

Gum Arabic–Acrylic Superabsorbing Hydrogel Hybrids: Studies on Swelling Rate and Environmental Responsiveness

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ABSTRACT: The swelling rate and the environmental sensitivity of novel superabsorbent gum arabic–acrylic hydrogel hybrids were investigated. The swelling kinetics of the hydrogel hybrids was studied by means of a Voigt-based viscoelastic model. The effects of concentration of the initiator, crosslinker, and the monomer ratio on the swelling rate were studied. The superswelling properties of the hydrogel hybrids were evaluated in various environmental pH, salinity and solvent–water mixtures. The optimally prepared hydrogel, MR5, showed a reproducible on–off switching behavior when the swelling medium was alternatively changed between distilled water and alkaline solutions. The hydrogel hybrid MR5 was also tested to be swollen and deswollen alternatively in distilled water and sodium chloride solution. The sorption–desorption behavior was found to be quite repeatable. A similar

capability was interestingly observed when a calcium chloride solution with the same molar concentration was used. The swelling changes of the hydrogel hybrid were examined in various water–solvent systems including the aqueous solutions of methanol, ethanol, acetone, ethylene glycol, glycerol, and dimethylsulfoxide. One and/or two volume-phase transitions were induced by the nonsolvents. The transitions were explained according to the solubility parameters of the solvents and water–solvent mixtures. The swelling–deswelling capability of the hydrogel in alternatively changed solvent–water mixtures was also studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5667–5674, 2006

Key words: gum Arabic; hydrogel; superabsorbent; swelling; volume phase transition

INTRODUCTION

Hydrogels, hydrophilic polymer networks, are being increasingly used in various applications from medical/pharmaceutical to agricultural sciences. They have occupied a unique position in the field of medicine and pharmacy^{1,2} because of the ways in which the imbibed water strongly influences the transport, surface, and mechanical properties of the polymers. During the past decade, we focused on special types of hydrogels, i.e., lightly crosslinked networks with ultra-high water absorption capacity (superabsorbent polymers, SAPs).^{3–12} Recently, we modified SAPs via incorporating inorganic materials or biopolymers to improve the swollen gel strength, minimize the cost, and modify the properties of the product.^{9–11}

Gum arabic (acacia gum) is a highly branched, branch-on-branch, complex acidic hetero-polysaccharide with main chain of (1→3)- β -D-galactopyranosyl units and side chains containing L-arabinofuranosyl, L-rhamnopyranosyl, D-galactopyranosyl, and D-gluco-

pyranosyl uronic acid units (Scheme 1). This hydrocolloid is the most widely used natural gum in industry and extensively used in a wide range of application such as confectionery, beverage or liquid flavor emulsions, pharmaceuticals, cosmetic products, inks, etc.¹³

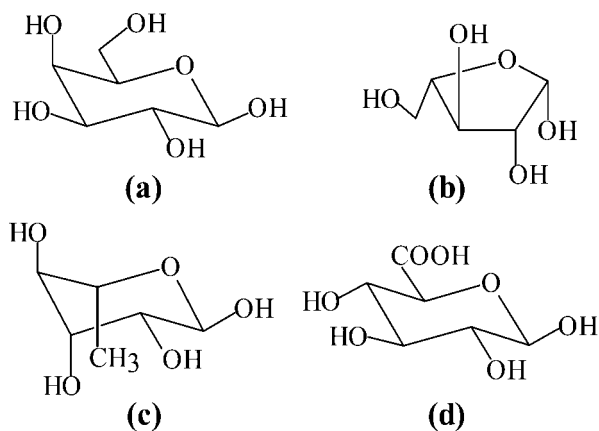
A literature survey based on the “Chemical Abstracts” revealed that no report had been published on the synthesis of hydrogels composing arabic gum and acrylic monomers. In a previous article,¹¹ we reported the first chemical modification of arabic gum through graft/crosslinking copolymerization of acrylic monomers to prepare superabsorbent hydrogel hybrids. The present article deals with studies on the swelling kinetics and environmental sensitivities of the SAP hybrid previously prepared.

EXPERIMENTAL

Materials

Gum arabic (AG, from Merck), acrylic monomers (acrylic acid, AA, and acrylamide, AM, from Fluka), ammonium persulfate (APS), sodium metabisulfite (SMBS), and other inorganic salts (all from Fluka) were of analytical grade and used without further

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Scheme 1 The main chemical building blocks of the carbohydrate biopolymer arabic gum. (a) D-galactopyranose, (b) L-arabinofuranose, (c) L-rhamnopyranose, and (d) D-glucopyranosuronic acid.

purification. The solvents (all from Merck) were used as received.

