Experimental Design for the Synthesis of Polyacrylamide Superporous Hydrogels

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ABSTRACT: An experimental design, based on L-18 Taguchi matrix, was used to examine the influence of formulation ingredients on a variety of aspects of gel formation during the synthesis of polyacrylamide hydrogels. Although a vast variety of formulations could lead to reasonable hydrogel networks, attempts were made to design a basic formulation that could be used to generate strong and elastic superporous hydrogels. The final properties of the hydrogels, especially when prepared in the presence of atmospheric oxygen, depended on events during their gel formation. Gelation features, including inhibition period, exothermic period and temperature increases, observed during the gelation, are dependent on the type and concentration of ingredients within the preparatory formulation. For this study, seven variables were chosen and their effects were examined within the frame of a L-18 Taguchi matrix. The parameters examined were inhibition period, exothermic period, maximum temperature due to exothermic reaction, and solubility feature along with the physical appearance at gelation point.

KEY WORDS: polyacrylamide, superporous hydrogels, Taguchi matrix, gelation, polymerization, polymerization induction period.

INTRODUCTION

Superporous hydrogels are hydrogels that, regardless of their size, swell to their equilibrium swelling in aqueous media in less than a

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couple of minutes. Superporous hydrogels were initially developed as gastric retention devices. Since the fast swelling of superporous hydrogels is size independent, they are useful in applications where large surface area and fast mass transfer are beneficial [1]. A few aspects of superporous hydrogels including synthesis [1–3], pore structure [4], gastric retention properties [5,6], characterization [7], swelling dependence on compression stress [8] and pH [9] and NMR characterization [10] have been studied. But, little attention has been paid to the events that occur during gel formation.

The final hydrogel properties are dependent on the events during gel formation, particularly when the reaction is carried out in the presence of oxygen. Existence of an inhibition period in the presence of oxygen is well-established for free radical polymerizations in general [11]. As shown by Barnes and others [12–15], a probable reaction of oxygen may be the formation of a copolymer with the monomer (M), i.e., polyperoxides (ROO$^{\cdot}$ and ROOM$^{\cdot}$). This reaction may compete with the normal polymer radicals (RM$^{\cdot}$) for monomer. Since the addition of monomer to the peroxy radical is much slower than the normal polymer radical [16], an inhibition or induction period is often observed. During the inhibition period, the degree of polymerization is low as reported by Flory [11]; nevertheless, each peroxide moiety is a potential source of free radicals to initiate polymerization. Therefore, the concentration of initiating radicals increase with time, leading to more polyperoxide formation and to a self-accelerating process. At some point, the concentration of initiating radicals become high enough to enable significant amounts of ‘‘normal’’ polymerization to occur, resulting in a rapid increase in viscosity, slowing of oxygen diffusion inwards and a rise in temperature during gelation [17]. Using DSC, Omidian *et al.* studied the inhibition period during the gel formation of conventional acrylic-based hydrogel polymers [18]. They evaluated various schemes for the inhibition period and the final polymer properties. They found that the duration of the inhibition period and the exotherm feature (amount and its state of occurrence, i.e., gradual/sudden) affected the reaction kinetics, polymer chain length, water absorbency, polymer sol fraction and physical consistency of the gel after synthesis.

In conventional hydrogel synthesis, reactions continue during the final drying process and influenced the gel consistency after its formation [15]. Thus, the swelling properties of the final dried polymer are affected not only by the inhibition period events, but also by the drying process. On the other hand, during the synthesis of superporous hydrogels, to maintain the superporosity, gels are dehydrated in ethanol almost immediately after the gel forms. Consequently, a superporous hydrogel is obtained in a dry and brittle state after dehydration. During dehydration, residual monomers and other soluble fractions are extracted from the gel polymer. Therefore, the extent of reaction in the final product is the same as the reaction at the time of gel formation. Likewise, kinetic chain length, polymer sol content and the final gel consistency are defined as obtained at the time of gel formation. Thus, events during the gelation or exothermic period in the synthesis of superporous hydrogels are expected to be much more critical than for conventional hydrogels.

