Superabsorbent Hydrogel Composed of Covalently Crosslinked Gum Arabic with Fast Swelling Dynamics

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ABSTRACT: A superabsorbent hydrogel (SH) with fast swelling dynamics and good mechanical stability in the swollen state was prepared. The SH was obtained from chemically modified gum arabic (MGA) with glycidyl methacrylate (GMA), acrylic acid (AAc), and acrylamide (AAm). The water-transport mechanisms and equilibrium swelling ratio (SR) were the parameters used to describe the water-absorption profile of SH. A 2^3 factorial design with a central point was built to evaluate the influence of the chemical modification of gum arabic (GA) on the SH sensitivity to water. The main effects of the temperature and amount of GMA and the interaction effect of the temperature and amount of GMA on the SR responses were statistically significant. It was demonstrated that the amount of GMA had a more prominent effect on gel swelling. Lower elastic modulus values for the SH were found when a decreased amount of GMA was used (0.05 g), which produced an SH with a high SR capacity. The SH matrix consisting of 3.0 g of AAc, 0.5 g of AAm, and 0.5 g of MGA was more suitable to absorb a large amount of water (SR = 503.17 ± 22.65 within 60 min of water immersion) without its mechanical stability being affected. Better GA modifying conditions to produce such an SH were as follows: 60°C for the temperature, 24 h for the time of MGA, and 0.05 g for the amount of GMA. It exhibited a diffusional exponent higher than 0.89, which corresponded to the supercase II type of penetrating transport mechanism, indicating that its water-absorption mechanism exclusively depended on the macromolecular relaxation of the polymer chains. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1500–1506, 2008

Key words: diffusion; hydrogels; mechanical properties; polysaccharides; swelling

INTRODUCTION

Over the past 5 decades, superabsorbent hydrogels (SHs) have received particular attention as promising materials for a series of applications in which the efficient use of water is required, such as soil conditioning, disposable infant diapers, and feminine napkins. From a physical–chemical point of view, SHs are three-dimensional polymer networks capable of expanding upon contact with water, and this results in the absorption and retention of a large amount of the liquid.[1–4] Because of the high water-absorption content, SHs exhibit properties in common with soft biological materials, and this enables them to be used in biomedical applications.[5] The

wide variety of applications of these materials has been a key factor in the rapid scientific advance of the field of SHs.[6,7] Esposito et al.[8] developed SHs for the removal of water for the treatment of edemas. Rodrıguez et al.[9] synthesized cationic cellulose hydrogels, using ethylene glycol, as anionic drug delivery systems. Zhang et al.[10] investigated the swelling profile of polyacrylamide–attapulgite superabsorbent composites to be used as an ecological water-managing system for the renewal of arid and desert environments. Kabiri and Zohuriaan-Mehr[11] developed SHs composed of acrylic acid (AAc) networks consisting of kaolin suitable for agricultural applications. Bajpai and Johnson[12] synthesized SHs based on sodium acrylate and acrylamide for the removal of divalent toxic ions from aqueous environments. Recently, there has been increasing interest in developing biodegradable materials that do not cause damage to the environment or living organisms. In this context, polysaccharide-based SHs have emerged as promising substitutes[13–16] because the polysaccharides are nontoxic and/or biodegradable materials and are widely available in the environment;[17–19] here gum arabic (GA) is referenced.[20,21] However, there are two challenges that remain to be

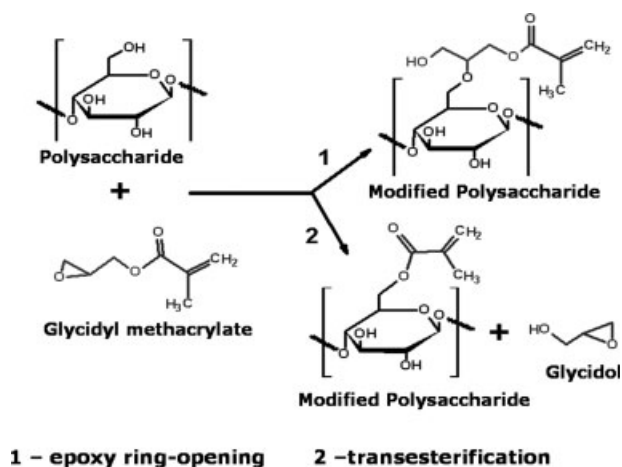**WILEY InterScience®**
DISCOVER SOMETHING GREAT