Hydrogel preparation

Acrylic acid (partially neutralized with potassium hydroxide) and acrylamide were copolymerized in the presence of AG and a crosslinker using a redox pair initiator under conditions reported previously.¹¹ The product was dried, ground, screened, and classified.

Swelling measurements

A 40–60 mesh-sized fraction of sample particles were used for the swelling measurements.

In the measurements of swelling capacity at various pHs, each individual solution pH was obtained by dilution of aqueous NaOH (pH 13.0) or HCl (pH 2.0) solutions to achieve $\text{pH} \geq 6$ and $\text{pH} < 6$, respectively. The pH values were precisely checked by a pH-meter (Consort C533, Belgium, accuracy ± 0.1).

The equilibrium swelling capacity (g/g) was measured according to a conventional “tea bag” method.^{6–8} The accuracies of the data obtained from the method of swelling measurements in distilled water and in ionic solutions were determined to be 0.8% and 2.8%, respectively.

Swelling rate (SR, g/g s) was determined based upon the previously reported relationship^{10,12} as follows:

$$\text{SR} = S_{\text{mr}}/r_{\text{min}} \quad (1)$$

where S_{mr} stands for swelling at the time related to the minimum rate parameter r_{min} (s) obtained from superabsorbents from a set of similar experiments. The rate parameter is the time required to reach 0.63 of the equilibrium swelling. It is based on a Voigt-like model for the swelling of SAPs.¹⁴

RESULTS AND DISCUSSION

Hydrogel preparation

A practical preparative system was investigated to produce novel hydrogel hybrids having superswelling properties.¹¹ The gum arabic-based superabsorbent hydrogels were synthesized via free radical copolymerization of acrylamide (AM) and partially neutralized acrylic acid (AA–AK) onto the gum. The crosslinking polymerization process was studied by varying the reaction parameters (i.e., concentration of gum, crosslinker, initiator, monomers, and the AM/AA–AK ratio) affecting the ultimate swelling and gel content of the final hydrogel.¹¹ The concluded optimized conditions are follows¹¹ (sample MR5): AG 7.9%, AM/AA–AK 60 : 40 (AA 76 mol % neutralized with KOH), total monomer concentration 24.6%, methylenebisacrylamide crosslinker concentration 0.079%, initiator (i.e., APS/SMBS mole ratio 1 : 1) 0.27%, room temperature. In the present article, the influence of three important synthetic parameters on the swelling rate (i.e., initiator and crosslinker concentration, and the AM/AA–AK ratio) is investigated. The environmental responsiveness of the hydrogel hybrids is studied as well.

The swelling kinetics–structure relationship

The swelling kinetics of the SAP hydrogel hybrids was studied by means of a previously reported Voigt-based viscoelastic model:¹⁴

$$S_t = S_e \left(1 - e^{-t/r}\right) \quad (2)$$

where S_t is amount of swelling (g/g) at any moment, S_e , the equilibrium swelling, is swelling at infinite time or maximum water-holding capacity, t is the swelling time (s), and r , the rate parameter (s), is the time required to reach 0.63 of the equilibrium swelling.

The data obtained from the swelling of the hydrogels prepared under different synthetic conditions were fitted into eq. (2), using suitable software like Easyplot, to find the values of the rate parameters (Table I). Figure 1 representatively exhibits such a fitted curve for an optimally prepared SAP hydrogel hybrid, MR5. The values of swelling rate for the individual samples were calculated using the eq. (1) and given in Table I.

In the series I (Table I), the equilibrium swelling (S_e) in water and also the rate parameter (r) is increased with increasing of the initiator concentration; however, no considerable change is observed in the swelling rate (SR). In fact, although in the crosslinking polymerization, higher crosslinker concentration causes shorter chain formation leading to imper-

TABLE I
Values of r , S_e , S_{mr} , and SR Obtained from the Voigt-Based Model [Eqs. (1) and (2)] for the Three Series of the Synthesized AG-Acrylic SAP Hydrogel Hybrids

Sample code ^a	r (s)	S_e (g/g)	S_{mr} (g/g)	SR (g/g s)
I1	63	115	69	1.14
I2	72	122	74	1.2
I3	81	139	72	1.2
I4	83	128	67	1.1
I5	92.6	141	73	1.2
I6	94.9	170	72	1.2
I7	104	157	71	1.2
C1	142	322	107	1.78
C2	104	191	90	1.5
C3	92.3	141	72	1.2
C4	91.9	92	46	0.75
C5	76	89	47	0.8
C6	69	77	44	0.75
MR1	742	70	10	0.17
MR2	143	263	110	1.8
MR3	150	265	109	1.8
MR4	121	264	107	1.7
MR5	89	238	99	1.6
MR6	80	189	97	1.6
MR7	60 ^b	139	90	1.4
MR8	59	125	81	1.3

The swelling medium is distilled water.

