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New Super-Absorbing Hydrogel Hybrids from Gum Arabic and Acrylic Monomers

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Novel super-absorbing hydrogel hybrids composing arabic gum (AG) and acrylamide (AM)/acrylic acid (AA)-potassium acrylate (AK) were prepared using a highly practical, homogenous solution polymerization process, conducted under normal atmospheric conditions. The unique characteristics of the gum and the redox pair initiating system (persufate/metabisulfite) favored the crosslinking polymerization, run under concentrated conditions without a need to heat. To produce hydrogel hybrids having the highest gel content and the highest swelling capacity, the preparative process was systematically studied through investigation of the certain reaction variables, i.e., the concentration of AG, initiator, crosslinker, monomer, and AM/AA-AK mole ratio. The spectral and thermal characteristics of the optimally prepared hydrogel were studied using FTIR spectroscopy and thermogravimetric analysis, respectively.

Keywords arabic gum, hydrogel, super-absorbent, acrylic, polymerization

Introduction

Gum arabic, sometimes known as acacia gum or arabic mucilage, is unique in that it forms homogeneous solutions of greater than 50% concentration (1). Although gum arabic function is based primarily on its properties as a protective colloid and emulsifier, its unique characteristics is usually due to its comparatively very low viscosity. This gum is the amber, amorphous, nontoxic, odorless, colorless, tasteless and dry exudate of the acacia tree. 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. (2).

Gum arabic is a highly branched arabinogalactan polysaccharide with rhamnose and glucuronic acid end units. Its molecular weight has been estimated to be M_w 500 000 and M_n 170 000 g/mol (2–4).

Hydrogels, hydrophilic polymer networks, are increasingly being used in various applications, from pharmaceutics to agriculture. They have occupied a unique position in the field of medicine and pharmacy (5, 6) due to the way the imbibed water strongly

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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 (super-absorbent polymers, SAPs) (7–14). Recently, we modified SAPs via incorporating inorganic materials to improve the swollen gel strength and to minimize the cost of the product (13, 14).

A literature survey based on a "Chemical Abstracts" search revealed that no report was published on the synthesis of hydrogels composed of arabic gum and acrylic monomers. This study deals with the first chemical modification of arabic gum through graft crosslinking copolymerization of acrylic monomers to prepare super-absorbent hydrogel hybrids. Thus, acrylamide (AM) and partially neutralized acrylic acid (AA) were graft copolymerized onto arabic gum in the presence of a crosslinking agent to form a hydrogel network, with super-swelling properties.

Experimental

Materials

Gum arabic, (AG, from Merck), *N,N′*-methylenebisacrylamide (MBA, from Fluka), ammonium persulfate (APS, from Fluka), sodium metabisulfite (SMBS, Merck), acrylamide (AM, from Fluka), acrylic acid (AA, from Fluka) were of analytical grade and used without further purification.

Polymerization

Acrylic acid was partially neutralized with KOH solution (18.0 g KOH + 16.0 g H_2O + 30.0 g AA). Definite quantities of AG, AM, APS, and SMBS were dissolved in distilled water. A 200 mL beaker was charged with AG and the monomer solutions; the crosslinker MBA and the initiators were subsequently added to the beaker. The reaction started instantaneously, once the redox initiator components were added.The temperature and viscosity of the reaction mixture rapidly increased to a gelation point, when the magnetic stirrer was stopped. The product was removed from the beaker followed by scissoring and then drying in an air-circulating oven for 7 h at 65°C to reach a constant weight. The dry product was ground with a hammer type mini-grinder, screened and classified.

Measurements

The equilibrium swelling (g/g) was measured according to a conventional "tea bag" method (15). To determine the gel content values, a weighed sample was dispersed in 0.90 wt% NaCl solution to swell for 72 h. After filtration, the extracted gel was dried (65°C, 5 h) and re-weighed. Gel content (Gel, %) was calculated using Equation (1).

$$Gel = \frac{m_f - 0.009A}{m_i} \times 100 \tag{1}$$

where m_i, m_f, and A stand for initial weight of sample, final weight of sample, and the equilibrium swelling of the sample in the saline solution, respectively.

