

Undesirable Effects of Heating on Hydrogels

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Received 22 August 2007; accepted 26 January 2008

DOI 10.1002/app.28148

Published online 15 September 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Heating is the most conventional drying method for removing water from as-synthesized hydrogels in laboratory and industry. In this article, the effects of the heating temperature (60–200°C) and time (10 min–24 h) on swelling properties of highly absorbent hydrogels based on 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylic acid (AA), potassium acrylate (KA), and acrylamide (AM) were studied. Crosslinkers methylene bisacrylamide (MBA) and poly(ethyleneglycol) dimethacrylate (PEGDMA) were used in the syntheses. Depending on the hydrogel structural composition and its drying temperature and time, the swelling capacities were extremely changed. Generally, AA-, KA-, and AM-based hydrogels showed more hydrolytic-thermal stability than the corresponding AMPS-based hydrogels. MBA-crosslinked hydrogels generally exhibited higher vulnerability against heating. Swelling of

PEGDMA-crosslinked poly(AM-KA-AA) hydrogel was greatly increased after heating, whereas its analogous AM-free sample exhibited huge loss of swelling. PEGDMA-crosslinked poly(AMPS) samples also exhibited swelling reduction after drying. Rheological studies showed that the storage modulus was highly reduced (~ 5200 Pa) after heating of MBA-crosslinked poly(AMPS) hydrogels, which reconfirmed the crosslink cleavage. Mechanistic discussions were proposed for the thermal-induced swelling changes. It was concluded that the chemical nature of both crosslinker and monomer must be taken into consideration to choose the temperature and time of the hydrogel drying. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3420–3430, 2008

Key words: hydrogels; swelling; 2-acrylamido-2-methylpropane sulfonic acid; methylenebisacrylamide; rheology

INTRODUCTION

Hydrogels are hydrophilic polymers that can absorb and retain large amounts of water and physiological solutions.¹ Special hydrogels are being used in hygienic and agricultural applications,^{1–2} controlled drug delivery,^{1–5} water swelling rubber,⁶ coal dewatering,⁷ and so on.

Hydrogels are mostly prepared based on acrylic monomers such as acrylic acid and its salts^{1,8,9} and acrylamide.^{10,11} Compound 2-acrylamido-2-methylpropanesulfonic acid (AMPS) is an interesting acrylic monomer, which can be used for hydrogel preparation. It is a strong organic acid that is sufficiently dissociated to give mobile ions without need of neutralization stage.¹² The AMPS-based hydrogels have electroresponsive properties.⁷ They can be particularly used in biochemistry for skin contact electrodes⁷ and muscle actuator (gel robots).¹³

Bifunctional acrylic compound *N,N'*-methylenebisacrylamide (MBA) is the most common water-soluble crosslinking agent that is vastly used for preparing nearly all hydrogels.^{8–12,14–23} A literature review showed no published report on the synthesis and study of full-AMPS hydrogels. However, in few

articles dealing with very limited study of full-AMPS hydrogels,^{12,21,23} the oven-drying method (i.e., direct heating; the most conventional method for laboratory and commercial drying) has not been used for the drying of the as-synthesized homopoly (AMPS) hydrogels. Instead, freeze drying,²³ nonsolvent dewatering,²¹ or room-temperature drying¹² have been applied.

On the other hand, during several-year working on hydrogels,^{8–12} we sometimes used to encounter with undesired swelling capacity enhancement for some of lengthily hydrated or exceedingly heated hydrogel samples crosslinked by MBA.

Infrequently, the unwanted phenomenon was extensive, so that it used to lead to a loosening state, becoming mushy or slimy. Most recently, in a research on MBA-crosslinked poly(AMPS) nanocomposite hydrogels, we found that the oven-dried hydrogels were surprisingly dissolved in water. This unfavorable behavior motivated us to study deeply the effect of heating time and temperature on hydrogels, typically poly(AMPS) in comparison with other important commercial hydrogels, i.e., poly(AA-KA) and poly(AM-AA-KA).

It is occasionally reasoned that the chemical nature of crosslinker MBA is probably the origin of the hydrogel network loosening. It has been mentioned that an extremely slow cleavage of MBA residue was occurred in some MBA-crosslinked hydrogels

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used as bioerodible microspheres tested *in vivo* or used for enzyme immobilization carriers.²⁴ In fact, it is experienced that MBA itself can be cleaved via hydrolysis in hot water to form acrylamide.²⁵ To obtain organized practical evidences for the decrosslinking of MBA residue, we aimed some practical investigations on the important phenomenon.

To the best of our knowledge, no prearranged work has yet been published on the effects of heating of MBA-crosslinked hydrogels on their swelling and rheological behaviors, even for those based on the conventional acrylic monomers such as acrylic acid, acrylamide, and AMPS. These studies are also important industrially. It has been previously implied that the drying stage should not be simply taken a step for removing water from the as-synthesized hydrogel after polymerization stage. We have previously exhibited, via DSC studies on MBA-crosslinking polymerization of neutralized acrylic acid, which the extent of reaction (i.e., the overall value of the reaction advancement) was at most around 56% after the gelation point.²⁶ It means the rest of the network would be formed during the next stage of production, that is, oven drying. Therefore, drying is an imperative stage in the related hydrogel manufacturing process as well.

This work deals with the study of thermal effects on MBA-crosslinked poly(AA-KA), poly(AM-KA-AA), and poly(AMPS) hydrogels. Polyethyleneglycol dimethacrylate (PEGDMA), as a water-soluble macrocrosslinker, is also used to practically compare the crosslinker nature-swelling property relationships. The behavioral evidences, swelling capacity, and rheological properties were investigated for studying the unfavorable effects of heating on the hydrogels.

EXPERIMENTAL

Materials

AMPS, acrylamide (AM), ammonium persulfate (APS), *N,N'*-methylenebisacrylamide (MBA), and acrylic acid (AA) were purchased from Merck and used as received. When desired, AA was partially neutralized (75 mol %) by potassium hydroxide solution to obtain a mixture of potassium acrylate (KA) and AA. Polyethyleneglycol dimethacrylate 330 (PEGDMA), the macrocrosslinker manufactured by Aldrich, was used without further purification.