^a I: initiator series (0.098–0.583 wt %); C: crosslinker series (0.028–0.233 wt %); MR: series AM/(AA–AK) monomer mole ratio (100–0). The ratios for MR1 to MR8 are 100, 90, 80, 70, 60, 50, 30, and 0, respectively.¹¹

^b The accepted minimum rate parameter, r_{min} .

fect hydrogel networks (and hence higher S_e),¹⁵ this imperfection, however, does not substantially affect the rate of water absorption of the SAP hydrogels.

In the series C, a known power law decreasing relationship between S_e and the crosslinker concentration is observed,¹¹ so that the higher the crosslinker concentration, the lower the swelling capacity (Table I). On the other hand, higher crosslinker concentration results in lower rate of swelling. This observation is also reasonable, because water cannot easily and rapidly diffuse into a hydrogel network having high density of crosslinking.¹²

In the series MR, swelling S_e is increased with increasing of the AM/AA–AK ratio up to 70–90%. The swelling of the sample containing 100% polyacrylamide as the synthetic part (MR1) is intensively decreased in water due to lack of ionic groups in the crosslinked chains. As we rationalized previously¹¹ from the gel content variation in this series of samples, the crosslinker MBA tends to react with AA–AK more readily than with AM. This is why the swelling S_e is increased from the AM/AA–AK ratio 0–90%. In addition, according to the foresaid argument, the higher content of acrylic acid and its salt results in networks with higher crosslink density leading to lower swelling rate, which is obvious from the SR data recorded in the table.

The environmental sensitivity

pH

The equilibrium swelling of the AG-acrylic SAP hydrogel hybrids with different AM/(AA–AK) mole ratios was studied at various pHs ranged from 2 to 12.5 (Fig. 2). To clearly observe the net effect of pH, buffer solutions containing lots of ionic species, were not used as the swelling media, because the swelling of a SAP is strongly decreased by ionic strength. Therefore, stock concentrated NaOH and HCl solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively.

In the sample MR1, full-AM AG-acrylic SAP hydrogel hybrid, since poly(AM) chains are nonionic, the sample MR1, shows the least swelling capacity at all pHs (Fig. 2). In fact, glucuronic acid moieties of the arabic-gum parts as well as the hydrophilicity of the amide groups are mainly determine the swelling of this sample. As seen in Figure 2, at all pHs, the presence of acrylic acid (AA) and its salt (KA) in the SAP increases the swelling up to a certain range of the AM/AA–AK mole ratio of 50–60. The repulsive forces between the ionic groups (COO^-) located mainly on the acrylic polymer chains are the major reason for the super absorbency. However, the environmental ionic species disfavor the higher swelling when the ionic groups are more than the certain value due to a shielding (screening) effect.^{7,8}

In each individual sample (except MR1), the highest swelling is detected at nearly neutral to alkaline pHs (~ 6 to ~ 11). The hydrogels are contracted at very acidic conditions due to the conversion of ionic COO^- to nonionic COOH groups and absence of the electrostatic repulsive forces in the network. At very basic pHs, although the powerful repulsive anion-

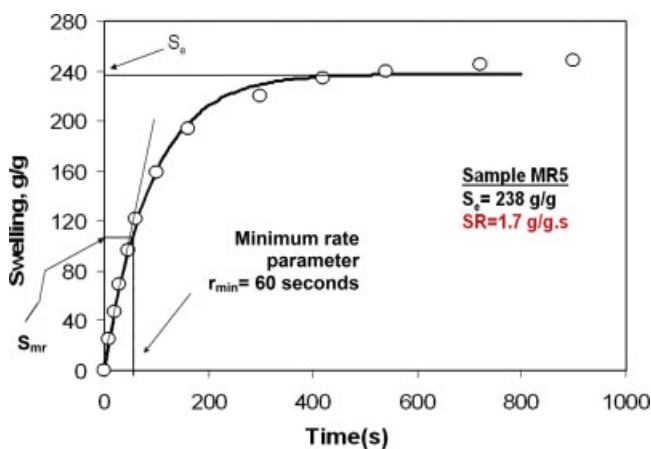


Figure 1 Representative curve for swelling kinetics of the optimally synthesized AG-acrylic SAP hydrogel hybrid (sample MR5) in distilled water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