Experimental design, based on the Taguchi matrix, has already been found useful in different disciplines in the study of the effects of various parameters on final product properties, for screening parameters and optimizing the synthesis or production procedures [19–23]. The Taguchi method was used here to study the effects of the ingredient concentrations on the gelation features of polyacrylamide (PAAm) hydrogel formulation as well as on the synthesis of acrylamide-based superporous hydrogel polymers.

EXPERIMENTAL

Materials

Acrylamide (C_3H_5NO, AAm, Sigma), *N*,*N*′-methylenebisacrylamide ($C_7H_{10}N_2O_2$, BIS, Sigma), Pluronic® F-127 (PEO-PPO-PEO, BASF), ammonium peroxydisulfate ($N_2H_8S_2O_8$, APS, Aldrich), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine ($C_6H_{16}N_2$, TMEDA, Sigma), glacial acrylic acid ($C_3H_4O_2$, AAc, Aldrich) inhibited with 200 ppm monomethylether hydroquinone (MEHQ) and crosslinked carboxymethylcellulose (croscarmellose, Ac-Di-Sol® from FMC) were used as received. Distilled water was used to prepare the solutions. All solutions were freshly made at room temperature before use.

General Synthetic Procedure

To make the superporous hydrogel, a monomer, crosslinker, water (if necessary), foam stabilizer, acid, polymerization initiator, initiation catalyst (if any), and foaming agent were added sequentially to a test tube (typically 130 mm height and 100 mm outer diameter) [3]. As in Table 1, 500 μL of 50 wt.% aqueous AAm solution was placed into a test tube; to this solution, 100 μL of Bis solution, distilled water (500, 750, and 1500 μL), 50 μL of aqueous F127 solution (5 and 10 wt.%) and acrylic acid (50 and 100 μL) were added under mild shaking. Ac-Di-Sol®

Table 1. Features of the materials used in hydrogel preparations.

Ingredients	Amounts and Concentration	Role
Aqueous acrylamide (AAm 50%) solution	500 μL	Base monomer
Aqueous methylenebisacrylamide (Bis) solution	100 μL of 0.0*, 1.0 and 3.0 wt.% solution	Crosslinker
Distilled water	As in Table 2, 500, 750 and 1500 μL	Diluent
Aqueous pluronic F127 solution (F127)	50 μL of 0.0, 5.0 and 10.0 wt.% solution	Foam stabilizer
Glacial acrylic acid (AAc)	0.0, 50.0 and 100.0 μL	Comonomer, Foaming aid
Crosslinked carboxymethylcellulose (Ac-Di-Sol)	0.0–200 mg	Foam strengthener
Aqueous ammonium peroxydisulfate (APS)	40 μL of 10.0, 20.0 and 40.0 wt.% solution	Redox initiator (oxidant)
Aqueous tetramethylethylenediamine (TMEDA)	40 μ L of 10.0, 20.0 and 40.0 v/v.% solution	Redox activator (reductant)

*To keep the monomer concentration constant, additional distilled water was added accordingly.

was then added under vigorous shaking. Once a homogeneous dispersion was obtained, 40 μL of TMEDA solution (10, 20, and 40 v/v%) was added under shaking and homogenized for 30 s. This was followed by the addition of 40 μL of APS solution (10, 20 and 40 wt.%). Thermocouple was put into the reacting mixture after the APS was added and dispersed. After the APS was added and dispersed, a thermocouple was put into the reacting mixture. The reaction was monitored using an instrument with a timed thermocouple. Temperature increases (with the nearest of ± 1.0°C) due to the reaction were recorded at timed intervals. To gain a more accurate measurement of the onset of reaction, in each temperature/time profile, intersection of horizontal axis (temperature of 27°C) and line through the points of early temperature rises was obtained and considered as the inhibition period (A-B in Figure 1). Time difference between corresponding times to reach the maximum temperature ($t_{T\max}$) and the inhibition period was recorded as the exothermic period (B-C in Figure 1). Temperature rise during the gelation process (C-D in Figure 1) was used as a measure of polymerization that occurred during the gelation process.