Synthesis of poly(AMPS) hydrogels

The monomer AMPS (30.0 g) was dissolved in 30 g distilled water, and crosslinker (MBA or PEGDMA) and the initiator APS solutions were then added to the monomer solution. The concentration of the initiator and crosslinker were fixed at 0.065 and 0.32 mM, respectively. After heating at 70°C and gelation,

the elastic samples were removed from the reactor, cut to small pieces, and kept at different temperatures in a forced draft oven. AM-KA-AA (mole ratio 60 : 30 : 10) and AA-KA (mole ratio 25 : 75) hydrogels have been synthesized according to a previously reported method.¹⁰

Swelling measurements

A 0.200-g sample of polymer (W_1) was dispersed in 500 mL of distilled water and allowed to swell for 2 h to reach equilibrium. The dispersion was filtered through polyester gauze, and excess water was removed thoroughly. The hydrated gels were then reweighed (W_2). Water absorbency or swelling capacity (W_e , g/g) was calculated by dividing W_2 to W_1 eq. (1).

$$W_e = F \left(\frac{W_2}{W_1} \right) \quad (1)$$

For the majority of samples (i.e., completely dried samples), the coefficient F is equal one. In the few cases of the as-synthesized and partially dried samples, F was calculated as follows:

For as-synthesized samples:

$$F = \frac{W_{\text{mix}}}{W_{\text{mc}}} \quad (2)$$

For partially dried samples:

$$F = \frac{W_{\text{pd}}}{W_{\text{cd}}} \quad (3)$$

where W_{mix} , W_{mc} , W_{pd} , and W_{cd} stand for total weight of reaction mixture, weight of monomer(s) and crosslinker, weight of partially-dried sample, and weight of completely dried sample, respectively.

Instrumental measurements

The rheological measurements were performed using a Paar-Physica oscillatory rheometer (MCR300, Germany) at 25°C with parallel plate geometry (plate diameter of 25 mm, gap of 3 mm). The detailed procedure was previously reported.²⁷ Sample/water ratio was identical for all of the measurements. Elemental analysis was performed by a CHNOS analyzer system (elementar, model vario EL III).

RESULTS AND DISCUSSION

MBA-crosslinked poly(AMPS) hydrogels

In the course of preparation of a series of MBA-crosslinked copolymeric hydrogels based on AMPS,

some full-AMPS samples were also synthesized and, as usual, oven-dried at above 60°C. They were unexpectedly dissolved in water instead of absorbing water and swelling. Because crosslinking is the most important structural/property issue of a polymer network, this strange behavior, preliminarily attributed to a kind of crosslink cleavage, encouraged us to study the undesired phenomenon systematically. For this purpose, swelling capacity of the samples at different drying time and temperature was measured.

Figure 1 shows swelling capacity variation of MBA-crosslinked poly(AMPS) hydrogel heated at 60°C for 0–12 h. The heating time of zero is related to the as-synthesized hydrogel product before drying. The swelling capacity of the as-synthesized sample was 10 g/g. It was increased to 41.3 g/g after 12 h heating at 60°C. Therefore, the swelling capacity increase was not considerable when it was oven-dried at this temperature. However, the slight swelling enhancement may be preliminarily attributed to some crosslink degradation.

In another series of experiments, swelling capacity of the MBA-crosslinked poly(AMPS) hydrogel oven-dried at 80°C was measured at different times. Two distinctive regions can be seen in the swelling-heating time profile (Fig. 2). In the first region (left part), swelling capacity was slowly increased with time. In this region, swelling capacity was increased from 44 g/g after 2 h, to 281 g/g after 12 h oven drying. In the second region, swelling capacity was vastly increased with increasing of the drying time. It was increased to 505 and 900 g/g after 13 and 15 h oven drying, respectively. The samples were completely soluble in water after 15 h of heating at 80°C. This indicated that, most probably, the MBA-originated crosslinks were cleaved during the drying stage at 80°C, so that the gel network was completely decrosslinked after 15 h.

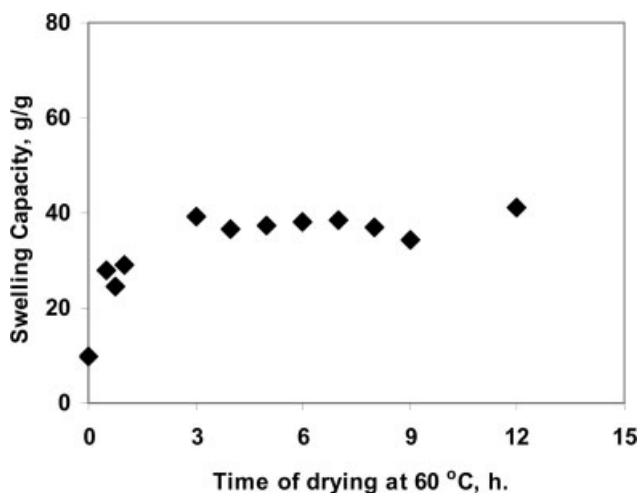


Figure 1 Swelling capacity versus time of drying at 60°C for MBA-crosslinked poly(AMPS) hydrogel.

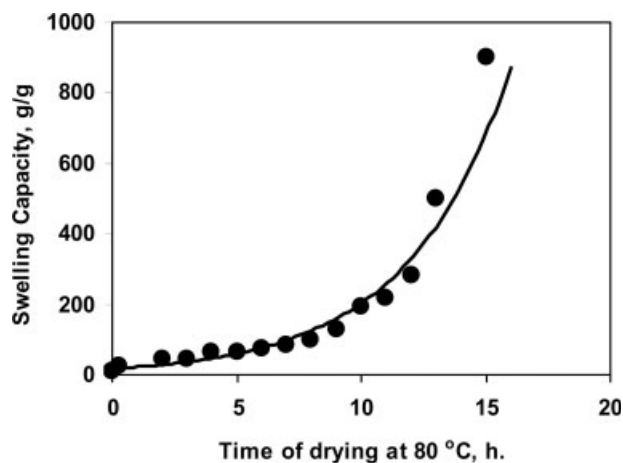


Figure 2 Swelling capacity versus time of drying at 80°C for MBA-crosslinked poly(AMPS) hydrogel.

Thermoaccelerated behavior of swelling enhancement versus drying temperature was examined at higher temperatures. According to Figure 3, swelling capacity was increased initially from 10 to 161 g/g after 2 h heating at 100°C. Then, the swelling was immensely increased with the drying time, so that it was enhanced to 427 g/g after 3.20 h. This sharp swelling increase was continued to reach to 790 and 945 g/g after 4 and 6 h, respectively. After 6 h heating at 100°C, the MBA-crosslinked poly(AMPS) hydrogel sample was totally soluble in water. Severer destructive effect of temperature was observed when the hydrogel was dried at 120°C (Fig. 3). At this temperature, swelling capacity was enhanced up to 231 and 724 g/g just after 45 and 60 min, respectively. Therefore, at 120°C, the time of the hydrogel dissolution (the time required for the hydrogel to become completely water soluble) was immensely reduced to just about 1 h.