Instrumental Characterization

The product samples were spectroscopically analyzed by a Brucker Equinox 55 Infrared spectrophotometer (FTIR), using thin KBr discs. The samples were thermally characterized using differential scanning calorimetry (DSC, Polymer Laboratories) and thermogravimetric analysis (TGA, Perkin-Elmer, Pyris 1) under nitrogen atmosphere and a heating rate of 20°C/min.

Results and Discussion

A gum arabic-based super-absorbent hydrogel was synthesized by free radical copolymerization of AM and partially neutralized AA onto the gum. The crosslinking polymerization process was studied by varying the reaction parameters (i.e., concentration of gum, crosslinker, initiator, monomers, and AM/AA-AK ratio) affecting the ultimate swelling and gel content of the final hydrogel.

Preparation and Characterization

A free radical polymerization process was chosen to prepare the hybrid super-absorbing hydrogels. The initial synthetic procedure was based on concentrated solution polymerization systems published previously by our group (8, 9, 14). High solubility characteristics of gum arabic favored the concentrated reaction system. Therefore, the gum was incorporated into the formulation to design a copolymerization process in the presence of a water-soluble crosslinker, i.e., MBA. The process proceeded well under normal atmospheric conditions without a need to protect the reaction from air. In addition, the redox initiation system used in the process acted almost instantaneously at room temperature, i.e., no heating was necessary to initiate and conduct the polymerization. Table 1 shows the conditions of the preliminary reactions and the swelling properties of the corresponding products. Because of higher swelling capacity and higher gel content, entry 2 was chosen to employ for investigating the relevant reaction variables.

Since the process is exothermic, the temperature increase can easily be recorded vs. time to follow and simply monitor the process progression (Figure 1). Once the initiator pair is added to the mixture, the temperature is increased while the viscosity is enhanced until gelation. The latter point (gelation time ~ 3–8 min) is indicated by stopping the magnetic stirrer. Then, the slope of the temperature enhancement is increased due to propagation of the polymerization. The process is finished at the end of this step, and the temperature is slowly decreased.

Table 1

Preliminary formulations for the polymerization processes. The quantities are in weight percent

	Reactants						Product properties	
Entry	AG	AA[a]	AM	SMBS	APS	MBA	Gel%	Swelling in water, g/g
1	10.84	0	16.26	0.080	0.080	0.108	44.6	14
2	10.61	6.96	9.55	0.079	0.079	0.106	80.4	60
3	10.39	16.56	0	0.077	0.077	0.104	57.2	47

[a] Acrylic acid partially (76 mol%) neutralized with KOH.

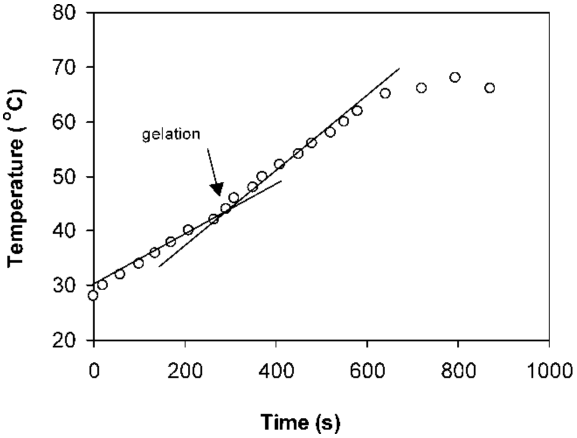

Figure 1. Typical temperature-time profile for the crosslinking graft copolymerization conducted in the present work (AG 7.92%, AM:AA-AK mol ratio 60 : 40, AA 76 mol% neutralized with KOH, total monomer 24.62%, MBA 0.079%, APS 0.147%, SMBS 0.124%).

