Notes

Modification of a Crosslinked Poly(acrylic acid) Based New Dehumidifying Agent and Its Moisture Absorbing Characteristics

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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. Among those, alkaline halides exhibit the highest moisture absorbing capacity (MAC) as well as fast moisture absorbing rate (MAR). However, the applications of alkaline halides are limited because of their tendency to liquefy after absorbing moisture. Thus, silica gel and zeolite have been utilized as desiccants for preserving foods, electrical cables, electronic assemblies, etc., even though they have disadvantages such as lower MAC and slower MAR than calcium chloride, difficulty in reuse, and fast aging in high humid condition. Therefore, researchers have been trying to develop a new class of dehydrating agents that are stronger, reusable and robust and 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 interest 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: They absorb and release more moisture per mass from air than does silica gel. Their MAC depends on the relative humidity (RH) of the atmosphere. With these characteristics they have been used as a desiccant or humid controlling material.[1,6] 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.[7-9] Modified acrylic acid based superabsorbents have been synthesized to enhance absorbency,[9] and to prepare composites with other materials.[5,10,11] Studies on fast-swelling superabsorbent,[12] and swelling kinetics of these polymers have been performed thoroughly,[13] but studies on high MAC and fast MAR at low humidity are seldom.[14]

In our previous study, therefore, a crosslinked poly(acrylic acid) based new dehydrating agent beyond the MAC and MAR of conventional materials was prepared for the first time via solution polymerization technique using the Taguchi method, a robust experimental design: The most important parameters for controlling MAC and MAR were found to be the kind of alkaline base used as a neutralizing agent of acrylic acid monomer and the degree of neutralization. As a result, a relatively high MAC of 30-39% relative to the weight of new dehydrating agent at 2 h at low RH below 50% was achieved when KOH was used as a base and the degree of neutralization was 90%, respectively. In addition, the swollen gel retained the shape of original particles even after absorbing the maximum MAC (138%) in a highly humid condition of 90% for 24 h. The gel can also be dried back to the original shape under reduced pressure and reused as a dehumidifying agent.[15] On the basis of these excellent performances, the new crosslinked poly(acrylic acid) based samples are expected to be useful as a dehydrating agent for foods and electrical assemblies packaging. However, a polymer suitable for high efficiency regenerative evaporative cooler system (HERECS) has not yet found since it requires high MAC and fast initial MAR even at low RH of 50%.[14,16]

In this work, additional treatment of potassium hydroxide to the crosslinked poly(acrylic acid) based new dehydrating agent, which is prepared by the previous Taguchi method,[17] was carried out to produce a novel dehumidifying polymer with high MAC and fast MAR that is applicable to HERECS that is now a hot issue for energy saving. We also investigated the effects of the surface crosslinking and the particle size on the MAC and MAR of the resulting modified polymers.

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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. Potassium persulfate (KPS), sodium metabisulfite (SMBS), sodium hydroxide, and calcium chloride dihydrate were used as received without further purification. Silica gel was purchased 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.

Preparation of Partially Crosslinked Poly(acrylic acid potassium salt) (PAA-K). A reference sample as a dehumidifying material was prepared by the procedure reported in our previous article:[15] 0.45 g of MBA was dissolved in 100.0 g of AA and added to a 1,000 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, 38.9 g of potassium hydroxide was dissolved in 105 mL water, and the solution was added into the reactor slowly and temperature of the resulting solution was kept lower than 40 °C. After purging with nitrogen for 30 min to remove oxygen in the solution, the reactor was heated to 60 °C and then 0.45 g KPS dissolved in 20 mL water, and 0.32 g of SMBS dissolved in 20 mL water were dropped into it with 2 min of interval. After stirring it for 5 min, the viscous polymer solution was moved to a petri-dish (150 mm of diameter) and put into a convection oven maintained at 60 °C and kept for 3 h. The obtained hydrogels were cut into small pieces with a diameter of less than 5 mm, transferred to a 20-mesh screen and placed in a convection oven at 105 °C for 12 h. The product were milled and screened to obtain a particle size in the range of 30-50 mesh (300-600 μm), 50-140 mesh (104-300 μm), and smaller than 104 μm and dried at 105 °C for 1 h, and finally stored in dry, cool, and dark condition.