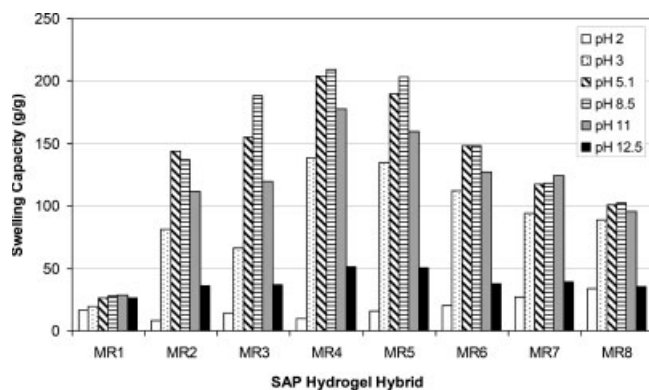


Figure 2 Effect of pH variation on the swelling capacity (g/g) of the AG-acrylic SAP hydrogel hybrids having different AM/(AA-AK) mole ratio. From MR1 to MR8, the monomer mole ratio AM/(AA-AK) is varied from 100 to 0, i.e., MR1 and MR8 are the full-AM and AM-free AG-acrylic hydrogel hybrids, respectively.

anion forces are in function, however, at the same time, a shielding effect of the counterions (Na^+) limits the absorbency and opposes the swelling.⁷ The overall swelling-pH dependency is similar to those observed for the fully anionic acrylic hydrogel,¹⁶ cross-linked carboxymethylated cotton,¹⁷ hydrolyzed starch-graft-polyacrylonitrile (H-SPAN),⁷ and starch-graft-poly(potassium acrylate-co-acrylamide)¹⁸ SAP hydrogels.

In the case of MR1, the swelling loss at very high pH is nearly not observed, because the synthetic part of this hydrogel is composed of nonionic (amide AM) moieties, so it is not a highly pH-sensitive SAP hydrogel.

The optimally prepared pH-sensitive hydrogel, MR5, showed a reproducible on-off switching behavior when the environmental pH of the sample was alternatively changed between 6.8 (distilled water) and alkaline conditions (Fig. 3). This responsiveness behavior may be of significant importance in controlled delivery of drugs to colon¹ having alkaline medium. Such swelling-deswelling behavior was not observed when pH alternatively varied between 2 and 6.9, i.e., after swelling at pH 6.9 and then deswelling at pH 2, it cannot reswell at pH 6.9, because the neutral pH (6.9) is not enough high to be able to effectively dissociate the molecular COOH groups and regenerate carboxylate anions.

Salinity

The swelling of the SAP hydrogel hybrids in saline solutions appreciably decreases comparing to the values measured in deionized water.^{1,2} This phenomenon, commonly observed in the swelling of all ionic hydrogels, is often attributed to a screening effect of the additional cations causing a nonefficient anion-anion electrostatic repulsion, led to a decreased os-

motonic pressure (ionic pressure) difference between the hydrogel network and the external solution.¹⁶

In a series of evaluation, the AG-acrylic hydrogel hybrid MR5 was tested to be swollen and deswollen alternatively in distilled water and 0.15M sodium chloride solution. As shown in Figure 4(a), the sorption-desorption behavior is quite repeatable. Interestingly, a similar capability was observed when a CaCl_2 solution with the same molar concentration was used [Fig. 4(b)]. According to our previous study on the starch-acrylic SAP hydrogels, the SAP particles that had once been immersed in the multivalent cations solution will not be reswollen in water again.¹⁹ Jianqi and Lixia have reported a similar observation in the case of poly(vinyl alcohol)/poly(acrylic acid) hydrogel fibers.²⁰ The nonreversible phenomenon has been explained by complexing ability arising from the coordination of the multivalent cations with the carboxylate pendant groups. This ionic crosslinking mainly occurs at surface of particles and makes them rubbery and very hard when they swell in multivalent cation solutions. In the case of the AG-acrylic hydrogel hybrid, however, the carboxylate- Ca^{2+} -carboxylate bridges are weak enough to break and the network reswell in distilled water. It can preliminarily be attributed to highly branched arabic gum sections of the hybrid network. The steric hindrances of the branches disfavor the formation of stable ionic crosslinks. Based on a similar possible reason, the hydrogel hybrid shows a good ion-exchange capability, i.e., it can repeatedly be swelled and collapsed when its swelling medium is alternatively changed between two media of the chloride solutions of Na^+ and Ca^{2+} with a same molarity [Fig. 4(c)].