Figure 1 Drawing of the modification routes of polysaccharides with GMA: (1) epoxy ring-opening and (2) transesterification mechanisms.

overcome: (1) GA does not possess water-superabsorbing properties and (2) the low mechanical strength of equilibrium-swollen SHs limits their use in many applications. With the intention of finding a GA-based SH that shows excellent performance for water absorption and good mechanical strength in the swollen state, a polymer matrix consisting of chemically modified gum arabic (MGA), AAc, and acrylamide (AAm) was used. The chemical modification of GA consisted of coupling vinyl groups of C=C coming from glycidyl methacrylate (GMA) onto the polymeric structure of polysaccharide.[22] In the modification of polysaccharides by GMA, two mechanism routes were considered: transesterification and epoxy ring-opening pathways, as described in Figure 1. A 2^3 factorial design with a central point was built to evaluate the influence of the chemical modification of GA on the SH sensitivity to water. The data for the swelling ratio (SR) were used as the responses. The equilibrium SR and water-absorption mechanism were the parameters used to explain the water-absorption profile of SH.

EXPERIMENTAL

Materials

Arabic gum (Company, Sudan), GMA (Acros Organics, NJ), sodium persulfate (Sigma, Belgium), dimethyl sulfoxide (Labsynt, Brazil), N,N,N',N'-tetramethylethy-

lenediamine (TEMED; Sigma, Belgium), 99.5% stabilized AAc (Acros Organics), and all other reagents of analytical grade were used without further purification.

MGA

A GA modifying solution was prepared by the addition of 10 g of GA to 100 mL of distilled and deionized water under constant stirring for 30 min at room temperature. Afterward, a known amount of GMA (as the modifier) and 0.13 mM TEMED (as the accelerator) were introduced. The mixture was stirred for 24 h at 50°C. The polysaccharide was precipitated by the addition of the required amount of ethanol to the resultant mixture, separated by centrifugation, and remixed in water. The cycle of dissolution and precipitation was repeated three times. The formed product was dried by lyophilization.

Factorial design

Main and interaction effects were evaluated with Design-Expert software (Minneapolis, MN). Table I shows the inferior (−1) and superior (+1) levels and central point (0) of the data fed into a computer. The variables—the temperature, time of MGA, and amount of GMA—were the factors selected to build the model. The limits of the levels were selected as follows: 40 and 60°C for the temperature, 12 and 24 h for the time of MGA, and 0.05 and 0.10 g for the amount of GMA.

Fourier transform infrared (FTIR) analyses

FTIR spectra of unmodified GA and lyophilized MGA were taken on a Bomen FTIR model MB100 spectrometer (Quebec, Canada). Powdered samples were prepared with KBr to make pellets.

Synthesis of the SHs from MGA

Known amounts of AAc and KOH (molar ratio of 1:1) were dissolved in 10 mL of distilled water and deionized. After, 0.5 g of MGA, 0.5 g of AAm, and 84 μM sodium persulfate (as the initiator) were introduced. The resultant solution was transferred to a cylindrical glass tube and heated to 50°C. The gel formation was observed within 15 min. The formed hydrogels were cut into smaller cylinders and stored in fresh distilled and deionized water for 24 h.

TABLE I
Factors and Levels Selected to Build the 2^3 Factorial Design with a Central Point for the Chemical Modification of GA with GMA

Factor	Name	Unit	Type	Level −1	Level 0	Level +1
A	Temperature	°C	Numerical	40.0	50.0	60.0
B	Time of MGA	h		12.0	18.0	24.0
C	Amount of GMA	mL	Numerical	0.05	0.075	0.10

Swelling dynamics of the hydrogels

Dry hydrogels (1-cm^3) of known weight were immersed into a buffer solution with pH 7 at 25°C. The hydrogel were taken out from the buffer solution and weighed at a specified time. The SR values were estimated with the following equation:

$$SR = \frac{(W_s - W_d)}{W_d} \quad (1)$$

where W_s is the weight of the hydrogel swollen at a specified time and W_d is the weight of the dried hydrogel. Before the samples were weighed, the excess water droplets on the hydrogel surface were wiped off carefully.

Determination of the water-absorption mechanism

The water-absorption mechanism of the hydrogel was determined through the plotting of curves of the fractional swelling (W_t/W_∞) and time (W_t is the mass of absorbed water in the hydrogel at any given time, and W_∞ is the mass of absorbed water in the fully swollen hydrogel). The W_t/W_∞ values were estimated with the following equation:[23]

$$\frac{W_t}{W_\infty} = kt^n \quad (2)$$

where k is the proportionally constant of the polymer structure of the hydrogel and n is the diffusional exponent.

