline metal used as a neutralization agent greatly affect the water and moisture absorbing natures of the samples: Potassium cation that has higher ionization tendency and larger ion radius than sodium and lithium cations is likely to result in higher MAC and faster WAR.

Main Effect Plots for WAC. Main effects analysis was done for the WAC, and the plots are shown in Figure 2. The most important parameters for the WAC were the concen-

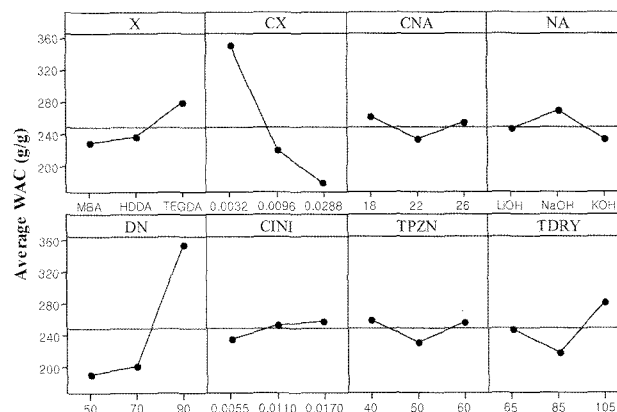


Figure 2. Main effect plots for water absorbing capacity (WAC).

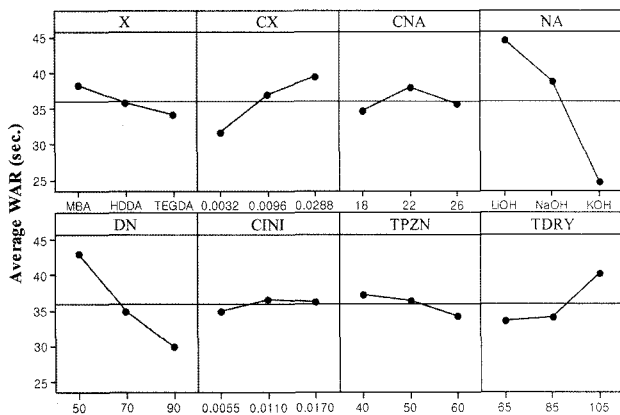


Figure 3. Main effect plots for water absorbing rate (WAR).

tration of the crosslinker and the degree of neutralization. The WAC increases drastically as the crosslinker concentration decreases and as the degree of neutralization increases. A type of crosslinker, a neutralizing agent, and the drying temperature also affect the WAC, but not as much as the crosslinker concentration or the degree of neutralization.

Main Effect Plots for WAR. Main effects analysis was carried out for the WAR, and the plots are shown in Figure 3. The most important parameters for the WAR were the type of a neutralizing agent and the degree of neutralization. KOH showed very fast WAR (the trials #9, 12, and 24) while LiOH exhibited slower WAR (the trials #1, 14, and 25). Moreover, the WAR increases as the degree of neutralization increases. Low crosslinker concentration, low drying temperature, and high polymerization temperature result in faster WAR.

Main Effect Plots for MAC after 2 h. Main effects analysis was examined for the MAC after keeping the samples in a humidity chamber for 2 h, and the resulting plots are shown in Figure 4. The most important parameters for the MAC were the type of a neutralizing agent and the degree of neutralization as those for the WAR. KOH was the best

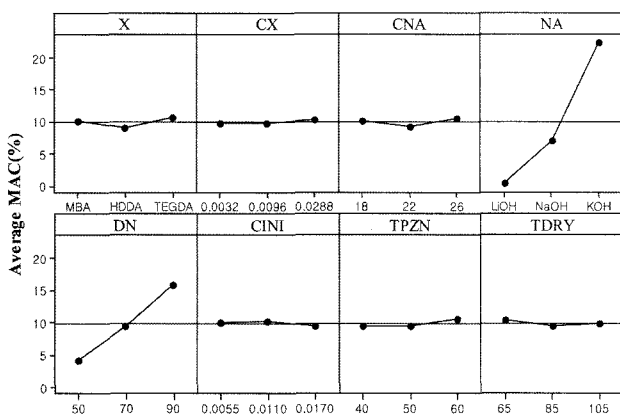


Figure 4. Main effect plots for maximum absorbing capacity (MAC) at 50% RH after 2 h.

neutralizing agent, and the degree of neutralization showed the direct proportionality to the MAC. Contribution of other parameters is negligible to the MAC.

Main Effect Plots for MAC after 24 h. Main effects analysis was investigated for the MAC after keeping the samples 24 h in a humidity chamber for 24 h, and the resulting plots are shown in Figure 5. The tendency was almost the same as the MAC after 2 h, but the average MAC after 24 h was higher than that of 2 h. The NaOH treated samples showed increasing tendency by time but LiOH applied samples did not show much change. The parameters affecting the MAC of 24 h and the results were the same as those of 2 h. Other parameters were very small contribution to the MAC.