Spectral Analysis

Figure 2 shows the FTIR spectra of the gum arabic (a), gum-free acrylic-based hydrogel (b), and the sol-free AG-acrylic hydrogel hybrid (c). As indicated in Figure 2(c), both characteristic bands of the gum and of the poly(acrylamide-co-AA/potassium acrylate) are presented in the hydrogel hybrid. The strong, broad peak at 3427 cm^{-1} is related to the OH stretching of the carboxylic and hydroxyl groups of either acrylic or carbohydrate parts. The medium peaks at 1030–1070 cm^{-1}, due to stretching vibration of C–O–C and C–O–H bonds, confirms the saccharide structure of the hydrogel hybrid. The very sharp peak at 1668 cm^{-1} and its left shoulder are attributed to the primary amide C=O stretching (16). The amide bond is reconfirmed by (i) a weak and obvious band at 1453 cm^{-1}, which is due to the C–N bending vibration, and (ii) an intensive shoulder located at ~3200 cm^{-1}. The two strong peaks at 1560–1630 cm^{-1} are related to the carboxylate C=O stretching, originating mainly from the acrylate part of the hydrogel hybrid. Since the hybrid had already been extracted to remove the soluble contents, its FTIR analysis proved that the gel network was not a physical mixture and chemical linkages have been formed during the free radical polymerization reaction (15). Therefore, the hybrid is composed most likely of a grafted, crosslinked copolymeric structure. In addition, the semi-interpenetrating polymer network (semi-IPN) structure is probable. The exact chemical structure of the hybrid remains a subject of debate at this stage of our study.

Thermal Analysis

TGA method was employed to thermally characterize the hydrogel hybrid in comparison with the intact gum and the gum-free acrylic hydrogel (Figure 3). In contrast to the untreated AG that showed a two-stage pattern with an initial decomposition temperature (IDT) of 275°C without a char residue at ~700°C, the hydrogel hybrid exhibited a multistep pattern with a char yield of ~15%, and an IDT around of 320 was observed in its thermogram. In addition, one of the decomposition peaks appeared at ~350°C was attributed

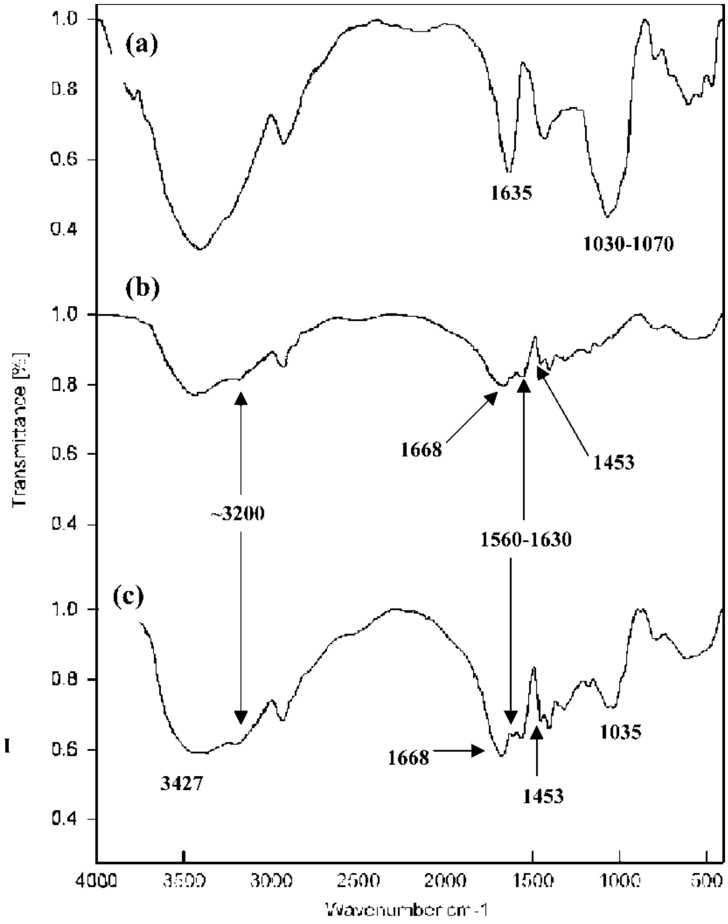

Figure 2. FTIR spectra of (a) arabic gum, (b) gum-free crosslinked poly(AM-co-AA-co-AK) hydrogel, and (c) arabic gum-acrylic hydrogel hybrid, MR5, prepared under conditions given in Figure 1.

to the AG moiety of the hydrogel (Figure 3(c)). In the intact gum, this main decomposition occurred at a lower temperature, i.e., 325°C (Figure 3(a)). Therefore, it may be concluded that the synthetic part of the hydrogel hybrid improves its thermal stability. No non-degradative thermal transition, e.g. T_g, was observed in DSC traces of the hydrogels.