Determination of the elastic modulus (E)

E of SH was determined through the method of short-time static loading. The choice of such a method was made because the SH had a soft polymer structure in the swollen state. Over the experimental tests, the loading was applied gradually and allowed for all parts of a hydrogel sample to reach equilibrium simultaneously at any time. The mechanical tests were conducted on a texture analyzer (TATX2i stable microsystem, Haslemere, Surrey, United Kingdom) equipped with a 5-kg load cell and adjusted to a compressive mode. A circular probe 12.7 mm in diameter was adjusted to descend to the SH surface at a constant speed of 0.2 mm/s. The data obtained from the equipment were the compressive force (F) and displacement. E was obtained from the proportionality of the compressive stress (σ) and strain:[24,25]

$$\sigma = \frac{F}{A} = E(\lambda - \lambda^2) \quad (3)$$

where λ is the relative deformation of the specimen and A is the cross-sectional area of the strained spec-

imen. $\lambda - \lambda^2$ is the strain calculated with the following equation:

$$\lambda = \frac{\Delta L}{L_0} \quad (4)$$

where ΔL is the deformation of the sample and L_0 is the initial sample length. In determining the stress by the compressive mode, it is important to note that the final sample length (L_F) is always lower than L_0. Thus, eq. (3) can be rewritten to fit the F data. By the integration of eq. (3) with respect to ΔL between the limits L_F and L_0, it can be rewritten as follows:

$$\lambda = 1 - \frac{L_F}{L_0} \quad (5)$$

RESULTS AND DISCUSSION

Characterization and statistical treatment

Figure 2 shows the FTIR spectra of unmodified GA and MGA for runs 1–4. The different experimental conditions used to modify GA and the gel SR responses for each one of the runs are described in Table II. The band in the spectral range of 1707–1586 cm^{-1} in the unmodified GA spectrum was assigned to the wave number of the carboxylate groups of glucuronic acid present in raw GA. The bands appearing at 1716 cm^{-1} in spectra of runs 1–4 were attributed to the C=O stretching frequency groups of the conjugated system coming from GMA, which are indicative of the GA modification.

The analysis of variance model and main and interaction effects were obtained from data of the SR responses, and their values are summarized in
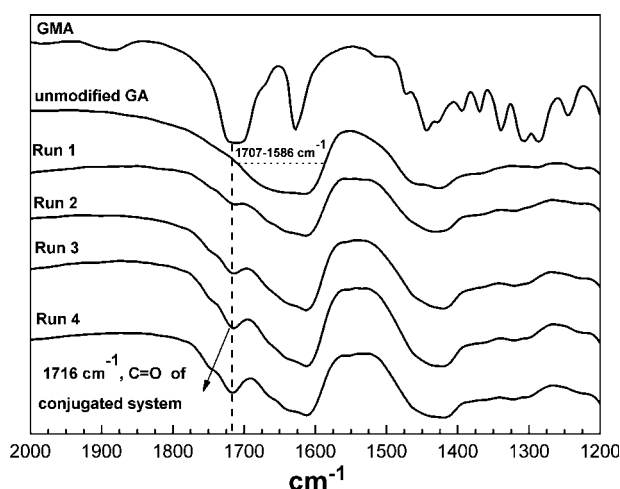

Figure 2 FTIR spectra of GMA, unmodified GA and GA modified under different conditions: temperature, time of MGA, and amount of GMA (for runs 1–4).

TABLE II
SR Responses Used to Build the 2^3 Factorial Design with a Central Point

Run	Factor			SR response $(g/g)^a$
	Temperature (°C)	Modification time of GA (h)	Amount of GMA (g)	
1	40.0 (−)	12.0 (−)	0.05 (−)	709.96 ± 20.02
2	40.0 (−)	12.0 (−)	0.10 (+)	172.07 ± 16.22
3	40.0 (−)	24.0 (+)	0.05 (−)	741.74 ± 25.04
4	40.0 (−)	24.0 (+)	0.10 (+)	219.66 ± 18.48
5	60.0 (+)	12.0 (−)	0.05 (−)	463.98 ± 19.92
6	60.0 (+)	12.0 (−)	0.10 (+)	237.07 ± 15.18
7	60.0 (+)	24.0 (+)	0.05 (−)	503.17 ± 22.65
8	60.0 (+)	24.0 (+)	0.10 (+)	177.15 ± 16.78
9	50.0 (0)	18.0 (0)	0.075 (0)	188.46 ± 15.24

^{a} The amounts of the gel components were 3.0 g of AAc, 0.5 g of AAm, and 0.5 g of MGA. In this case the gel is labeled as 3.0–0.5–0.5.