Additional Neutralization. The PAA-K prepared as a reference sample was additionally neutralized by KOH solution: 14.7 g of PAA-K sample was dispersed uniformly in a rectangular stainless steel reservoir. Then 1.56-4.67 g of KOH dissolved in 13.44 mL of water was sprayed on the sample and mixed homogeneously. The after-treated sample was stored for 1 h at room temperature and then placed in a convection oven at 105 °C for 6 h. The dried product was milled by using a ball mill and screened to obtain a constant range of particle size.

Surface Crosslinking. 15 g of the prepared PAA-K was mixed with 0.015 g ethylene glycol diglycidyl ether (EGDE) dissolved in 0.7 mL of water and 1.0 mL of methanol. The mixed sample was mixed uniformly by using a food mixer for 3 min and then placed in a convection oven at 120 °C for 1 h to give a crosslinking on the surface of reference sample. The resulting product was milled by using a ball mill and screened to obtain a constant range of particle size.

Measurements of MAC and WAC. MAC and WAC (water absorbing capacity) were measured according to the procedures reported in our previous paper.[15]

Moisture Absorption-Desorption Behavior. 1.0 g of 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. The swelled sample was put into a convection oven preset at 120 °C to remove the absorbed moisture. The change of weight of the sample was measured after 30 min and 1 h. Then the same procedures were repeated 7 times to confirm the reliability of moisture absorption-desorption behavior for the modified dehumidifying samples. The behavior is shown as a function of time for the MAC.

Results and Discussion

Polymerization and Modification. As a reference sample, the PAA-K based new dehumidifying agent was prepared by the solution polymerization described earlier. For the solution polymerization, MBA and potassium hydroxide were used as a crosslinker and a neutralizing agent of the acrylic acid monomer. To initiate the polymerization at low temperature, KPS and SMBS were applied as a redox initiator system. The prepared reference sample was modified by three after-treatment methods such as additional neutraliza-

Table I. Effect of Particle Size and After-treatment Method on WAC and MAC

Sample	NA[a]	DN[b]	SX[c]	AN[d]	PS (μm)[e]	WAC (g/g)	MAC (%)[f]
1	KOH	90%	X	X	50	155	39
2	KOH	90%	X	X	200	141	40
3	KOH	90%	X	X	450	118	39
4	KOH	90%	O	X	450	105	38
5	KOH	90%	X	10%	450	210	49
6	KOH	90%	X	20%	450	133	51
7	KOH	90%	X	30%	450	120	52

[a]Neutralizing agent. [b]Degree of neutralization. [c]Surface crosslink. [d]Additional neutralization. [e]Average particle size. [f]Moisture absorbing capacity at 50%RH, after 2 h.

tion, surface crosslinking, or excess addition of potassium hydroxide. Table I shows their effects on WAC and MAC of the sample.

Effect of Modification on WAC and MAC. The prepared PAA-K was screened using a stainless sieve before modifying it with 90% degree of neutralization to investigate the effect of particle size: As the particle size of the reference sample decreased from 450 to 50 μm, its WAC greatly increased from 118 to 155 g, whereas its MAC (39-40%) was independent on the particle size (Sample # 1-3). Therefore, WAC and MAC for the modified samples were measured by using the large particle of average 450 μm, which is easy to handle and process from an industrial point of view.

In order to produce a new modified dehumidifying agent with better WAC and MAC than the reference sample #3, we tried to polymerize the acrylic acid potassium salt monomer solution of 100% degree of neutralization with the same procedure mentioned earlier. However, the rate of polymerization for this sample was five times slower than the monomer solution of 90% and also the productivity of the resulting polymer was about two times lower because of the decreased solubility of the acrylic acid potassium salt against water. Thus, instead of using a 100% neutralized monomer solution, the sample #3 was after-treated with potassium hydroxide aqueous solution to additionally neutralize the 10% acrylic acid that is still remaining inside the PAA-K chains after the polymerization. As a result, the modified sample #5 showed almost two times increase in WAC and about 25% increase in MAC even at 50%RH than the reference sample #3.

On the other hand, in case of excess addition of potassium hydroxide to the sample #3, the MAC of the samples # 6 and 7 increased slightly (from 49 to 51 and 52%), but their WAC decreased in half (from 210 to 133 and 120 g). Such a significant decrease results from electrostatic repulsion between negative charges of PAA-K and excess potassium hydroxide ions of 10-20%.[1] Besides these modifications, the introduction of surface crosslinking into the sample #3 resulted in the decrease of WAC without the increase of MAC (sample #4). The correlation between WAC and MAC was not found in this study. In our previous article,[15] we reported that MAC and MAR was independent on degree of crosslinking incorporated into dehydrating polymers.