Solvent-induced phase transition

Hydrogels are recognized as hydrophilic materials that swell in water. However, the swollen hydrogels

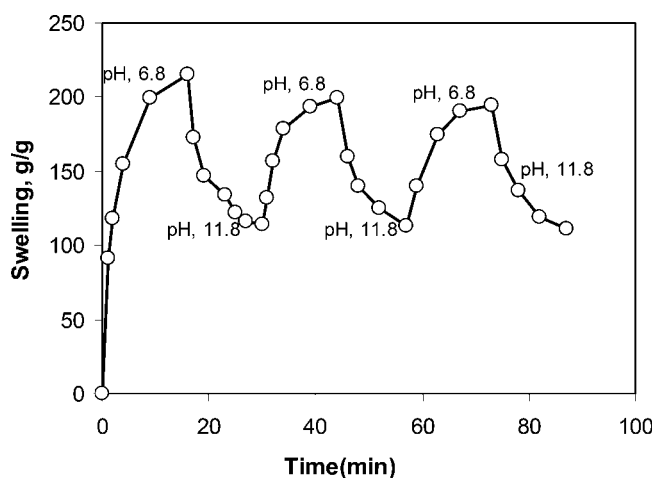


Figure 3 The pH-sensitive on-off switching behavior of the AG-acrylic SAP hydrogel hybrid MR5.