For superporous hydrogel preparation, the same procedure was applied except that sodium bicarbonate (50 mg) was added. The latter was added 15 s before the end of the inhibition period. Once this period ended, an exothermic reaction started and the reaction mixture was converted to a foam. Foaming was extended up to its final expansion,

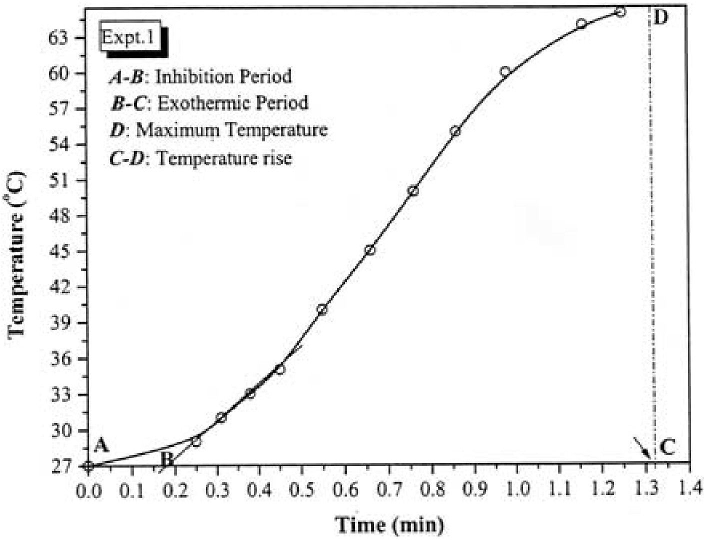

Figure 1. Kinetics of temperature change during the hydrogel synthesis.

after the temperature declined to about 30°C the mixture was placed in ethanol and dehydrated for about 1 h. Complete drying was done in an oven at 60°C for 1 h. The dried foam was weighed and placed into distilled water to measure swelling. To calculate the swelling capacity, the water-swollen foam was blotted with filter paper and weighed again.

Load–Deformation Measurement

A simple bench comparator consisting of a weight, weight holder (upper touch), spindle, gauge, lower touch and a laboratory jack was used. The individual hydrogels after their exothermic period were placed on the jack (below lower touch). Weights were applied to the upper touch of the bench comparator and the corresponding amounts of hydrogel deformations were read from the gauge.

RESULTS AND DISCUSSION

General Observations

The amounts of crosslinker, diluent, foam stabilizer, comonomer, foam strengthener and redox couple used are listed in Table 1 and the changes are shown in Table 2. The common observation with all

Table 2. Variables and parameters in our experimental design based on L-18 Taguchi matrix.

Experiment Number	XCMC	Bis	D.W	F127	AAc	APS	TMEDA	Inhibition Period (Min)	Exothermic Period (Min)	T_{max} (°C)	Solubility Status	Physical Appearance at Gel Point
	mg	w/w%	μL	w/w %	μL	w/w %	v/v%					
1	0	0	500	0	0	10	10	**0.18**	**1.15**	**65.5**	Soluble	Grease-like
2	0	0	750	5	50	20	20	**5.7**	**5.5**	**53**	Soluble	Grease-like
3	0	0	1500	10	100	40	40	**8.8**	**8.2**	**45**	Soluble	Oily
4	0	1	500	0	50	20	40	**1.8**	**2.3**	**68.5**	Swellable	RH*-tough
5	0	1	750	5	100	40	10	**15.5**	**10**	**51.5**	Swellable	RH-tough
6	0	1	1500	10	0	10	20	**0.32**	**2.08**	**48.3**	Semisoluble	RH-soft
7	0	3	500	5	0	40	20	**0.08**	**0.72**	**69.5–70**	Swellable	RH-very tough
8	0	3	750	10	50	10	40	**5.7**	**4.8**	**57.5**	Swellable	RH-tough
9	0	3	1500	0	100	20	10	**46**	**34**	**32**	Semisoluble	Grease-like
10	200	0	500	10	100	20	20	**12.5**	**5.8**	**63**	Soluble	Grease-like
11	200	0	750	0	0	40	40	**0.08**	**0.81**	**64.5**	Soluble	Grease-like
12	200	0	1500	5	50	10	10	**41.25**	**25.5**	**34**	Soluble	Grease-like
13	200	1	500	5	100	10	40	**7.8**	**4.25**	**68**	Swellable	RH-tough
14	200	1	750	10	0	20	10	**0.43**	**1.27**	**60.5**	Swellable	RH-very tough
15	200	1	1500	0	50	40	20	**8**	**5.8**	**45**	Semisoluble	RH-soft
16	200	3	500	10	50	40	10	**5.05**	**2.8**	**67**	Swellable	RH-very tough
17	200	3	750	0	100	10	20	**25**	**8.5**	**52**	Swellable	RH-tough
18	200	3	1500	5	0	20	40	**0.18**	**1.59**	**52**	Swellable	RH-tough