Tables III and IV, respectively. For a confidence interval of 95%, the P values for the main effects of the temperature and amount of GMA and the interaction effect of the temperature and amount of GMA are less than 0.05, and this indicates that they are statistically significant. This argument may be strengthened through a normal distribution plot of both the main and interaction effects, as shown in Figure 3. The points corresponding to significant effects do not fit on a straight line. This implies that alterations in the levels of these factors lead to substantial changes in the SR response. The statistical data found for both kinds of effects are described in Table IV. It is important to report that the data for the main effect of the amount of GMA had a more prominent effect on the SH sensitivity to water.

Modulus of Elasticity

Table V shows the values of E obtained for equilibrium-swollen hydrogels produced from GA modified under different experimental conditions, as described in Table II. The E values were calculated from the linear slope of the stress–strain curves, as shown in Figure 4. The correlation of the stress to the strain implies that the SH experienced elastic deformation when it was under an applied load. There was a macromolecular rearrangement of polymer chains inside the SH to accommodate the deformation. After the removal of the applied load, the polymer chains tended to return to their original formation because of the retractive elastic force that developed in the three-dimensional polymer networks.

The higher E values were observed for runs 2, 4, 6, 8, and 9, in which an increased amount of GMA (0.1 g) to prepare the SHs was used. More crosslinking points formed, and they reduced the mobility of polymer chains within the gel structure; therefore, a loader was needed to compress the SHs. This may be related to the low SR values of these SHs because they had a tighter polymer structure that hindered network expansion upon contact with water. On the order hand, lower E values were observed when a decreased amount of GMA was used (0.05 g), which produced SHs with a high SR capacity, as described in runs 1, 3, 5, and 7. These SHs had a softer polymer structure that was more suitable to expand in water. However, the lower E values of the SHs described in runs 1, 3, and 5 considerably limit their use in a series of applications. Furthermore, those SHs were brittle in the equilibrium swollen state. The E findings and the statistical treatment demonstrate that the experimental conditions described in run 7 are more suitable to produce SHs with good mechanical stability and high water-absorption capacity.

TABLE III
Analysis of Variance Data for the 2^3 Factorial Design with a Central Point

Source	Sum of squares	Degree of freedom	Mean square	F	P
Model	$3.932 \times 10^{+5}$	3	$1.311 \times 10^{+5}$	70.03	0.0007
Temperature	21,137.74	1	21,137.74	11.30	0.0283
Amount of GMA	$3.460 \times 10^{+5}$	1	$3.460 \times 10^{+5}$	184.90	0.0002
AC	26,014.80	1	26,014.80	5.73	0.0203
Lack of fit	43,412.26	1	43,412.26	23.0	0.0085
Pure error	7485.29	4	1871.32		
Total (sum of squares)	$4.441 \times 10^{+5}$	8			

TABLE IV
Main and Interaction Effects for the 2^3 Factorial Design
with a Central Point Described in Table II

A	B	C	AB	AC	BC	ABC
−102.81	27.37	−415.94	−12.32	114.05	−33.54	−41.44

A = temperature; B = time of MGA; C = amount of GMA.