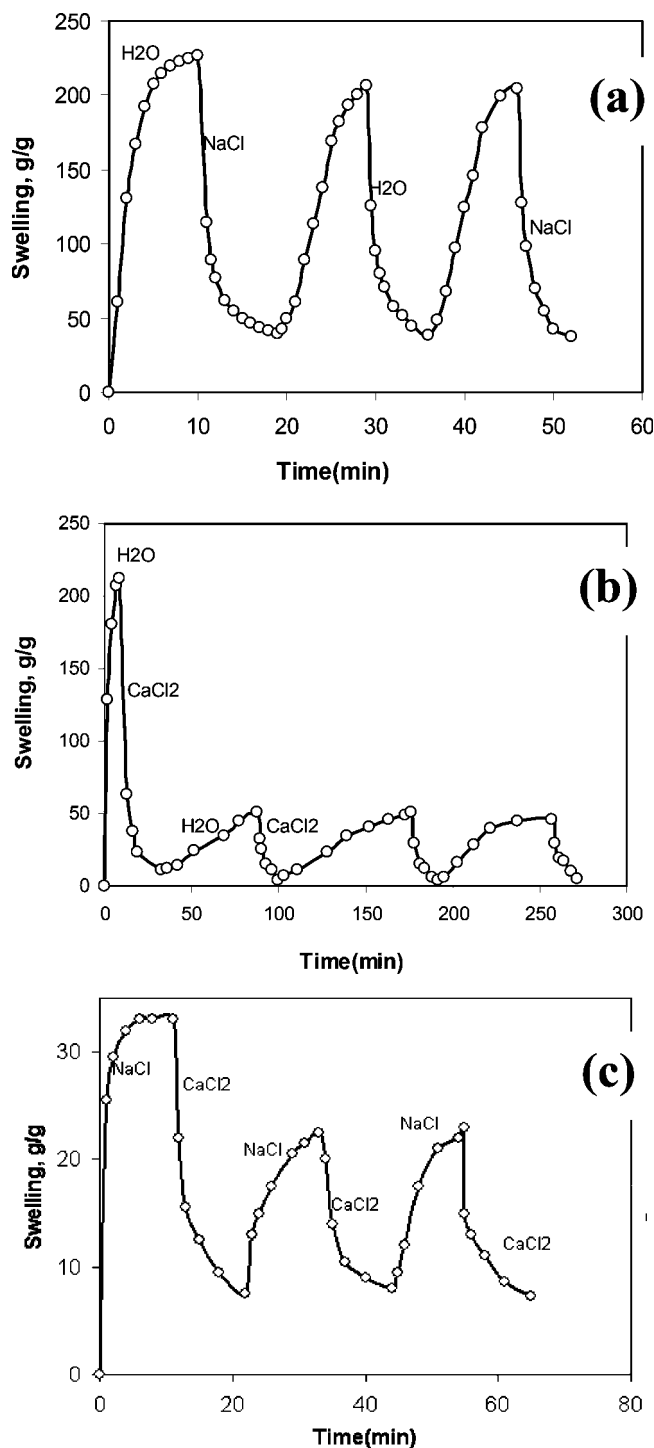


Figure 4 Responsiveness behavior of the AG-acrylic SAP hydrogel hybrid MR5 when the ionic aqueous swelling media is alternatively changed. (a) Distilled water - 0.15M NaCl, (b) distilled water - 0.15M CaCl₂, (c) 0.15M NaCl - 0.15M CaCl₂.

shrink or collapse when a water-miscible nonsolvent is added to the water. Depending upon the gel chemical structure, the solvent nature and water/solvent composition, the gel shrinkage may be gradual (continuous) or abrupt (discontinuous). The latter phe-

nomenon, currently known as the volume phase transition (VPT), was first reported by Tanaka²¹ in the case of saponified polyacrylamide gels. Since then, many researchers have focused on the phenomenon²²⁻²⁴ mainly because of its smartness aspects.^{25,26}

In the present study, the swelling changes of the gum arabic-acrylic-based SAP hydrogel hybrid were examined in various water-solvent systems. As shown in Figure 5, both one and two solvent-induced phase transitions are observed. The first transition (if any) is a minor transition at a range of 10–57 wt % solvent (in the case of acetone, ethanol and methanol, swelling-loss 30–40%) and the second (the major gel collapse) is ranged 50–97 wt % solvent (swelling-loss 92–97%). Similar VPTs have been observed in the hydrogel/water-solvent systems based on the hydrolyzed starch-g-polyacrylonitrile²⁷ and poly(acrylic acid)-attapulgit superabsorbent composites.²²

According to Rodehed and Ranby,²⁷ the first transition may be attributed to the polymer-polymer affinity causing the free liquid in the gel to be forced out and is an effect of increased solvent content. The second transition (the gel collapse) is due to an interaction between the polar groups in the liquid and the ionic groups in the polymer, and the collapse of the gel is a result of the total depletion of water from the solvated polymer network. In our study, to investigate the swelling-solvent polarity relationship, we selected six water-miscible solvents (i.e., methanol, ethanol, acetone, ethylene glycol, glycerol, and dimethylsulfoxide (DMSO)) having different polarities. The swelling decreased slowly from 10% to 45% acetone, from 10% to 50% ethanol, and from 10% to 57% methanol (Table II). The main transition for the acetone-water, ethanol-water, and methanol-water systems was a sharp reduction of the swelling at 50–60%

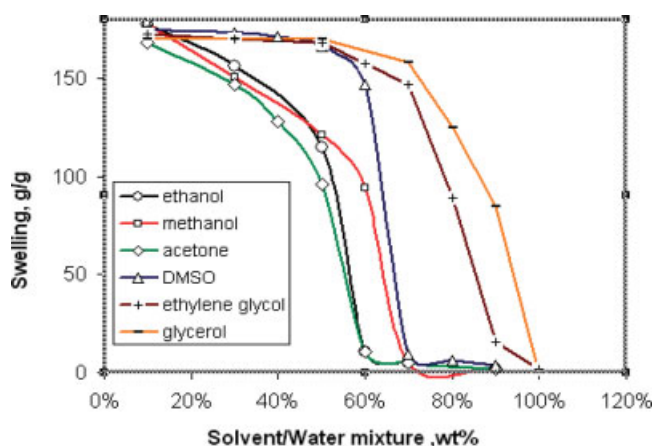


Figure 5 Sensitivity of the AG-acrylic SAP hydrogel hybrid MR5 swelled in different solvent-water media with varied composition. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
The Solvent–Water Concentrations in Which the Hydrogel Hybrid MR5 Exhibits
Minor and/or Major Volume-Phase Transition

Solvent (δ)	Minor transition			Major transition		
	Solvent wt % range	δ_{mix}	Swelling-loss (%)	Solvent wt % range	δ_{mix}	Swelling-loss (%)
Acetone (9.9)	10–45	22.05–17.32	34	50–60	16.65–15.3	92
Ethanol (12.7)	10–50	22.33–18.05	37	52–60	17.84–16.98	94
Methanol (14.5)	10–57	22.51–18.33	41	60–70	18.06–17.17	96
DMSO (14.5)	NOT	–	–	57–70	18.33–17.17	97
Ethylene glycol (14.6)	NOT	–	–	60–90	18.12–15.48	92
Glycerol (16.5)	NOT	–	–	70–97	18.57–16.7	94