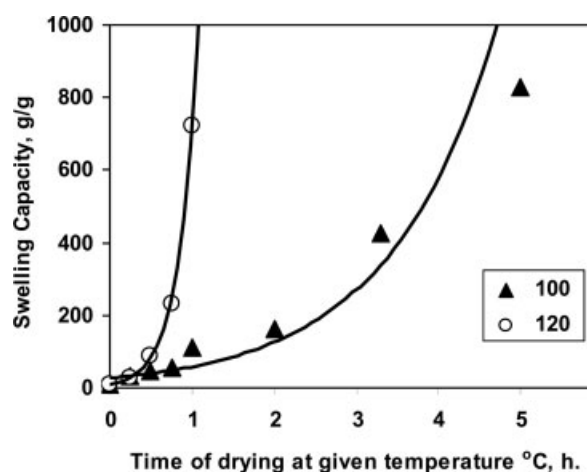


Figure 3 Swelling capacity versus time of drying at 100 and 120°C for MBA-crosslinked poly(AMPS) hydrogel.

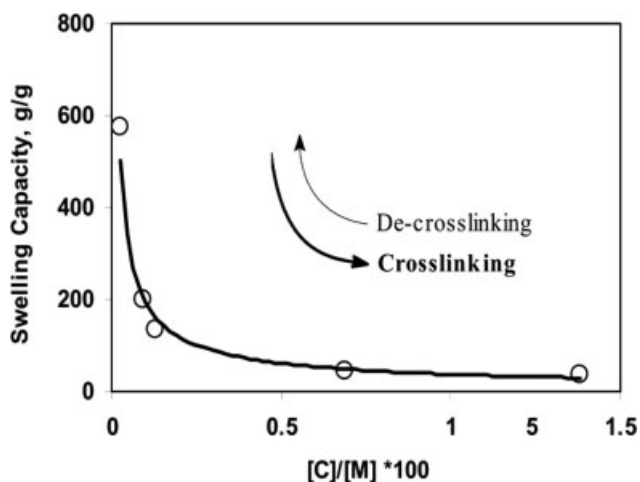


Figure 4 An archetypal plot of swelling capacity versus [crosslinker]/[monomer] for an acrylic acid based hydrogel. Data extracted from ref. 28.

Finally, it should be pointed out that thermal studies of poly(AMPS) hydrogels at higher temperatures could not be carried out due to fast polymer degradation. At 180–200°C, for example, it was vigorously decomposed, and the remained parts had foamy hydrophobic characteristics. Therefore, this heat treatment did not yield a measurable product.

Indirect effect of drying time on crosslink density and swelling

This is well-known that the swelling capacity of hydrogels has power law relationship with the crosslink density or crosslinker concentration. As a representative example, the relationship for the crosslinked poly(AA-KA) is exhibited in Figure 4.²⁸ Swelling capacity is highly dependent on crosslinker concentration, $[C]$, at very low levels of $[C]$. Conversely, it became nearly $[C]$ -independent at high-crosslink densities. The overall behavior is often shown in eq. (4).

$$\text{Swelling} = k[C]^{-n} \quad (4)$$

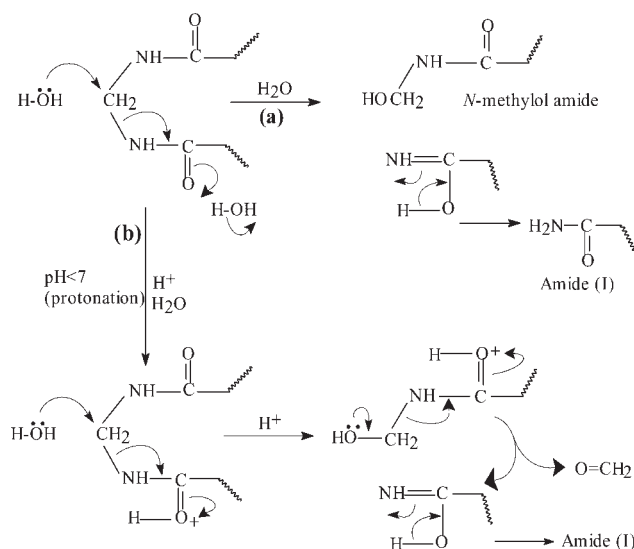
Here, inverse relationship was observed during heat treatment of the MBA-crosslinked hydrogels (Figs. 2 and 3). The as-synthesized sample has high-crosslink density. At the early minutes of heat treatment, MBA crosslinks are partially degraded, but still there are lots of crosslinks, therefore swelling is enhanced very slowly. Gradually, more and more crosslinks are cleaved during heat treatment, and the crosslink density is decreased so much that small changes in the crosslink density has much influence on swelling capacity. Consequently, swelling capacity is highly increased at long time of drying at a given temperature. Therefore, power law relationships with

reverse trends can be seen from Figures 2 and 3. The reverse trends are originated from the opposite occurrence of crosslinking (i.e., de-crosslinking) that is happened during the oven-drying (see Rheological study).

Cleavage of MBA crosslinks

To find the reasons for the hydrogel degradation, chemical structure of the crosslinker methylenebisacrylamide (MBA) can be considered. It was previously reported that bisacrylamide and bismethacrylamide crosslinkers, which have more than one methylene group in their structure, were hydrolytically stable.²⁹ This stability characteristic has not been mentioned for MBA. It can be implicitly concluded that MBA is not hydrolytically stable. However, MBA is the most conventional crosslinking agent for hydrogel preparation. In this organic molecule, two electronegative atoms are bonded to one carbon atom. According to organic structural principles, such bonding cannot be very stable at normal electronical and sterical conditions. The methylene group has a relatively positive charge; therefore, it can be attacked easily by a nucleophile such as the protic solvent water under normal or acidic conditions (Scheme 1).

The reaction is catalyzed and progressed more easily (Scheme 1b). The oxygen of carbonyl groups is protonated via H^+ abstraction. Then, the nucleophilic attack of H_2O is facilitated, and the decrosslinking reaction is accelerated. On the other hand, some crosslink formation through cyclization of the AMPS residues is not impossible (see the next sec-



Scheme 1 Noncatalyzed (a) and acid-catalyzed (b) hydrolytic degradation of a crosslinker originated from the crosslinker N,N' -methylene bisacrylamide in a polymer network.

tion); however, its extent and role are very insignificant in comparison to the cleaving behavior of the MBA crosslinks.

Pegdma-crosslinked poly(AMPS) hydrogels

In another series of experiments, for synthesizing full-AMPS hydrogels, a different crosslinker, PEGDMA, was replaced with MBA. It is a water-soluble macromolecular crosslinker with an aliphatic polyether long linear chain terminated to methacrylate groups. Again, the as-synthesized hydrogel products were dried by heating, as the most conventional method of drying.