Comparison of MAC for Different Dehumidifying 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 RH and 32 °C, and was compared with that of the new dehumidifying agents (sample #3, 5, and 7) as shown in Figure 1. From the viewpoints of MAC, 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 calcium chloride became an aqueous solu-
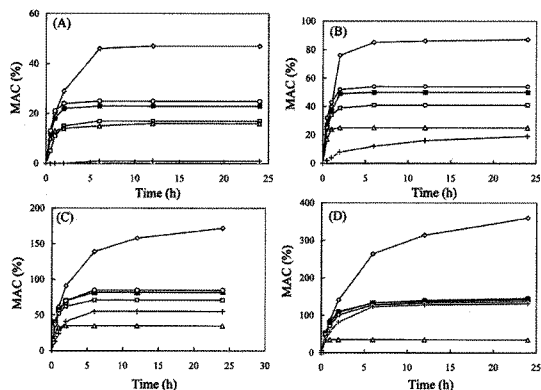
Figure 1. Moisture absorbing behaviors of different dehumidifying agents at 32 °C under different relative humidity: 30 (A), 50 (B), 70 (C), and 90%RH (D); sample #7 (○), sample #5 (■), sample #3 (□), calcium chloride dihydrate (◇), silica gel (△), and K-SAM (+).
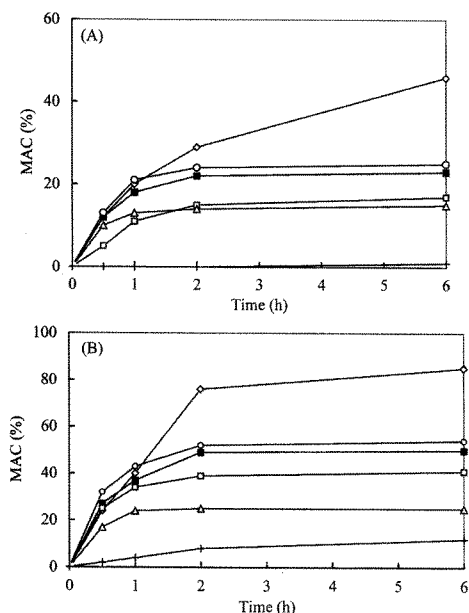
tion after absorbing moisture in air at highly humid condition of more than 50%. Therefore, it is used only as a simple desiccant, not as a dehumidifying agent for HERECS as well as food and electronic packaging. Silica gel showed 16-35% of MAC under the test conditions. At the lowest RH of 30%, the MAC of silica gel was similar to that of the reference sample #3. However, the maximum MAC of silica gel was reached at 70%RH and did not increased any further even with increasing RH concentration. On the other hand, the K-SAM displayed dramatic change of MAC from 1 to 131% depending on the concentration of RH: At low RH of below 50%, it showed much lower MAC than silica gel. On the contrary, at higher RH of above 70%, it exhibited more than twice of MAC than silica gel. However, it is still hard for silica gel and K-SAM to be applicable to the HERECS that requires high MAC and fast initial absorbing rate at low RH of below 50%.

In addition to these conventional dehydrating agents, the new modified samples #5 and 7 showed much better MAC and faster moisture absorbing rates than either silica gel or the reference sample #3 as well as the K-SAM at all test conditions. The distinct improvement of the modified samples was shown especially at the low RH of below 50%. Their MAC was about 1.5 times of the MAC of the reference sample #3 (22-24% vs. 15%) after 2 h at 30%RH and also 1.25-1.33 times at 50%RH. However, the effect of the modification of the reference sample (1.33 to 1.08 times) becomes less significant as the RH increases from 50 to 90%. Moreover, the maximum MAC (23-54%) for the modified samples was almost achieved within 2 h at below 50%RH. On the other hand, the sample #7, which is added in 20% excess of potassium oxide, was 5-10% high in both MAC and initial absorbing rate compared with the sample #5 with 100% degree of neutralization. However, the pH of the
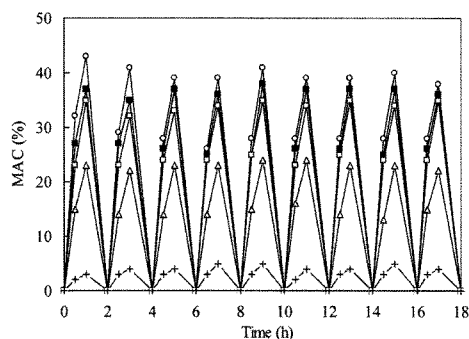
resulting swollen gel was much higher (10.7) than that of the latter gel (8.6). Such high pH offsets the merits because of safety issues in scale up processing and corrosion problems in practical applications. In addition, the swollen gel of the new samples retained the shape of the original particles even after reach 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 under pressure. The gel can be dried to the original shape under reduced pressure and reused as a dehumidifying agent. Such characteristics are essential requirements for the development of HERECS for energy saving.