Symbols δ and δ_{mix} [(cal/cm³)^{1/2}] are the solubility parameters for the solvent and the solvent–water mixture, respectively. NOT, No transition was observed.

acetone, 52–60% ethanol, and 60–70% methanol, respectively. In the case of DMSO–water, ethylene glycol–water, and glycerol–water systems, no transition was observed up to $\sim 50\%$ DMSO, $\sim 60\%$ ethylene glycol, and $\sim 70\%$ glycerol, respectively (Fig. 5). Instead, a very large and sharp transition was occurred at 57–70% DMSO (swelling-loss 97%), 60–90% ethylene glycol (swelling-loss 92%), and 70–97% glycerol (swelling-loss 94%) (Table II). When the concentration was greater than $\sim 60\%$ (in the case of acetone–water and ethanol–water systems), $\sim 70\%$ (in the case of methanol–water and DMSO–water systems), and $\sim 95\%$ (in the case of ethylene glycol–water and glycerol–water systems), the water absorbency dropped almost to zero (Fig. 5).

The solvent-induced swelling-loss of the SAP hydrogel hybrid can be explained using the solubility parameter variations. A solvent that can dissolve a linear polymer can also swell its crosslinked network of the same polymer. Therefore, the swelling of the network would conform of the dissolving rules of linear polymer or the Hildebrand eq. (3).²⁸

$$\Delta H_m / (V\phi_1\phi_2) = (\delta_1 - \delta_2)^2 \quad (3)$$

where ΔH_m is the enthalpy change on mixing of a polymer and a solvent, V is the whole volume of the solution, ϕ_1 and ϕ_2 are the volume fractions for the solvent and the polymer, δ_1 and δ_2 are the solubility parameters for the solvent and the polymer, respectively.

By means of this equation, we can predict that a solvent can dissolve a polymer if the solubility parameters for the solvent and the polymer are close to each other. The maximum swelling capacity of the SAP hydrogel hybrid is occurred in water with the solubility parameter of 23.4 (cal/cm³)^{1/2}. So, this value can be regarded as the solubility parameter of the hydrogel hybrid.

The solubility parameter for a mixing solvent (δ_{mix}) can be calculated using the eq. (4).²⁹

$$\delta_{\text{mix}} = \delta_1\phi_1 + \delta_2\phi_2 \quad (4)$$

where ϕ_1 and ϕ_2 are the volume fraction for the two solvents, and δ_1 and δ_2 are the solubility parameters of the two solvents.

It can be seen from Figure 5 and Table II that with increasing of δ_{mix} values toward 23.4, the hydrogel can be highly swollen as in pure water. It means the swelling capacity of the hydrogel in the solvent–water mixture will be close to that in pure water when δ_{mix} is close to $\delta_{\text{water}} = 23.4$ (cal/cm³)^{1/2}. Similarly, it can also be concluded from Figure 5 that in a fixed ratio of solvent–water (e.g., a 1:1 w/w mixture), the swelling capacity is enhanced with increasing the individual solvent solubility parameter, so that the swelling is increased in order of glycerol \sim ethylene glycol \sim DMSO $>$ methanol $>$ ethanol $>$ acetone. Meanwhile, the most intensive gel collapsing was observed in DMSO–water mixture (swelling-loss 97% in DMSO wt % range of 57–70). This may be explained by this fact that δ values are the sum of the contribution of dispersion (δ_d), polar (δ_p), and hydrogen bonding (δ_h) forces [eq. (5)].²⁸

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (5)$$

According to the data given in Table III, in the case of DMSO, the values δ_d and especially δ_p are the high-

TABLE III
The Values of Parameters [(cal/cm³)^{1/2}] Contributed
in the Solubility Parameters of the Solvents Used
in the Present Study²⁸

Solvent	δ_d	δ_p	δ_h
Acetone	7.6	5.1	3.4
Ethanol	7.7	4.3	9.5
Methanol	7.4	6.0	10.4
DMSO	9.0	8.0	5.0
Ethylene glycol	8.3	5.4	12.7
Glycerol	8.5	5.9	14.3
Water	7.6	7.8	20.7

est among those of the other solvents. The polyhydric alcohols ethylene glycol and glycerol having higher hydrogen bonding functionality (the highest δ_H) exhibit very high swelling-loss as well.