The macrocrosslinker PEGDMA-crosslinked samples were also studied at different times and temperatures similar to what done for the MBA-crosslinked samples. Swelling capacity versus time of drying at 80°C for PEGDMA-crosslinked poly(AMPS) hydrogels is shown in Figure 5. Swelling capacity was 86 g/g after heating for 1 h. It was slowly increased to 124 g/g after heating for 22 h. Considerable swelling enhancement was not observed for PEGDMA-crosslinked poly(AMPS) sample dried at 80°C. Therefore, it can be obviously concluded that at this drying temperature (i.e., 80°C), PEGDMA crosslinked-hydrogels are more stable than MBA-crosslinked samples. In addition, drying temperature should not be more than 60°C for MBA-crosslinked hydrogels, but PEGDMA-crosslinked AMPS hydrogels can be dried at 80°C without considerable adverse effect on the swelling properties (see also Rheological study). It may also be taken as an industrially important advantage of PEGDMA in comparison with MBA, because the time-consuming stage of drying will be relatively shortened for the PEGDMA-crosslinked hydrogels.

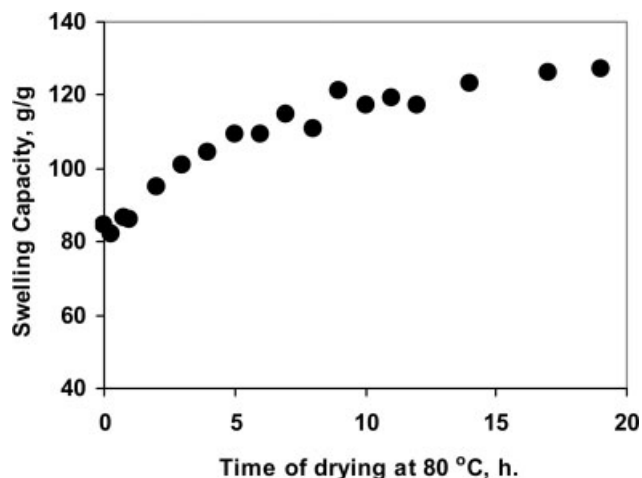


Figure 5 Swelling capacity versus time of drying at 80°C for PEGDMA-crosslinked poly(AMPS) hydrogel.

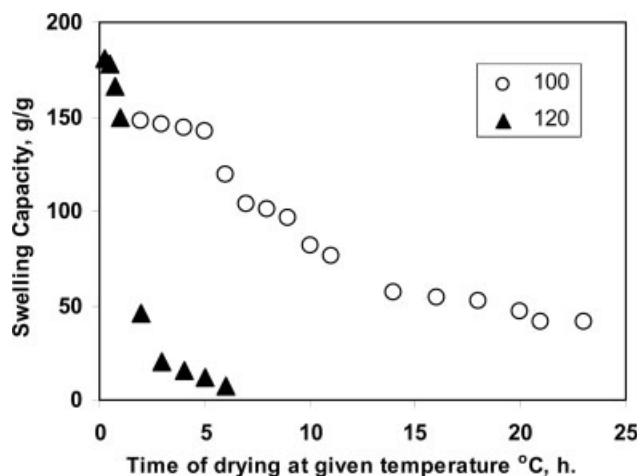
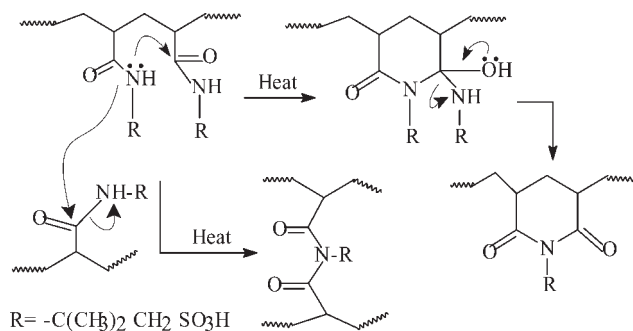


Figure 6 Swelling capacity versus time of drying at 100 and 120°C for PEGDMA-crosslinked poly(AMPS) hydrogel.

Swelling capacity of the PEGDMA-crosslinked AMPS hydrogels versus drying time was also studied at higher temperatures 100 and 120°C, as shown in Figure 6. It is clearly observed that heating of this sample is totally different from that of MBA-crosslinked hydrogels illustrate in Figure 3. Swelling capacity is measured to be 181 g/g after drying at 120°C for 15 min. It is smoothly decreased to 150 g/g after 1 h. Then, a remarkable loss of swelling capacity was observed with the drying time increase, so that the swelling capacity was reduced to 46 g/g after 2 h heating at 120°C. Swelling capacity was then gradually decreased to lower amounts, e.g., 7.4 g/g after 7-h drying at 120°C.

Physical appearances of PEGDMA- and MBA-crosslinked AMPS hydrogels before and after drying at 120°C are also different. Both as-synthesized samples were transparent before heat treatment. After oven drying, MBA-crosslinked sample became transparent brownish, but the PEGDMA-crosslinked sample was a brittle opaque solid with light yellow color. When its particle was put in water, it automatically started to be shattered to smaller particles, while making sound (quiet rattling). This surprising macroscopic destruction produced tiny sandlike particles without the ability of swelling.

All the obvious visual and behavioral differences between the MBA- and PEGDMA-crosslinked AMPS hydrogels are rationally attributed to the difference in the chemical nature of the crosslinking agents. It seems that the PEGDMA crosslinks have not been disconnected during oven-drying at high temperature (e.g., 120°C); otherwise, swelling capacity had to be increased as observed in the case of the MBA-crosslinked samples (cf. Figs. 3 and 6). Conversely, the swelling capacity is decreased with the increase of drying time. It generally guided us to two proba-



Scheme 2 Proposed thermal promoted cyclization and postcrosslinking of PEGDMA-crosslinked poly(AMPS) hydrogel.

ble phenomena happened during the drying stage: (a) gradual loss of hydrophilicity via removing and/or transforming the hydrophilic groups to hydrophobic functions, (b) a kind of crosslink formation.

A simple mechanism proposes a partial scissoring of SO₃H groups of poly(AMPS) to evolve sulfur trioxide gas. Losing the water soluble sulfonic acid groups of the hydrogels has to reduce hydrophilicity and swell ability in water. This occurrence, however, was not confirmed by elemental analysis data. The elements content, particularly sulfur content, of the PEGDMA-crosslinked poly(AMPS) sample dried at 120°C during 7 h (S 12.61, C 34.19, H 6.65, N 5.45%) was measured to be nearly identical with that of the same sample dried at the same temperature for 1 h (S 12.39, C 34.38, H 6.77, N 5.50%). As a result, thermal scissoring and the removing of SO₃H groups were disproved.

An intramolecular cyclization may also be probable (Scheme 2). Aggour³⁰ reported the possibility of such reaction during ion beam irradiation of poly(AMPS) resulted in brittleness and insolubility of the irradiated samples. Actually, our samples dried at 120°C are either water insoluble or brittle, being in agreement with the reported work.³⁰ Indeed, such reaction is also possible between the pendant groups of adjacent polymer chains. Because of the chemical and macromolecular restrictions, such interchain reaction is not very favorable; however, this fewer probable crosslinking interaction can extremely affect the swelling capacity. Because the intensive effect of crosslink density on swelling capacity is very well known to be a power-law relationship (Fig. 4), the very similar trend, power-lawlike decreasing behavior, exhibited in Figure 6, may be taken as a confirmation of such postcrosslinking.