Study of the Reaction Variables

The Gum Concentration. The concentration of arabic gum (AG) was varied from 5.6 to 26.26 wt%. No certain trend was observed in the gelation times in this series of reactions (Table 2). The variation of the hydrogel swelling in distilled water and saline vs. AG concentration in the initial feed of polymerization are presented in Figure 4 and Table 2, respectively. According to Figure 4, although a higher AG amount resulted in hydrogels with higher swelling, considerable loss of gel content was determined for the samples prepared from the reactions conducted with AG concentration higher than 10.6 wt%. The gel reduction was related to enhancement of soluble materials mostly

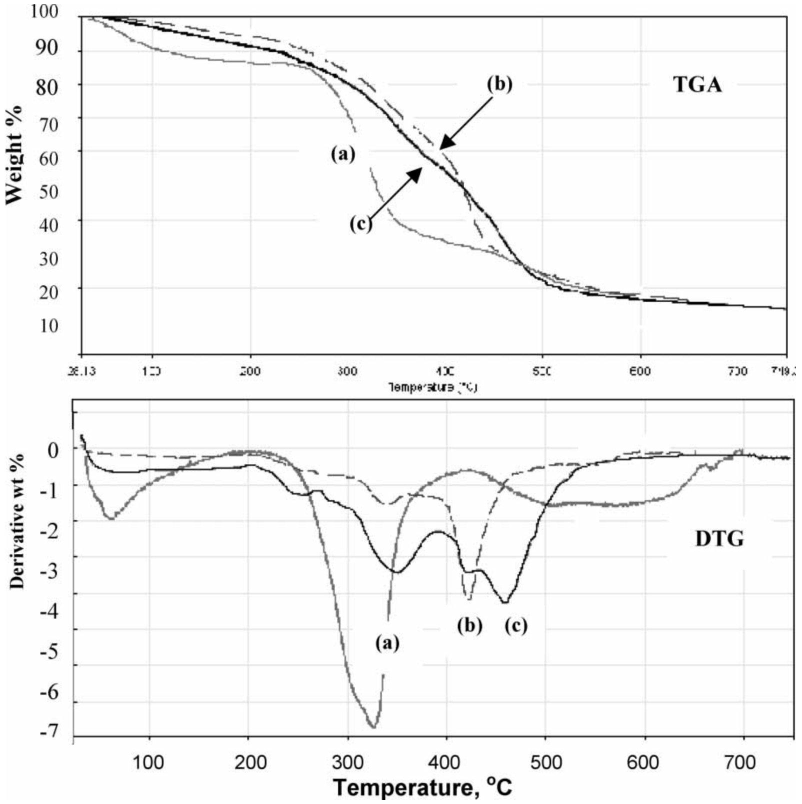

Figure 3. TGA and DTG thermograms of (a) arabic gum, (b) gum-free crosslinked poly(AM-co-AA-co-AK) hydrogel, and (c) arabic gum-acrylic hydrogel hybrid, MR5, prepared under conditions given in Figure 1.

included the non-reacted arabic gum. Since the swelling of hydrogel networks is highly sensitive to the crosslink density, because of unwanted automatic decrease of the crosslinker concentration in the mixture, the swelling is enhanced versus increasing of the gum concentration. The sample AG2 also comprised the highest swelling in saline.