Swelling dynamics of the hydrogels

The water-superabsorbing properties of a crosslinked polymer matrix are related to the flexible chains and chemical nature of polymers that form three-dimensional networks, such as functional ionic groups throughout the polymer chain.[4] These factors are essential components to produce a polymer matrix with high water-absorption efficiency. When an SH is immersed in an aqueous medium, the water molecules diffuse into the hydrogel through pores and interact with functional ionic groups in the polymer networks. Upon contact with water, the functional ionic groups are converted to fixed-charge groups, which cause electrostatic repulsions among the polymer chains, increasing the dimensions of gel networks. Figure 5 shows the ratios of the time-dependent swelling of SHs composed of different amount of AAc at room temperature. In this section, the SHs were produced from GA modified with better experimental conditions demonstrated by a statistical treatment: 60°C for the temperature, 24 h for the time of MGA, and 0.05 g for the amount of GMA. The 3.0–0.5–0.5-composition SH exhibited the
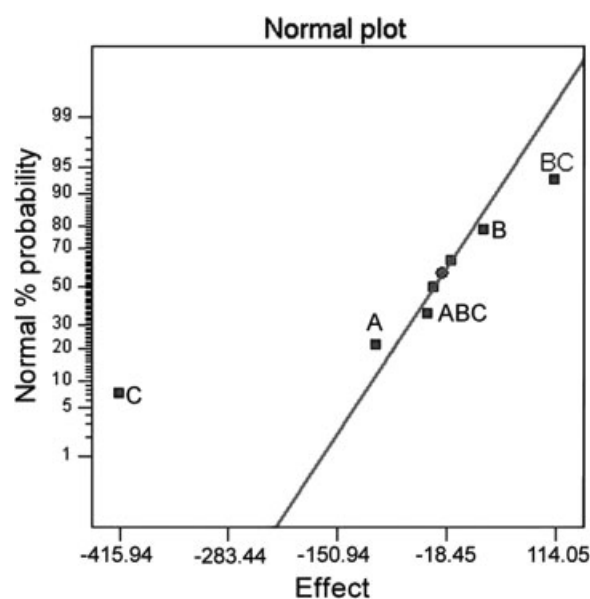
TABLE V
Values of E for SHs Prepared from MGA

Run	E (kPa)
1	2.52
2	22.70
3	2.81
4	25.58
5	9.60
6	17.78
7	10.71
8	30.52
9	23.88

highest performance for water absorption. It swelled nearly 500-fold, with respect to its dry weight, within 60 min of water immersion. The lower water-absorption capacity of the 2.0–0.5–0.5-composition SH was attributed to the decreased number of functional ionic groups in its polymer networks. On the order hand, the increased number of functional ionic groups of the 4.0–0.5–0.5-composition SH was unable to absorb more water because of its high polymer concentration, which made it more difficult for SH networks to be expanded.

Water-absorption mechanism

The penetration of water molecules into flexible polymer networks is usually viewed as a contribution of two water-absorption mechanisms.[23,26] First, the water molecules that diffuse into dry polymer networks result from the physical–chemical interactions of the solvent with the hydrogel. Upon contact with the dry hydrogel, the water molecules primarily interact with more exposed polar groups at the gel surface, and in this way the hydration process is
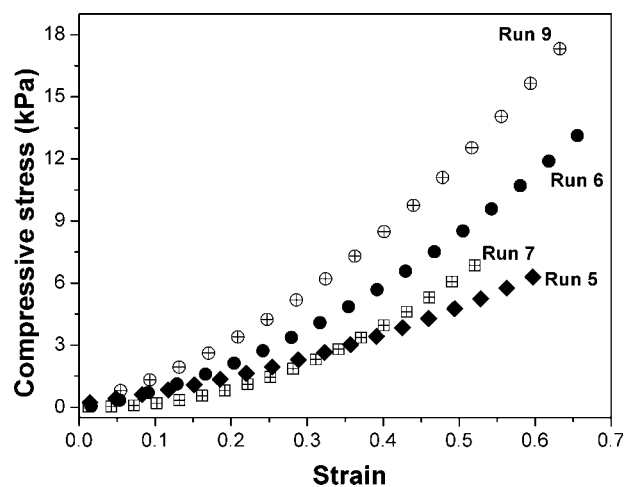
Figure 3 Normal distribution plot of the main and interaction effect build for the 2^3 factorial design with a central point: (A) temperature, (B) time of MGA, and (C) amount of GMA.

Figure 4 Applied stress versus the strain of the SH composed of MGA, AAc, and AAm. The SH was prepared from GA modified with the experimental parameters described in runs 5–7 and 9.