Surprisingly, at all test conditions of 30-90%RH, MAC of all of our samples was higher within 30 min than that of calcium chloride, the best desiccant material. In particular, the initial MAR of the modified sample #7 was faster than that of calcium chloride up to 1 h even at the 50%RH, as shown in Figure 2. These also are a critical quality for HERECS.
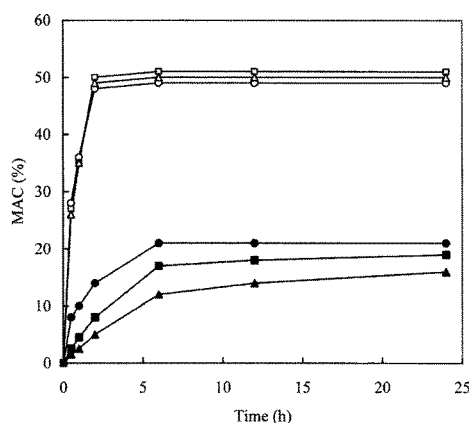
Moisture Absorption-Desorption Behavior. The MAC for different dehumidifying agents was measured as a function of either time or number of repeats to confirm the reliability of their moisture absorption-desorption behaviors, as shown in Figure 3. According to the data, the sample #7 had the highest MAC and their MAC was in order of #7 > #5 > #3> silica gel > K-SAM at 50%RH. Such trend was consistent with that of the moisture absorbing characteristics described earlier. All the synthesized samples were excellent in reli-

Figure 3. Moisture absorption-desorption behaviors of different dehumidifying agents at 32 °C and 50%RH: MAC by time; sample#7 (○), sample #5 (■), sample #3 (□), silica gel (△), and K-SAM (+).

Figure 4. Moisture absorbing behaviors with different particle sizes at 32 °C and 50%RH for the sample #5 (50 μm, ○; 200 μm, □; 450 μm, △) and K-SAM (50 μm, ●; 200 μm, ■; 450 μm, ▲).

ability as their MAC was remained even after repeating the absorption-desorption test nine times. On the other hand, calcium chloride dehydrate turned into liquid even after repeating the absorption-desorption test three times.

Effect of Particle Size. Figure 4 exhibits the effect of the particle size on the MAC of the modified sample #5 and K-SAM. The MAC of the commercial superabsorbent K-SAM gradually increases (about 2 times after 6 h) as its particle size becomes smaller (450 to 50 μm). However, the MAC of the sample #5 was almost constant regardless of its size. On the contrary, its MAC slightly increases as the size decreases.

Therefore, we concluded that the differences of MAC and MAR for the new dehumidifying agents do not result from their particle size. Such phenomenon results from low concentration of water molecules in moisture relative to the number of hydrophilic groups connected to the polymer chains.[15]

Figure 2. Comparison of initial absorbing rate for different dehumidifying agents at 32 °C under low RH of 30% (A) and 50% (B) RH; sample #7 (○), sample #5 (■), sample #3 (□), calcium chloride dihydrate (◇), silica gel (△), and K-SAM (+).

Conclusions

A crosslinked poly(acrylic acid potassium salt) based new dehumidifying agent was synthesized via solution polymerization. To achieve high MAC and fast MAR at low RH of below 50%, the resulting crosslinked polymer was additionally neutralized with potassium hydroxide or crosslinked after the polymerization. As a result, the modified polymers showed 25 to 33% increase in MAC relative to the sample before the modification and fast MAR with which they reached the MAC of over 80% within 1 h. Moreover, high MAC was maintained during repeated moisture absorption and desorption tests. The dependence of the MAC and MAR of the samples on surface crosslinking, particle size, or morphology was nearly not observed.

With high MAC, fast initial MAR, robust moisture absorbing property even after multiple use, and independence of MAC on surface crosslinking, particle size, and morphology, the new dehumidifying agents have advantages over conventional dehydrating agents such as silica gel and K-SAM. Therefore, the newly synthesized polymers could be very useful as a novel humidifying material for the carrier of HERECS as well as a dehydrating agent for food and electrical assemblies packaging.

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