The Initiator Concentration

This series of experiments was conducted to study the redox pair concentration (APS/SMBS 1 : 1 mole ratio). The results are given in Table 2 and Figure 5. The gelation time of the polymerization is increased when the initiator concentration is increased. This is due to of shorter chain formation leading to imperfect hydrogel networks, which is a known phenomenon in the crosslinking polymerization (17). Regarding the product properties, swelling in either water or saline is increased with increasing of the initiator concentration. This is a well-known behavior in hydrogel networks that has been investigated previously (9, 14). On the other hand, the gel content is reached to a maximum value at an initiator concentration of 0.362 wt%. The hydrogel samples prepared with the initiator concentration higher than this amount, produced hydrogels with reduced gel contents. The higher soluble content is originated from the imperfection in the networks

Table 2

Experimental series designed for investigating the synthetic process to prepare carbohydrate-acrylic super-absorbing hydrogel hybrids (APS/SMBS mol ratio 1 : 1, AA 76 mol% neutralized with KOH, room temperature). Unless MR series, a 60 : 40 mol ratio of AM:AA-AK was used in all experiments

Exp. series	Exp. code	Reaction variable content[a]	Reaction gelation time, min.	Swelling of product (in 0.9% NaCl), g/g
Arabic gum[b]	AG1	5.6	4	28.0
	AG2	10.61	4.5	29.0
	AG3	15.11	3	27.5
	AG4	19.18	3	25.5
	AG5	26.26	4	25.0
APS-SMBS redox pair initiator[c]	I1	0.098	3	30.7
	I2	0.144	4.5	28.0
	I3	0.216	5	26.9
	I4	0.292	6	26.0
	I5	0.362	7	29.0
	I6	0.486	10	30.4
	I7	0.583	12	32.9
MBA crosslinker[d]	C1	0.028	37	31.3
	C2	0.064	18	29.7
	C3	0.106	7	28.0
	C4	0.148	6	24.1
	C5	0.19	5	25.0
	C6	0.233	3	22.5
AM-AA-AK monomer[e]	M1	14.14	8	30.0
	M2	16.48	7	32.0
	M3	20.6	6	34.0
	M4	24.62	5	35.7
	M5	27.31	3	36.8
AM/(AA-AK) monomer mole ratio[f]	MR1	100	5	25.0
	MR2	90	6.5	26.6
	MR3	80	4	28.0
	MR4	70	5.5	35.7
	MR5	60	5	36.5
	MR6	50	4	33.5
	MR7	30	3	32.0
	MR8	0	1.5	30.5

[a] With an exception of the MR series, all of the values are in weight percent.

[b] Unchanged reactants: total monomer 16.51%, initiator 0.157%, crosslinker 0.106%.

[c] Unchanged reactants: AG 10.61%, total monomer 16.51%, crosslinker 0.106%.

[d] Unchanged reactants: AG 10.59%, total monomer 16.48%, initiator 0.362%.

[e] Unchanged reactants: AG 10.59%, initiator 0.362%, crosslinker 0.106%.

[f] Unchanged reactants: AG 7.92%, total monomer 24.62%, initiator 0.271%, crosslinker 0.079%.

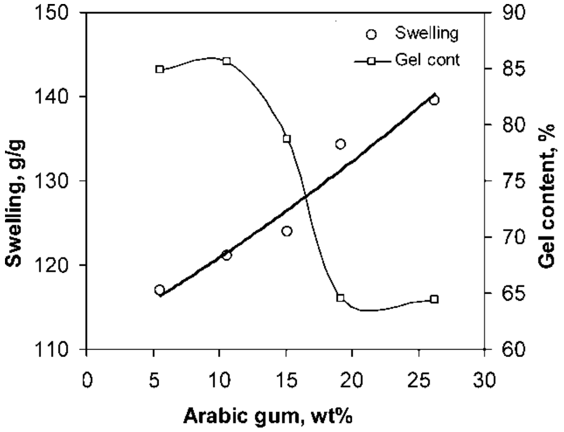

Figure 4. Variation of swelling in water and gel content of arabic gum-acrylic hydrogel hybrids vs. the gum concentration employed in the polymerization process (Total monomer 16.51%, initiator 0.157%, crosslinker 0.106%).

formed at higher concentrations of initiator (i.e., the same main reason for the above-mentioned gelation time and swelling enhancement).