*RH: Rubber hydrogel, a hydrogel that shows rubbery properties immediately after its gelation. Rubber hydrogels were obtained in different consistencies throughout the work. Their consistencies were evaluated in terms of their resistance to stretching. Soft hydrogels are readily torn apart, while tough and very tough hydrogels showed more and even more resistance to failure. Difference in consistencies of the rubber hydrogels obtained was quite clear.

experiments was a period of inhibition, which was followed by normal polymerization. As shown in Figure 1 (Experiment 1), the reaction started at room temperature after a certain period, i.e., inhibition period of about 0.18 min; the dynamic "normal" polymerization began after this phase and continued for about 1.32 min. These processes correspond to about 1.15 min of total exothermic period. Following this exothermic period (B-C period), the temperature declined to room temperature.

Using 18 experiments, a variety of gelation features were observed as shown in Figure 2. Almost, no inhibition period was observed for Experiment 7. On the other hand, in Experiment 9, normal polymerization took a very long time (about 46 min) to get started. The exothermic periods were very scattered (short and long). Shown in Figure 2 (for Experiments 7 and 9, respectively) are short and very long exothermic periods (0.72 vs. 34 min). During this evaluation, a broad value of temperature rises was also observed (minimum of 32°C vs. a maximum of 70°C, respectively, for the Experiments 9 and 7). Generally the shortest inhibition periods, the shortest exothermic periods and the highest temperature rises were obtained with formulations containing

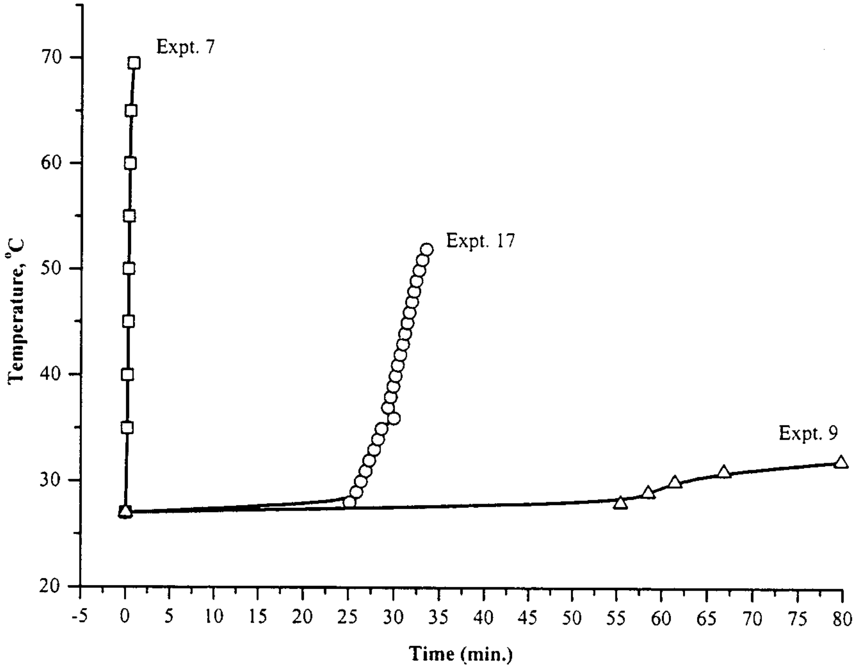

Figure 2. Time–temperature profiles of different experimental conditions.

no acrylic acid or the least amount of water as diluent (Experiments 1, 4, 11, 14, and 18) and vice versa (Experiments 5, 9, 12, and 17).