MBA-crosslinked AA- and AM-based hydrogels

Swelling capacity of AA-KA sample at two different drying temperatures (120 and 160°C) is illustrated in Figure 7. Swelling capacity is nearly unchanged for

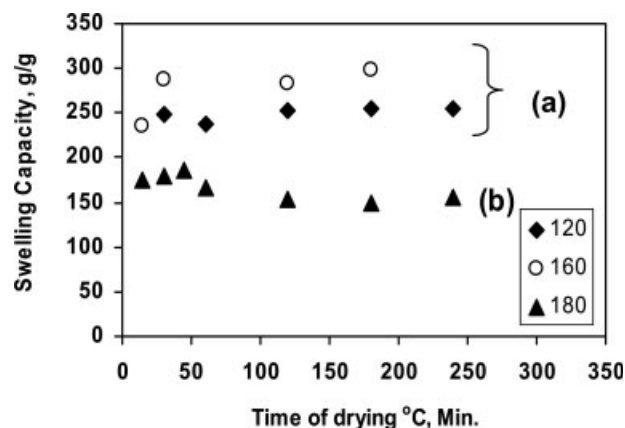


Figure 7 Swelling capacity versus time of drying at (a) 120 and 160°C for MBA-crosslinked hydrogel based on AA-KA with mole ratio 25 : 75, and (b) 180°C for MBA-crosslinked hydrogel based on AM-KA-AA with mole ratio 60 : 30 : 10.

this sample. For instance, swelling capacity only changes between 230 and 250 g/g for the sample, which was dried at 120°C for a few minutes to about 3 h. Similar behavior has been observed for the AM-KA-AA hydrogel (Fig. 7). The swelling capacity was not much changed with increase of drying time and an individual temperature. In conclusion, MBA-based crosslinks in AA-KA and AM-AA-KA-based hydrogels are thermally stable. These interchain linkages are stable at different temperatures up to 180°C.

For drying at 200°C, different swelling behavior was clearly observed for AA-KA and AM-KA-AA-based samples (Fig. 8). Swelling capacity of AA-KA-based sample was 320 g/g after heating at 200°C for 15 min. It was highly increased to 980 g/g after heating for 4 h, leading to a totally dissolvable product. However, swelling capacity increase obtained from heat treatment was lower for AM-AA-KA-based hydrogel. It was linearly increased by the drying

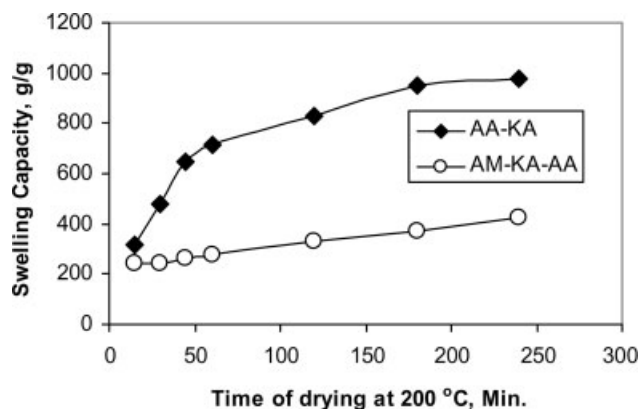
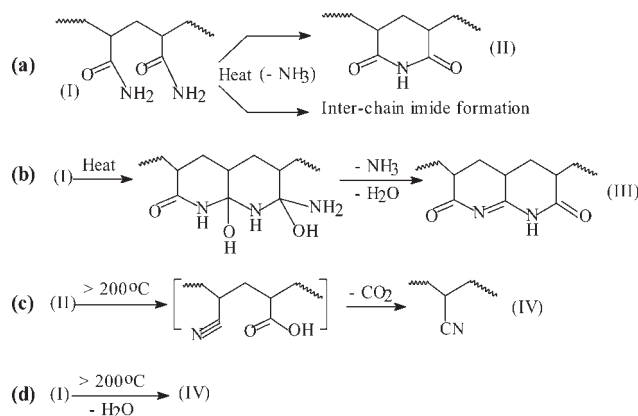


Figure 8 Swelling capacity versus time of drying at 200°C for MBA-crosslinked hydrogels based on AA-KA (mole ratio 25 : 75) and AM-KA-AA (mole ratio 60 : 30 : 10).



Scheme 3 Well-known nonchain breaking reactions for thermal decomposition of AM homo- and copolymers. (a) Deammoniation via monocyclic imidization (the corresponding interchain reaction is of less importance), (b) deammoniation dehydration via bicyclic imidization, (c) decarboxylation via imide breakdown, and (d) dehydration.

time gradually from 243 to 425 g/g after heating at 200°C for 4 h. The difference may be ascribed to the internal medium with slightly acidic nature locally formed from carboxylic acid groups having considerable effect on cleavage of crosslinkages originated from MBA (Scheme 1b). The AA-KA-based hydrogel composes 25 mol % acrylic acid, while AM-KA-AA-based sample contains only 10 mol %. The latter, that is, AM-KA-AA with mole ratio 60 : 30 : 10, is decrosslinked slower than the former. Meanwhile, less considerably, an interchain imide formation (Scheme 3a) may also be contributed in the swelling loss of the AM-contained hydrogels heated at 200°C.

PEGDMA-crosslinked AA- and AM-based hydrogels

Swelling capacity of PEGDMA-crosslinked AA-KA hydrogels versus drying time at 200°C is illustrated in Figure 9. Absorption capacity was 106 g/g after 15 min. It was considerably diminished to 29 g/g after 5 h. Again, a decreasing trend with a power-law-shape (see Fig. 4) indicates an increasing crosslinking similar to that of described for poly(AMPS) and poly(AA) hydrogel (see Fig. 6).