The Crosslinker Concentration

According to the C series in Table 2, higher crosslinker (MBA) concentrations cause a quicker time of gelation, as expected, since the network is formed faster in the presence of more amounts of the crosslinking agent. Figure 6 exhibits the swelling and gel content values of the hydrogel products versus the crosslinker (MBA) concentration. It is observed a well-known swelling-crosslinker power law relationship (8, 9, 18), so that

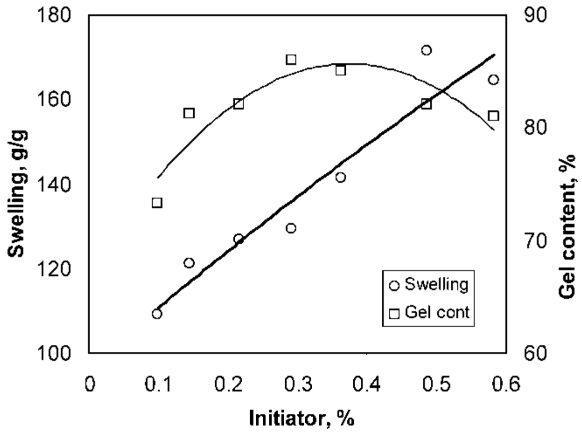

Figure 5. Variation of swelling in water and gel content of arabic gum-acrylic hydrogel hybrids vs. the initiator concentration (APS/SMBS 1 : 1 mole ratio) employed in the polymerization process (Arabic gum 10.61%, total monomer 16.51%, crosslinker 0.106%).

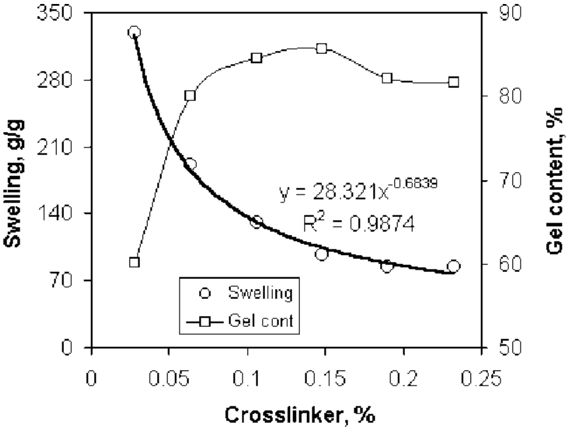

Figure 6. Variation of swelling in water and gel content of arabic gum-acrylic hydrogel hybrids vs. MBA crosslinker concentration employed in the polymerization process (Arabic gum 10.59%, total monomer 16.48%, initiator 0.362%).

the higher the crosslinker concentration, the lower the swelling capacity, either in water or in saline (Figure 6, Table 2). According to the C series in Table 2, a MBA concentration of 0.106% (sample C3) provides the best values of swelling and gel content. At lower than the latter amount, the gel content is diminished appreciably because of the formation of very loosely crosslinked networks, resulting in highly swollen hydrogels with very low gel strength. The slight loss of gel content of the next products (i.e., C4 and C5), prepared from higher crosslinker concentrations, may be attributed to the rapidly gelated system that prevents the monomers and gum to fully participate in the crosslinking polymerization.

The Monomer Concentration

The influence of the total monomer concentration was studied in this experimental series (Table 2, M series). According to the radical polymerization kinetics (19) the higher monomer concentration causes a higher rate of polymerization, and an observed gelation time decrease. On the other hand, because of the higher molecular weight chain formation between the crosslink points in the network (8, 9, 17, 18) both gel content and swelling capacity were increased when the monomer concentration was increased (Figure 7). The sample M4 was chosen as a hydrogel optimally prepared in this series.