Effect of Morphology. SEM analysis was done for samples that had different absorbing characteristics and the micrographs are shown in Figure 6. According to the analysis, the morphology was not much different among the samples. It is known that the morphology, the shape, and the

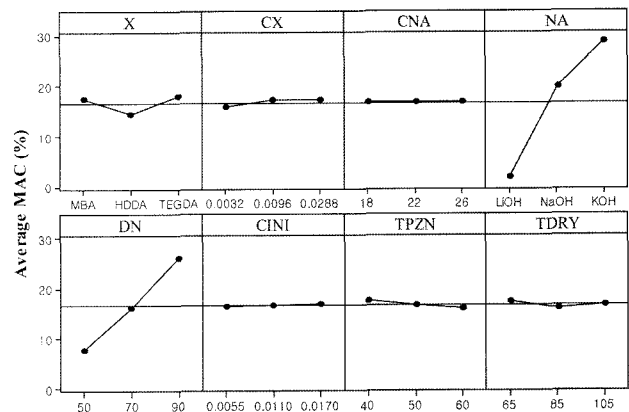


Figure 5. Main effect plots for maximum absorbing capacity (MAC) at 50% RH after 24 h.

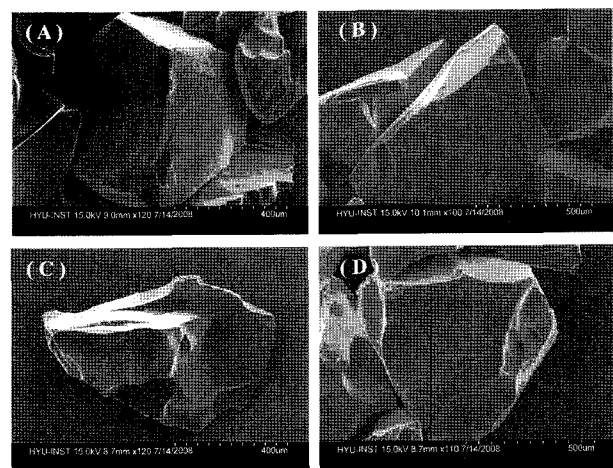


Figure 6. SEM photographs of crosslinked poly(acrylic acid) based dehydrating agents synthesized by a solution polymerization: (A) Trial #1, (B) Trial #5, (C) Trial #7, and (D) Trial #9.