A preliminary assumption can be decarboxylation; the scissoring of COOH and COO⁻ groups to evolve CO₂ gas and yield a less hydrophilic network. But, it has been proved that it could only be happened at the temperatures in excess of 200°C. According to the literature, linear poly(AA)³¹ and poly(KA)³² evolve CO₂ when they are heated around 300 and 400°C under nitrogen, respectively. At lower temperatures, before decarboxylation, however, dehydration could occur by intra- and/or intermolecular reaction of carboxyl groups to yield six-membered cyclic an-

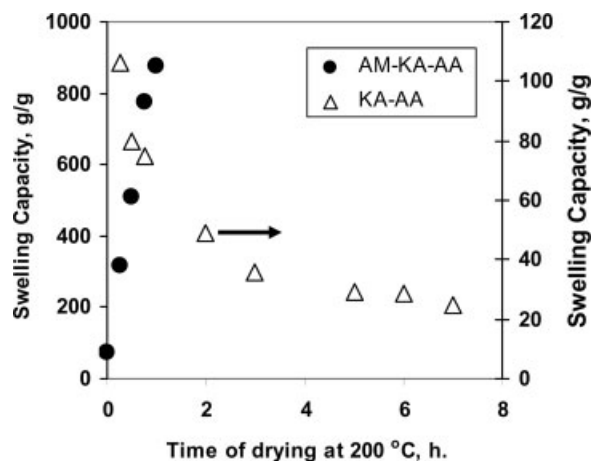
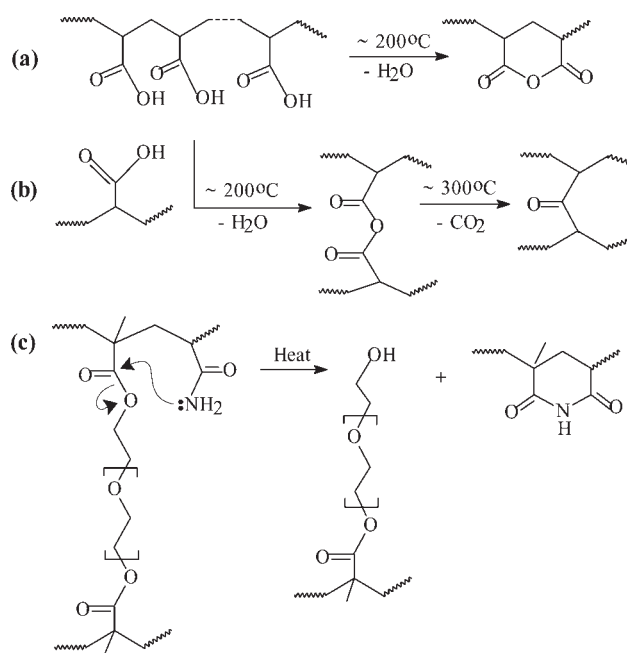


Figure 9 Swelling capacity versus time of drying at 200°C for PEGDMA-crosslinked hydrogel based on AA-KA (mole ratio 25 : 75) and AM-KA-AA (mole ratio 60 : 30 : 10).

hydride and/or anhydride crosslinks³¹ (Scheme 4a). Using solubility studies, researchers³² showed that the anhydride formation occurred almost exclusively by the intramolecular process when poly(AA) was heated at 170°C. If anhydride formation occurs by water elimination from among neighboring pairs, occasionally isolated COOH groups will be left, which cannot dehydrate by that mechanism, but must do so through intermolecular anhydride formation. Presumably, higher temperatures would be required to proceed; also, crosslinking would result



Scheme 4 Thermal promoted dehydration of AA-contained polymers lead to (a) cyclic anhydride and, less extensively, (b) interchain linkage formation, (c) a probable mechanism for disconnection of the crosslink PEGDMA moiety via attack of the neighboring amide group.

from the reaction.³³ The anhydride crosslink may be transformed to hydrolytically stable keto-crosslink via thermal removing of CO₂ (Scheme 4b). Eisenberg et al.³³ pointed out that a dehydration temperature of over 200°C caused an enhancement in the glass transition temperature (T_g) of poly(AA) from 103 to 180°C. They emphatically attributed this substantial increase to a high crosslinking density.

However, when acrylamide (AM) was incorporated, the terpolymeric hydrogel poly(AM-KA-AA) showed a surprising inverse behavior. Swelling capacity versus drying time at 200°C for the hydrogels based on AM-KA-AA (mole ratio 60 : 30 : 10) is shown in Figure 9. Swelling capacity of as-synthesized sample was 80 g/g. It was highly increased to 318 g/g after only 15 min drying at 200°C. After 1-h drying, it was immensely increased to 876 g/g. Longer time of drying at 200°C resulted in a completely soluble product. What happens when AM is incorporated in the polymer network?

According to several works on thermal behaviors of AM homopolymers³⁴ and copolymers,³⁵ AM (co)polymers start to degrade around 200°C (the first region of decomposition). Upon heating, after removing the absorbed and bonded water, deamination is occurred; that is, NH₃ is released by imidization between adjacent amide groups on a chain or between amide groups on neighboring chains. This reaction has been reported to be occurred even during AM polymerization conducting at temperatures higher than 140°C.³⁶ The intramolecular imidization produces both mono- and bicyclic functional groups to evolve NH₃ and H₂O (Scheme 3). The monocyclic imide decomposes to evolve CO₂. This reaction as well as a dehydration reaction produces nitrile groups in a lesser extent at the first decomposition stage (~ 200–340°C). The imidization and dehydration, initiated in this stage, continue but are of minor importance to chain-breaking reactions occurring in the next decomposition stages at higher temperatures.³⁴ Leung et al.³⁵ specified that no single reaction can be attributed to each decomposition regions, although a major reaction seems to dominate. Furthermore, degradation reactions usually occur in and continue beyond one decomposition stage.

Because all the above-mentioned reactions lead to decreasing the water-solubilizing amide groups, the swelling capacity of the resulting heated hydrogel has to be diminished. Inversely, the swelling of PEGDMA-crosslinked AM-KA-AA hydrogels was enhanced upon heating. In addition, the swelling enhancement was very significant (Fig. 10).

The most possible reason for such huge swelling increase should be related to a kind of cleavage of crosslinks, similar to what observed for the MBA-crosslinked AM-KA-AA sample (Section 3.3, Fig. 8). At first, it was assumed that PEGDMA crosslinks

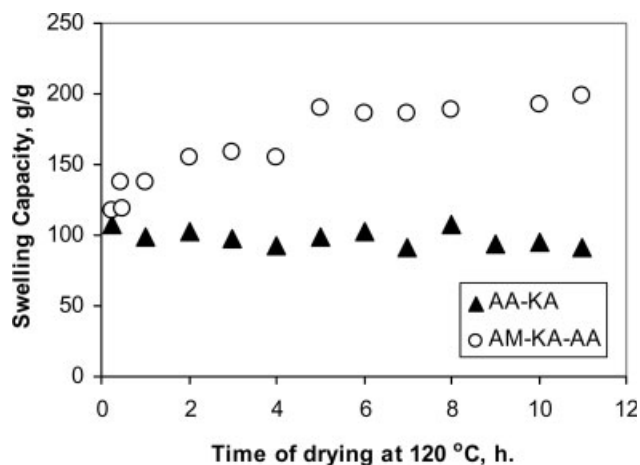


Figure 10 Swelling capacity versus time of drying at 120°C for PEGDMA-crosslinked hydrogel based on AA-KA (mole ratio 25 : 75) and AM-KA-AA (mole ratio 60 : 30 : 10).

were scissored to lead swelling enhancement and even dissolution of hydrogel. However, as described earlier and in PEGDMA-crosslinked poly(AMPS) hydrogels section, it was rationalized that PEGDMA was not cleaved in the heated AMPS- and AA-KA-based hydrogels. Therefore, the possibility of the thermal cleavage of PEGDMA crosslinks is obviated. Instead, a mechanism including disconnection of the crosslink PEGDMA by the neighboring amide is highly probable (Scheme 4c). Such reaction can also be chemically favored, because the formation of the cyclic imide (glutarimide) has been evidenced (Scheme 3a).