The Monomers Ratio

The mole ratio of AM/AA-AK was changed from 100 to 0 to investigate the influence of the amounts and type of the monomer on the gelation time, gel content and swelling capacity (Table 2, Figure 8). Overall, the gelation time is enhanced as the AM component is increased. On the other hand, swelling 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

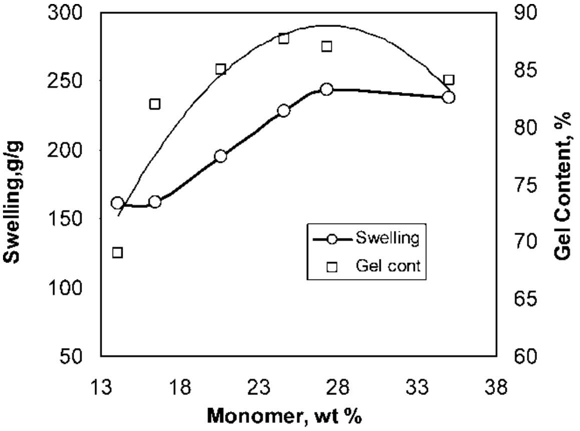

Figure 7. Variation of swelling in water and gel content of arabic gum-acrylic hydrogel hybrids vs. total monomer (AM/AA-AK) concentration employed in the polymerization process (Arabic gum 10.59%, initiator 0.362%, crosslinker 0.106%).

groups in the crosslinked chains. Due to the same reason, the swelling loss (from MR2 to MR1) in saline is not appreciable, so MR1 sample may be considered to as an anti-salt super-absorbing hydrogel hybrid. From the gel content variation shown in Figure 8, it can be proposed that, comparing with AM, AA-AK tends to react with the crosslinker MBA more readily. This is why the gel content is dramatically reduced at high AM compositions (90 and 100%). Due to the same reason, the swelling is increased from the AM/AA-AK ratio 0 to 90%. The ratio 100% (i.e. MR1), however, is an exceptional case because it forms a full-AM/AG hybrid network, which is not aimed in the present work.

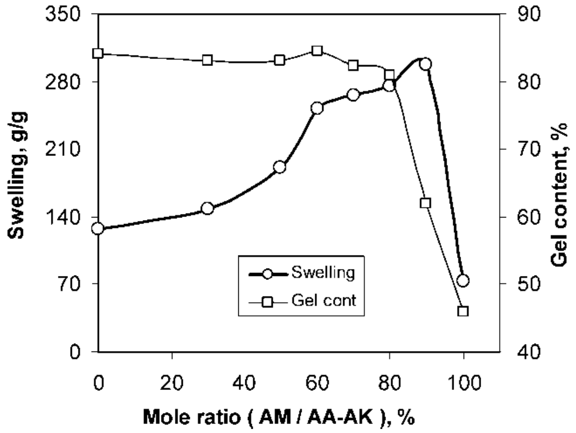

Figure 8. Variation of swelling in water and gel content of arabic gum-acrylic hydrogel hybrids vs. monomer mole ratio (AM/AA-AK) employed in the polymerization process (Arabic gum 7.92%, total monomer 24.62%, initiator 0.271%, crosslinker 0.079%).

Conclusions

Super-absorbing hydrogel hybrids, composed of arabic gum (AG) and AM/AA-AK, were prepared via a homogenous polymerization process under atmospheric conditions. The unique characteristics of the gum and the selected redox pair initiating system (APS/SMBS) permitted us to conduct the crosslinking polymerization in concentrated solutions without a need to heat. Indeed, the radical polymerization was started and proceeded without protecting the reaction from air. Thus, a highly practical preparative system was systematically investigated to produce novel hydrogel hybrids having super-swelling properties. Overall, the reaction conditions may be concluded as follows: AG 7.9%, AM/AA-AK 60 : 40 (AA 76 mol% neutralized with KOH), total monomer concentration 24.6%, MBA concentration 0.079%, initiator (i.e., APS/SMBS mole ratio 1 : 1) 0.27%, room temperature. The structural and thermal characteristics of the hydrogel hybrid were studied by FTIR and TGA, respectively.

The carbohydrate-acrylic super-absorbent hydrogel hybrids may potentially be used in agriculture, biomedicine, pharmaceutics and controlled delivery of bioactive agents.

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