The gel products were also examined in terms of their solubility or swellability in distilled water. A variety of solubility behavior was observed ranging from products of readily water-soluble to sparingly and highly water-swellable. Besides, various water-soluble and water-swellable products showed broad ranges of gel consistencies, i.e., oily, grease-like and rubbery (soft, tough and very tough).

All soluble products showed grease-like consistency after gel formation. With one experiment, in which all ingredients were introduced as their maximum concentrations, an oily product was obtained. A soluble product was generally observed with formulations with no crosslinker (Experiments 1–3 and 10–12). Although all the formulations that contained a certain amount of crosslinker were swellable in water, very soft and loose hydrogels were obtained at high water dilution (Experiments 6 and 15). On the other hand, stiff hydrogels were obtained with high crosslinker concentrations and low amounts of water (Experiment 16).

In comparing Experiments 1, 4, and 7, the strength properties of the hydrogels increase with increased crosslinker concentration. Despite the higher initiator concentration in Experiment 7 (that in turn favors shorter kinetic chain length and hence a higher water-soluble product), the final product in Experiment 1 was stronger and stiffer. This means that the strength properties of the hydrogels obtained were affected more by the crosslinker concentration than by the initiator concentration. Although high water dilution (which lowers the total monomer concentration) generally resulted in an oily and grease-like product, high crosslinker concentration produced a rubber-like hydrogel as a final product (Experiments 15 and 18).

A common feature of all the experiments that resulted in semi-soluble products (Experiments 6, 9, and 15) was high water dilution (using 1500 μL water). Even though a high amount of crosslinker was used in these experiments, there was still a large soluble fraction that gave a semi-soluble and a very loosely-structured hydrogel. At high water dilution or low monomer concentration, the polymer chain cannot reach the crosslinker molecule, so that the crosslinker molecule cannot take part in the network structure, which in turn results in loosely-structured hydrogels. A common feature of the experiments that resulted in a swellable product was medium water dilution (500–750 μL Experiments 4,5, 7,8, 13,14, and 17). All swellable products showed the consistency of a tough rubber after gel formation. Among the swellable products, very tough rubber-like hydrogels were obtained at low water dilution and at high crosslinker concentrations (Experiments 7 and 16). With one experiment, using medium water dilution, with definite amount of XCMC, a very tough rubber-like hydrogel was obtained (Experiment 14).

Since a strong and elastic superporous hydrogel should be generated based on a tough and strong polymer base, we examined conditions to make tough AAm-based hydrogels. Experiments 7, 14, and 16 produced very tough hydrogels that showed a close relationship between the desired strength property and the gelation features. The inhibition period was in the 0.08–5.05 min range, but most preferably less than 1 min. This means, the least exposure of the reaction mixture to atmospheric oxygen results in (presumably) purer and higher molecular weight polymer (oxygen does not take part as comonomer in the kinetic chain). The exothermic period was in the 0.72–2.8 min range. Rapid gelation in the case of hydrogel synthesis or sudden cell freezing in the case of superporous hydrogel preparation was favored, when the exothermic period was short. Apparently, the shorter the period, the more stabilized the cells . The $T_{\max}$ was also laid within the 60–70°C range which corresponds to a 33–43°C rise in temperature during gel formation.

Considering the results shown in Figure 2 and the conditions for very tough AAm-based hydrogels, it appears that the inhibition and exothermic periods should lie within the minimum shortest range and $T_{\max}$ lies at the extreme maximum. Thus, in order to design a base formulation to produce strong hydrogel, influencing parameters should be quantified in terms of their effects on gelation features.

Evaluation of Variables and Parameters

All parameter observations are listed in Table 3. The negative and positive effects of the parameters are displayed as − and +, respectively, and numbers indicate the significance of the effects. Considering the whole concentration ranges of different variables studied, results are summarized in Table 4.