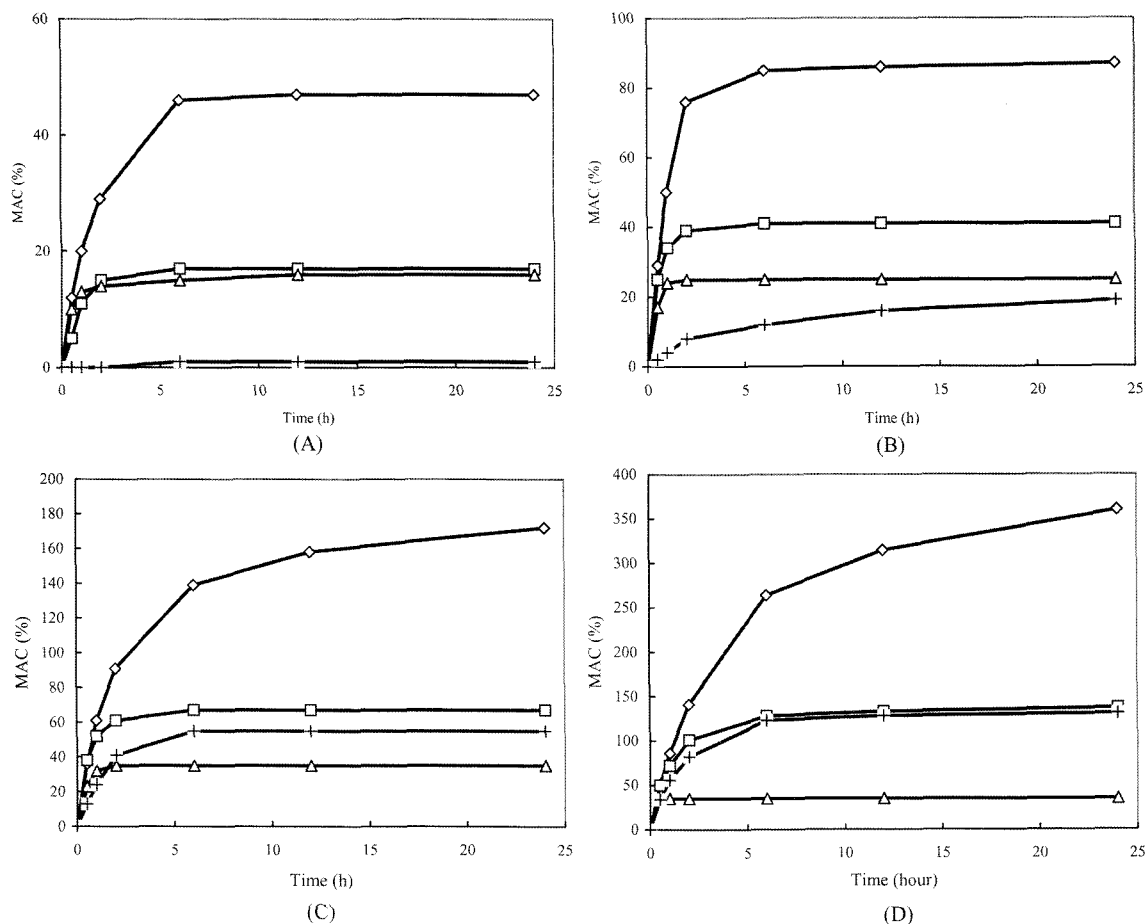


Figure 7. Moisture absorbing behaviors of different dehydrating agents at 32 °C under different relative humidity: 30(A), 50(B), 70(C), and 90% RH(D); calcium chloride dihydrate (◇), trial #9 (□), silica gel (△), and K-SAM (+).

particle size of the conventional superabsorbents affect their physical properties such as absorbing rate, absorbing capacity, and gel strength swollen in water.^{1,9,12} However, we observed that the differences of absorbing capacity and time for the poly(acrylic acid) based new dehydrating agents do not result from their morphological differences.

Comparison of MAC for Different Dehydrating Agents.

The MAC for conventional dehydrating agents (calcium chloride dihydrate and silica gel) and commercial superabsorbent K-SAM (Kolon Industries Inc.) was measured as a function of time at different relative humidity and was compared with that of the new dehydrating agent (trial #9) as shown in Figure 7. From the viewpoints of MAC and absorbing rates, calcium chloride dihydrate showed the highest value, 47% of MAC at 30% RH and 360% at 90% RH after 24 h, but within 2 h the calcium chloride became an aqueous solution after absorbing moisture in the air at highly humid condition of more than 50%. Due to its liquefying property after absorbing humidity, calcium chloride is used only as a simple desiccant, not as a dehumidifying agent for food and electronic packaging. Silica gel showed 16–35% of MAC under the test conditions. At the lowest RH of 30%, the

MAC of silica gel was similar to that of the new sample #9, and higher than that of the K-SAM, a commercial superabsorbent. The maximum MAC of silica gel was reached at 70% RH and not increased any more with increasing RH concentration. On the other hand, the K-SAM displayed dramatic change of the MAC from 1 to 131% depending on the concentration of RH: At low RH of below 50%, it showed lower MAC than silica gel. However, at higher RH of above 70%, it exhibited more than twice of MAC than silica gel. Also, its MAC was almost the same as that of the new sample at 90% RH.

In addition to these conventional dehydrating agents, the new sample #9 showed much better MAC and faster moisture absorbing rates than either silica gel or the K-SAM at all test conditions. The distinct improvement of the sample #9 was shown especially at the low RH of less than 50%: The MAC of trial #9 was 17 times of the MAC of the commercial superabsorbent (17% vs. 1%) at 30% RH, and more than 2 times (41% vs. 19%) at 50% RH. Moreover, the maximum MAC (17–138%) was almost achieved within 2 h. These results are essential requirements for the development of HERECs that is now a hot issue for energy sav-

ing.^{14,15} Unlike calcium chloride dihydrate, the swollen gel retained the shape of the prepared original particles even after absorbing the maximum MAC in a highly humid condition. The gel was robust under an appropriate external pressure and the moisture absorbed in the gel was also not released even with the pressure. The gel can be dried to the original shape under reduced pressure and reused as a dehumidifying agent.

Conclusions

We synthesized crosslinked poly(acrylic acid) based new dehydrating agents using solution polymerization. By Taguchi's experimental design, a standard L27 (3^8) orthogonal array with eight parameters and three levels was adopted. The eight parameters were a type of crosslinkers and its concentration, a type of neutralizing agents and its dilution concentration, degree of neutralization, initiator concentration, polymerization temperature, and drying temperature. Among these parameters, the type of alkaline bases used in neutralizing the acrylic acid monomer and its degree of neutralization were the most important parameters for the MAC and the WAR. The best results of the new dehydrating agents were achieved when KOH was used as a base and the degree of neutralization was 90%. The WAC was greatly affected by the concentration of the crosslinker and the degree of neutralization. We also found that there is no relationship between the MAC and the WAC. The novel dehydrating agents, which are synthesized for the first time, showed much more excellent characteristics in the MAC and the WAR than the conventional silical gel and the superabsorbent in the whole range of RH of 30 to 90%. In particular, the WAR was noticeably fast and the maximum MAC was reached within 2 h after absorbing the moisture even at low RH of 30% and the resulting swollen sample showed strong gel strength. On the basis of these excellent performances, the new crosslinked poly(acrylic acid) based samples could be very useful as a dehydrating agent for foods and electrical assemblies packaging or a novel dehumidifying material for the carrier of HERECs.

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