In other set of experiments, the beginning and final solvent-water composition related to the "major transition" was chosen for some alternative swelling measurements. When the hydrogel hybrid MR5 swollen highly in a solvent-water mixture (with $\delta_{\text{mix}(1)}$) was placed in another mixture with a lower solubility parameter, $\delta_{\text{mix}(2)}$, the swollen gel was not collapsed considerably. However, acetone with the smallest solubility parameter among the tested solvents produced different results. The hydrogel showed a reproducible swelling-deswelling behavior when the environmental medium was changed alternatively between the acetone-water mixtures 50 wt % ($\delta_{\text{mix}(1)} = 16.65$) and 60 wt % ($\delta_{\text{mix}(2)} = 15.3$) (Fig. 6). As mentioned earlier, the collapse of the gel is a result of the total depletion of water from the solvated polymer network. Nevertheless, such phenomenon was not observed in the case of other solvents, e.g., ethanol, methanol, DMSO, with slightly higher solubility parameter. The exceptional case of acetone may be attributed mostly to the very low value of hydrogen bonding (δ_H) contribution in δ of acetone (Table III). The capability of the hydrogen bonding formation between the molecules of the acetone-water and the hydrogel macromolecular network is at the minimum level. The nonsolvent acetone dissociates the water-hydrogel hydrogen bonding, and as a result, the hydrogel is collapsed at a certain concentration of acetone-water. The contracted gel is reswollen when it is located in another acetone-water mixture with higher δ_{mix} .

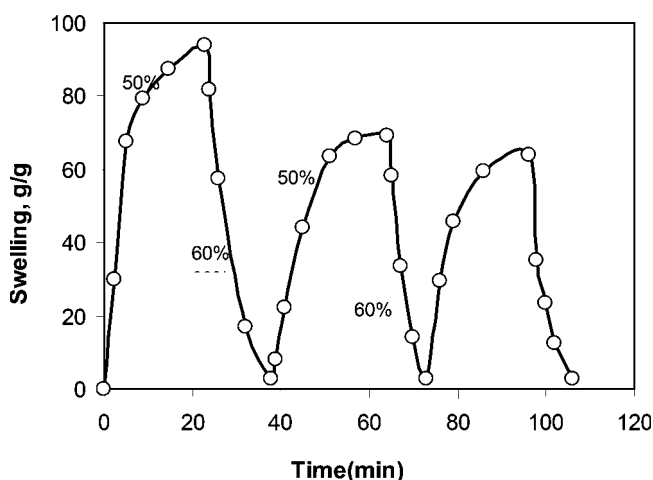


Figure 6 The water-acetone composition-responsiveness of the AG-acrylic SAP hydrogel hybrid MR5 when the swelling medium is alternatively changed between 50 and 60 wt % acetone.

CONCLUSIONS

The most important conclusion remarks may be summarized as follows:

- Regarding the synthetic and structural aspects, the higher content of acrylic acid and its salt results in networks with higher crosslink density lead to the hydrogel hybrids with lower swelling rate. The higher crosslinker concentration results in lower rate of swelling. No considerable swelling change was observed with increasing of the initiator concentration. The presence of acrylic acid (AA) and its salt (KA) in the hydrogel hybrids increases the swelling up to a certain range of the AM/AA-AK mole ratio of 50–60. In each individual sample (except MR1), the highest swelling is detected at nearly neutral to alkaline pHs (~ 6 to ~ 11).
- The optimally prepared hydrogel, MR5, showed a reproducible on-off switching behavior when the swelling environment (salinity and pH values) was alternatively changed. A quite repeatable sorption-desorption behavior was observed when hydrogel hybrid was tested to be swollen and deswollen alternatively in distilled water and 0.15M NaCl solution. Such a capability was observed when a CaCl_2 solution with the same molar concentration was used.
- The solvent-induced volume-phase transitions were observed when the swelling changes of the hydrogel hybrid were examined in various water-solvent systems. When the hydrogel hybrid highly swollen in a solvent-water mixture was placed in another mixture with a lower solubility parameter (unless acetone-water), the swollen gel was not collapsed considerably.
- The environmentally responsive gum arabic-acrylic hydrogel hybrids may be considered as good candidates to design intelligent systems of controlled delivery of bioactive agents (e.g., drugs and agrochemicals) and other applications.

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