In qualitative terms, increased concentrations of the foam stabilizer, redox couple and crosslinker (in a definite lower range of concentration) resulted in reduced inhibition and exothermic periods and also in increased temperature during gelation (Table 4).

Effect of the Initiator Concentration

Regardless of the source of the initiator generation, (sulfate ion or peroxy radicals) normal polymerization was favored at a critical initiator

Table 3. The effects of varying the parameters for gel formation.

Variables	Inhibition Period (min)	Exothermic Period (min)	T_{max} (°C)
XCMC (0–200)	+2.695	−2.073	+2.53
Bis (0–1)	−5.768	−3.54	+2.8
Bis (1–3)	+8.018	+4.448	−1.96
Bis (0–3)	+2.25	+0.90	+0.83
D.W (500–750)	+4.16	+2.308	−10.416
D.W (750–1500)	+8.689	+7.714	−13.78
D.W (500–1500)	+12.85	+10.02	−24.2
F127 (0–5)	−1.76	−0.836	+0.08
F127 (5–10)	−6.285	−3.768	+2.216
F127 (0–10)	−8.05	−4.605	+2.3
AAc (0–50)	+11.04	+6.51	−5.88
AAc (50–100)	+8.00	+4.00	−2.25
AAc (0–100)	+19.05	+10.52	−8.13
APS (10–20)	−2.26	+0.70	+0.61
APS (20–40)	−4.85	−3.69	+2.25
APS (10–40)	−7.12	−2.99	+2.86
TMEDA (10–20)	−9.46	−7.72	+3.38
TMEDA (20–40)	−4.53	−1.07	+4.11
TMEDA (10–40)	−13.99	−8.79	+7.5

Table 4. Qualitative relationship between gelation parameters and concentration of the ingredients.

⇑	Inhibition Period	Exothermic Period	T_{max}
⇓	Bis (0 – 1), F127 (0 – 10), APS (10 – 40), TMEDA (10 – 40)	XCMC (0 – 200), Bis (0 – 1), F127 (0 – 10), APS (10 – 40), TMEDA (10 – 40)	Bis (1-3), DW (500-1500), AAc (0-100)
⇑	XCMC (0 – 200), Bis (1 – 3), DW (500 – 1500), AAc (0 – 100)	Bis (1 – 3), DW (500 – 1500), AAc (0 – 100)	XCMC (0-200), Bis (0-1), F127 (0-10), APS (10-40), TMEDA (10-40)

concentration. At high concentrations of initiator, although the oxygen can still take part in the reaction, there was a sufficient amount of initiator radicals for normal polymerization to occur. Therefore, the inhibition period is shortened at high initiator concentration. Likewise, polymerization takes place faster at high initiator concentrations, therefore, gelation or exothermic reaction occurs faster.

Effect of the Stabilizer Concentration

The foam stabilizer used in this study (Pluronic® F127) is a block copolymer of poly(ethylene oxide) and poly(propylene oxide). The structure $EO_{100}PO_{65}EO_{100}$, with an average molecular weight of 12,600, PEO concentration of 70 wt.% and a HLB value of 18–23 [24]. This HLB value favors solubility in water at room temperature but at concentrations less than 10 wt.%. Micellization of PEO–PPO–PEO block copolymers can be induced at the polymer's critical micellization temperature. At this point, a temperature region of 10–15°C, has been recognized as the unimer-to-micelle transition region in which, significant amounts of both free and associated copolymer molecules coexist. Above this transition temperature, most of the copolymer molecules are in micelles [25]. If F127 assumes different morphologies during the inhibition (almost unimer) and exothermic periods (both unimer and micelle), then the dynamic morphology responsible for gelation is effected. On the other hand, at increased water dilution, comonomer concentration and crosslinker concentrations (in a high range of concentration) have a negative effect on desirable gelation features.

Effect of Water Concentration

At high dilution with water, i.e., low monomer concentration, there are at least two parameters that need to be considered. There is more molecular oxygen in the reaction mixture that can take a part in significant undesirable reactions as noted. Second, reduced collision of monomer units happens at high dilution with water. Both could extend the inhibition and exothermic periods to a considerable amount.