This cycloimidization crosslink-breaking reaction (decrosslinking) may be occurred even at lower temperatures very rarely; however, its effect is so great that it results in appreciable increase of swelling. This fact is shown in Figure 10 in comparison with the corresponding AM-free hydrogel. PEGDMA-crosslinked poly(AA-KA) hydrogel exhibited no swelling change when it was dried at 120°C. It also implies that a similar PEGDMA crosslink cleavage is not occurred in the AM-free hydrogels. In summary, as clearly exhibited in discriminating Figures 9 and 10, the presence of AM in the PEGDMA-crosslinked hydrogels causes an essential difference in their swelling behavior originated from the thermal treatment.

Rheological study

Rheological studies were carried out to follow gel strength of typical hydrogels heated during oven-drying process. We had previously shown that the swollen gel strength can accurately be determined by oscillatory rheometer with parallel plate geome-

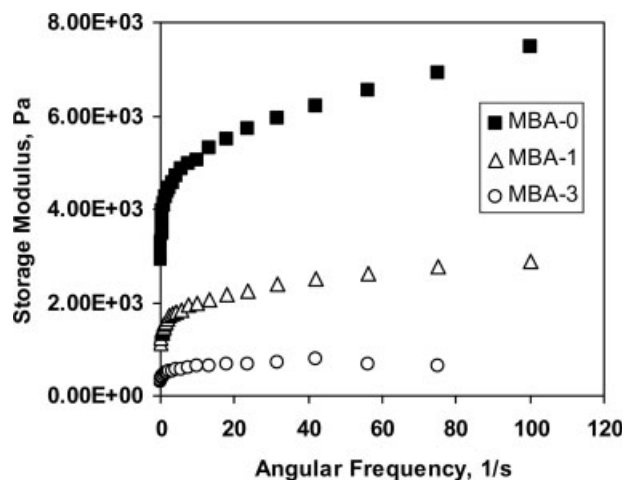


Figure 11 Storage modulus versus angular frequency for MBA-crosslinked poly(AMPS) hydrogel dried for different times. MBA-0 indicates the blank sample (as-synthesized gel dried overnight at room temperature). MBA-1 and MBA-3 are the same sample dried at 100°C after 1 and 3 h, respectively.

try.²⁷ The storage modulus can be taken as a measure of the mechanical strength of the hydrogel. Figure 11 shows storage modulus of MBA-crosslinked poly(AMPS) hydrogel dried at 100°C for different times comparing with a blank sample, MBA-0 or MBA-RTD (i.e., as-synthesized gel dried overnight at room temperature). It is obviously seen that storage modulus of the sample MBA-0 is considerably higher than that of the heated samples. In addition, it is reduced with the drying time from 1 to 3 h. Table I shows the storage modulus data obtained from the measurements run at 31.6 s⁻¹ angular frequency for the different samples. Storage modulus of MBA-RTD hydrogel was measured to be 5930 Pa. It was highly reduced (60%) to 2380 Pa after 1 h drying at 100°C. The modulus was further reduced to 716 Pa (87% reduction) after a 3-h drying.

Figure 12 shows the storage modulus of PEGDMA-crosslinked AMPS hydrogel. The modulus was nearly identical for corresponding blank sample and the

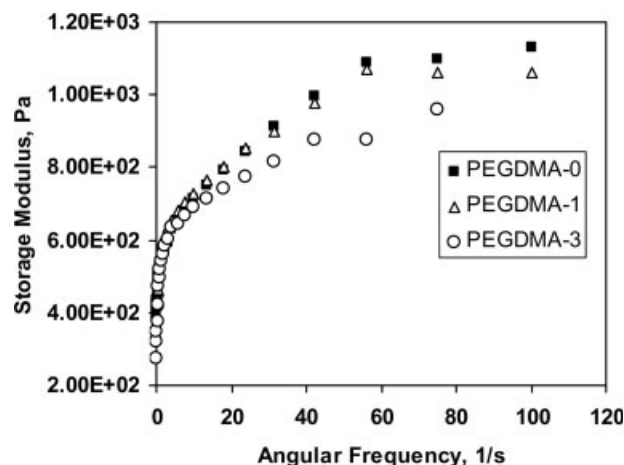


Figure 12 Storage modulus versus angular frequency for PEGDMA-crosslinked poly(AMPS) hydrogel dried for different times. PEGDMA-0 indicates the blank sample (as-synthesized gel dried overnight at room temperature). PEGDMA-1 and PEGDMA-3 are the same sample dried at 100°C after 1 and 3 h, respectively.

sample oven-dried for 1 h at 100°C. A small decrease in storage modulus is observed for the sample oven-dried for 3 h at the same temperature. A storage modulus of PEGDMA-RTD sample is 911 Pa. After heating for 1 and 3 h, it is only reduced to 898 and 818 Pa, respectively. A longer heating time (10 h at 100°C) diminishes the modulus to 634 Pa, that is, the mechanical strength of the swollen gel is reduced to the extent of 31% (Table I).

Storage modulus is related to the average molecular weight between crosslinks (M_c) through eq. (5):

$$G' = \frac{\rho RT}{M_c} \quad (5)$$

where G' is the relaxed rubbery modulus, ρ is density, R the gas constant, and T the temperature. The storage modulus has inversely changed with M_c . Increase of M_c means lower crosslink density leading to swelling enhancement. It is well known that swelling capacity and gel strength has inverse relationship, that is, the higher swelling capacity the lower gel strength will be.³⁷ It can be assumed that water acts like a plasticizer for acrylic hydrogel. Therefore, increase of water content causes decrease of storage modulus.

Here, swelling capacity of MBA-crosslinked poly(AMPS) hydrogels is highly increased with increase of drying time at high temperature (see MBA-crosslinked poly(AMPS) hydrogels section). Also, rheological studies show that storage modulus of these hydrogels is vastly decreased with the time of drying at a given temperature. These two observations indicate that MBA crosslinks has to be continuously degraded during oven drying. Therefore, M_c is

TABLE I
Rheological Properties of Poly(AMPS) Hydrogels Synthesized Using Crosslinkers MBA and PEGDMA

Crosslinker-drying condition	Storage modulus (Pa)	Modulus decrease (%)
MBA-0	5930	–
MBA-100°C, 1 h	2380	60
MBA-100°C, 3 h	716	87
PEGDMA-0	911	–
PEGDMA-100°C, 1 h	898	2
PEGDMA-100°C, 3 h	818	11
PEGDMA-100°C, 10 h	634	31

MBA-0 and PEGDMA-0 denote the hydrogel dried at room temperature. Angular frequency 31.6 s⁻¹.

increased with the drying time enhancing. Equation (5) shows a first-order inverse relationship between M_c and storage modulus. As a result, storage modulus will be decreased with drying time enhancement of the samples, as observed in the data given in Table I.