started. Over the initial hydration, there is a macro-molecular rearrangement of polymer networks to accommodate the absorbed water molecules. Second, when the swelling ratio (W_t/W_∞) of a gel linearly responds with the square root of time ($t^{1/2}$), there is diffusion of the water molecules into the hydrogel because of the random movement of the molecules, which is caused by a number of variables, such as the temperature, pressure, gradient concentration, and pH. When the second mechanism is the predominant cause of the gel swelling, it is believed that the swelling is governed by Fickian diffusion. However, if the first mechanism is the predominant cause, it is assumed that the penetration of water molecules into the hydrogel is controlled by a macromolecular relaxation mechanism. Exponent n, described in eq. (2), is a mathematical parameter that has been used to describe the water-absorption profile of the swellable polymer networks. However, n strongly depends on the geometrical form of the hydrogel matrix because of the progression in the swollen–dry boundary caused by the swelling process.[26] In this work, cylindered SH samples were used in water-absorption studies. It follows that n assumes the following values: (1) $n = 0.45$ for Fickian diffusion (case I), (2) $0.45 < n < 0.89$ for anomalous transport (contribution of Fickian diffusion and controlled relaxation), (3) $n = 0.89$ for zero order (case II; contribution of controlled relaxation of the polymer chains), and (4) $n > 0.89$ for supercase II (contribution of the macromolecular relaxation of the polymer chains). The n values of SHs with different concentrations of AAc are summarized in Table VI. The n values were higher than 0.45 for the three SHs, demonstrating that their water-absorption profiles were more dependent on the polymer relaxation. It is important to note that this typical swelling behavior of SHs is due to the ability of their ionic
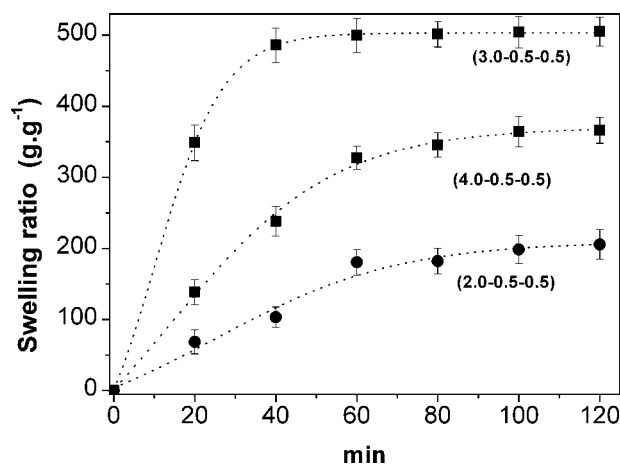
TABLE VI
Parameters n and k for SHs Swollen in a Buffer Solution of pH 7

Gel composition	$k \times 10^2$ (min$^{1/2}$)	n
2.0–0.5–0.5	1.87 ± 0.08	0.83 ± 0.04
3.0–0.5–0.5	2.84 ± 0.05	1.23 ± 0.03
4.0–0.5–0.5	1.80 ± 0.01	0.98 ± 0.09

The errors represent standard deviations for two experiments.

polymer networks to expand in water. Conventional hydrogels, called absorbent hydrogels, exhibit a water-transport mechanism more dependent on anomalous transport and/or transport Fickian diffusion[22] because of their lower water-absorption capacity. A lower n value was observed for the 4.0–0.5–0.5-composition SH because of the high polymer concentration, which hardly allowed gel networks to be expanded in an aqueous medium. The 3.0–0.5–0.5-composition SH exhibited an n value higher than 0.89 (supercase II type of penetrating transport mechanism), and this indicated that the water-absorption mechanism exclusively depended on the macromolecular relaxation of the polymer chains. The excellent performance for water absorption and E make the 3.0–0.5–0.5-composition SH suitable for further tests in various applications such as soil conditioning, disposable infant diapers, and feminine napkins.

CONCLUSIONS

An SH with fast water-absorption dynamics and good mechanical stability was obtained from MGA. From a statistical treatment, it was found that the main effects of the temperature and amount of GMA and the interaction effect of the temperature and amount of GMA on the SR responses were statistically significant. The amount of GMA had a more prominent effect on gel swelling. Lower E values were observed when a decreased amount of GMA was used (0.05 g), which produced SH with a high SR capacity. The 3.0–0.5–0.5-composition SH was more suitable to absorb a large amount of water (SR = 503.17 ± 22.65 within 60 min of water immersion) without its mechanical stability being affected. Better GA modifying conditions to produce such an SH were as follows: 60°C for the temperature, 24 h for the time of MGA, and 0.05 g for the amount of GMA. It exhibited an n value higher than 0.89 (supercase II type of penetrating transport mechanism), indicating that its water-absorption mechanism depended exclusively on the macromolecular relaxation of the polymer chains. The excellent performance for water absorption and E make the 3.0–0.5–0.5-composition SH a candidate suitable for

Figure 5 Ratios of the time-dependent swelling of the 2.0–0.5–0.5, 3.0–0.5–0.5, and 4.0–0.5–0.5 SHs swollen in a buffer solution of pH 7 at 25°C.

further tests in various applications such as soil conditioning, disposable infant diapers, and feminine napkins.

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