Effect of Acid Addition

An aqueous AAm-based hydrogel formulation has a pH around 4, at this pH, polymerization occurs rapidly even at high water dilution. Acid addition reduces the AAm solution to pH 2; polymerization is retarded at this pH even at low water dilution. Therefore, the inhibition and exothermic periods are extended upon acid addition.

Increased T_{max} is not an exact measurement of polymerization during the exothermic period except for the systems at the same monomer concentration. The heat generated during this period can cause more monomer to polymer conversion for the systems at low water dilution or at high monomer concentrations. On the other hand, the heat generated raised the water temperature for systems with high water dilution. Therefore, more heat can be lost during the exothermic period via convection and conduction rather than to attain higher reaction rates.

Effect of the Crosslinker Concentration

At low crosslinker concentrations (0–1), despite the increase in maximum temperature, the inhibition and exothermic periods were shorter. The reverse happens at high crosslinker concentrations (1–3). Theoretically, the crosslinker can shorten the inhibition and exothermic periods simply by raising the reaction viscosity created by the crosslinks between the growing chains. Although the observation at low concentration is as expected, this dual behavior of the bisacrylamide crosslinker at its low and high concentrations can presumably be accounted for in terms of its interaction with another variable like water.

Effect on the Inhibition Period

To start the exothermic reaction, maximum retardation or inhibition was observed as the concentration of acid was increased. Water dilution was shown to have a similar effect but less significant. On the other hand, increased TMEDA, APS and F127 concentrations resulted in promoting the gelation process. XCMC and Bis (in range of higher concentration) showed nearly negligible positive effects.

Effect on the Exothermic Period

Increased dilution with water and increased comonomer addition (AAc) similarly resulted in increased duration of the inhibition and exothermic events. On the other hand, increased TMEDA, F127 and APS concentration led to a fast gelation process. Again, increased XCMC and Bis concentration (at its lower concentration range) showed comparatively negligible negative effect, respectively.

Effect on the Maximum Temperature

The highest maximum temperature during gelation was obtained as a result of increased TMEDA concentration. Increased APS and F127 concentration showed a minor positive effect. The lowest temperature rises were obtained with increased dilution with water and increased acid comonomer concentration. These results were schematically shown in Figure 3.

Normal polymerization was favored by shorter inhibition and exothermic periods; since there is less possibility of oxygen reacting with monomers. Therefore, to attain higher molecular weight polymer or to attain high monomer conversion to polymer, shorter inhibition and exothermic periods are required. On the other hand, to obtain a successful well-structured and homogeneous superporous hydrogel, a kind of so-called ‘‘cell freezing’’ (very fast gelation) should be practiced.