Another interesting point can also be observed from Table I data related to the modulus of the blank sample. It is seen that the modulus of MBA-RTD sample is considerably higher than that of PEGDMA-RTD sample. Equation (6) shows relation between storage modulus and number of crosslink sites per unit volume (v).³⁷

$$G' = vRT \quad (6)$$

By using the data of Table I,

$$G'_{\text{MBA}}/G'_{\text{PEGDMA}} = v_{\text{MBA}}/v_{\text{PEGDMA}} = 5930/911 = 6.5$$

The practical and theoretical value for the ratio $v_{\text{MBA}}/v_{\text{PEGDMA}}$ is 6.5 and 1, respectively, (in the synthesis, the crosslinker mol % for MBA- and PEGDMA-crosslinked AMPS hydrogels was chosen identical. Therefore, theoretical $v_{\text{MBA}}/v_{\text{PEGDMA}}$ will be 1). The higher practical value of $v_{\text{MBA}}/v_{\text{PEGDMA}}$ shows that MBA was more effective than PEGDMA as a crosslinker for the network formation of AMPS hydrogels. It can be attributed to higher reactivity of MBA to react with AMPS. It has been previously reported that MBA has higher reactivity than the macrocrosslinker polyethyleneglycol diacrylate (PEGDA)^{2,38} in the acrylic acid polymerization. A similar reasoning can be assumed in the case of MBA and PEGDMA. On top of that, mobility of the low molecular weight crosslinker MBA is much higher than that of the macrocrosslinker PEGDMA. Therefore, probability of collision of MBA with growing poly(AMPS) chains will be higher than that of PEGDMA. In summary, MBA-based poly(AMPS) is more efficiently crosslinked during the synthetic polymerization stage; however, the PEGDMA-based counterpart is more stable during the next production stage, that is, oven drying.

Another point observed from Figures 11 and 12 is a gradual enhancement of storage modulus with angular frequency for individual samples. In higher frequencies, the polymer chains do not have sufficient time for relaxation; therefore, the chain flexibility is reduced. As a result, polymers become stiffer and storage modulus is increased.

CONCLUSIONS

Drying stage is an essential technical requirement in industrial production of hydrogels. There are different drying methods in laboratory scale for the

hydrogel dewatering, for example, freeze-drying, nonsolvent drying, and vacuum drying. These methods are not economically favorable due to consuming the time and cost. Only conventional heating method at high temperatures are industrially favorable for hydrogel drying for shortening the hydrogel drying time and production rate enhancement. In addition, oven drying is often taken as a necessary stage, not only for water removing, followed by grinding, but also for the advancement of the polymerization process to yield higher conversions.

This article was written based on the following well-established facts: (a) the crosslink density and chemical nature of the crosslinker are the most effective factors determining the swelling capacity of a polymer gel, (b) a very small change in the crosslink density causes huge changes in the gel-swelling capacity, and (c) if the crosslink density is very low (as in superabsorbents), the gel swelling change will be so much high that the changing trends may be accurately and precisely monitored just by simple swelling measurements. In this article, the huge change of swelling capacity was logically correlated with some certain changes happened in the level of crosslinking for heated hydrogels (compare the changing trends shown in Figs. 2, 3, 6, 8, and 9 with the typical plot of Fig. 4). Meanwhile, some processes with simultaneous probability of occurrence were also taken into consideration.

The hydrogels composing different commercial acrylic monomers (AMPS, AA, KA, and AM) and two different crosslinkers (MBA, PEGDMA) were synthesized and dried at different temperatures and times. Then, they were investigated by measuring the variation of their swelling and rheological properties. The AMPS-based hydrogels showed higher thermovulnerability in comparison with AA- and AM-based hydrogels.

For the MBA-crosslinked poly(AMPS) hydrogels, the temperatures $< 60^\circ\text{C}$ and times < 10 h were found to be suitable drying conditions without appreciable adverse effects of heating on the swelling (Figs. 1–3). Higher temperatures lead to fast enhancement of swelling capacity and appreciable loss of the storage modulus of the swollen gel (Fig. 11), which is attributed to thermoaccelerated hydrolytic cleavage of the crosslink MBA moieties (Scheme 1).

In the case of PEGDMA-crosslinked poly(AMPS) hydrogels, the suitable drying conditions were concluded to be 80°C (~ 19 h). Higher temperatures results in an extraordinary loss of swelling (Figs. 5 and 6), which may be related to the thermal-promoted cyclization and/or postcrosslinking reaction (Scheme 2).

The MBA-crosslinked hydrogels based on AA and KA can be dried by heating up to 160°C (~ 4 h)

without serious unfavorable effects (Fig. 7). Similar AM-contained hydrogels can even be dried at 180°C for 4–5 h (Fig. 7). However, at 200°C, appreciable thermoaccelerated decrosslinking causes undesirable increase of the swelling capacity (Fig. 8).

In the case of PEGDMA-crosslinked poly(AA-KA) hydrogels, heating at 120°C was recognized to be suitable for drying. At the same temperature, the similar AM-contained hydrogel shows a moderate increase of swelling when it is heated for 12 h (Fig. 10). Drying at 200°C, however, results in an extraordinary enhancement of swelling (from 120 to 900 g/g; see Fig. 9), which may be attributed to a thermal promoted decrosslinking via a cycloimidization reaction (Scheme 3c).

Overall, it was found that the type of crosslinker had certain effects on the thermal vulnerability of the hydrogel. The most common crosslinker for hydrogel synthesis, that is, MBA, exhibited high susceptibility to thermodegradation in hydrogels. The crosslinker cleavage was monitored through swelling and rheological studies. Storage modulus was considerably reduced with the increase of drying time in MBA-crosslinked hydrogels. All the MBA-crosslinked hydrogels were degraded at high-drying temperatures. Two distinctive different behaviors were observed for PEGDMA-crosslinked hydrogels at high-drying temperatures. AA-KA and AMPS-based hydrogels were postcrosslinked, while AM-KA-AA hydrogels were decrosslinked during the heating stage.

In summary, either the nature of crosslinker or monomer must be taken into consideration for choosing the temperature and time needed for drying of hydrogels.

Finally, it should be pointed out that the majority of mechanisms given in this article (Schemes 1–4) are based on the known reactions ascertained basically by other researchers. Therefore, they are proposed here, for the similar cases, just to explain the empirical observations. Providing meticulous mechanistic proofs is far from the scope of this applied research.

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