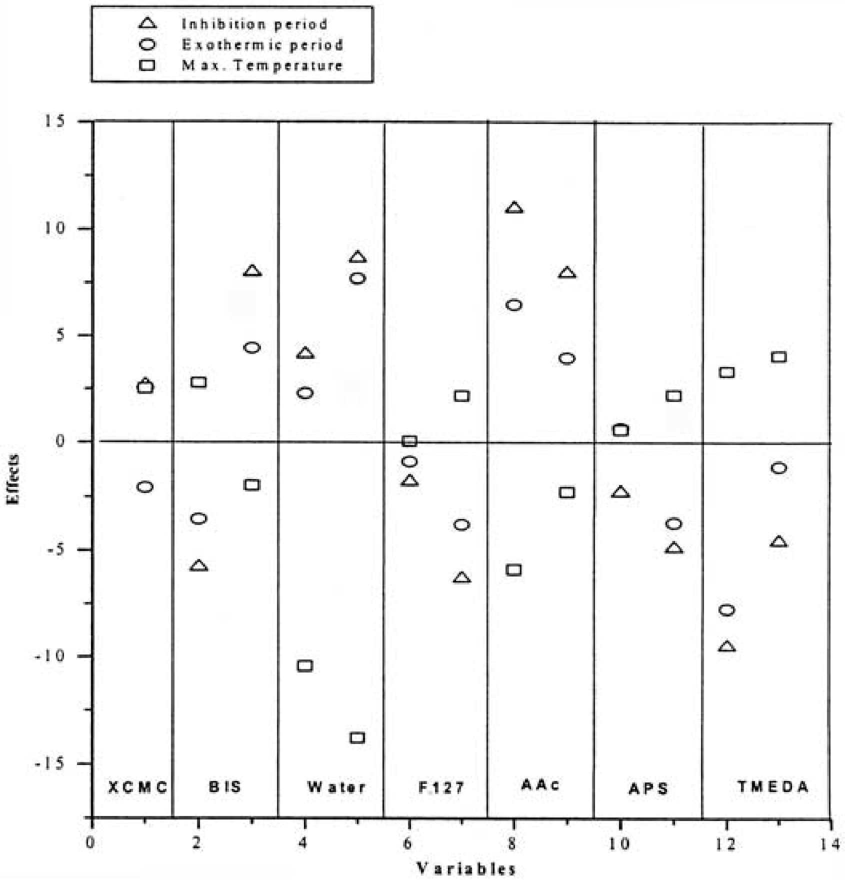

Figure 3. Effects of variables at different ingredient concentrations.

These requirements occur at high monomer concentration (less water dilution), low acrylic acid concentration and high F127 concentrations. Although increased TMEDA and APS additions gave similar results, care should be taken to avoid very low molecular weight polymer chains. Increased temperature during the exothermic process means more reaction, i.e., higher conversion of monomer to polymer. This is similar to superporous hydrogels that are mainly attained at high initiator concentration, and at high reductant concentration.

Based on the above evaluations and considerations, the following recipe (Table 5) was adopted in order to examine our approaches to make strong superporous hydrogels, which is the subject of forthcoming publications.

Table 5. Basic ingredients for superporous hydrogels.

Acrylamide (50 wt.% aqueous solution)	500 μL
Distilled water	500–750 μL
Methylenebisacrylamide (1–2 wt.% aqueous solution)	100 μL
Pluronic F127 (10 wt.% aqueous solution)	50 μL
Glacial acrylic acid	50 μL
Ammonium peroxydisulfate (10–20 wt.% aqueous solution)	50 μL
Tetramethylethylenediamine (20–40 v/v% aqueous solution)	50 μL

A number of hydrogel formulations were examined using 500 μL distilled water, 100 μL Bis solution (1–3 wt.%), 50 μL APS solution (20 wt.%) and 50 μL TMEDA solution (40 v/v%) TMEDA. Strength properties of these hydrogels were measured using a simple bench comparator. The results are shown in Figure 4.

The load–deformation behavior of all the hydrogels was nonlinear and resembled a viscoelastic material. It seems that an increase in the crosslinker concentration changed the behavior to an elastic material, as the shape of the curves appear to be more linear and with less deformation under load. As shown in Figure 5 under different loads, there is a nonlinear relationship between crosslinker concentration and the amount of hydrogel deformation, that means that the strength properties of the hydrogels increased with increased crosslinker concentration.

For a superporous hydrogel to be tough, optimized viscoelastic behavior is desirable. At extreme elastic behavior, where the crosslink density of the hydrogel is very high, there is no time for the polymeric chains to relax under certain stress or load. Like glass, hydrogels break apart under load. On the other hand, extremely viscous behavior in which the lowest crosslink density is applicable, the polymer chains are infinitely free to relax and display the behavior of a fluid under load. So that, there should be an optimum amount of the crosslinker concentration by which a reasonable chain stress relaxation is obtainable. Using 100 μL of 1 wt.% crosslinker solution was found to be optimum.

Superporous synthesis was tried with the above formulation using 500 μL distilled water, 100 μL Bis solution (1 wt.%), 50 μL APS solution (20 wt.%) and 50 μL TMEDA solution (40 v/v%). The final product showed a very high rate of absorption (10–15 s for its equilibrium swelling) and very high absorption capacity (150 g/g), while maintaining the reasonable strength.

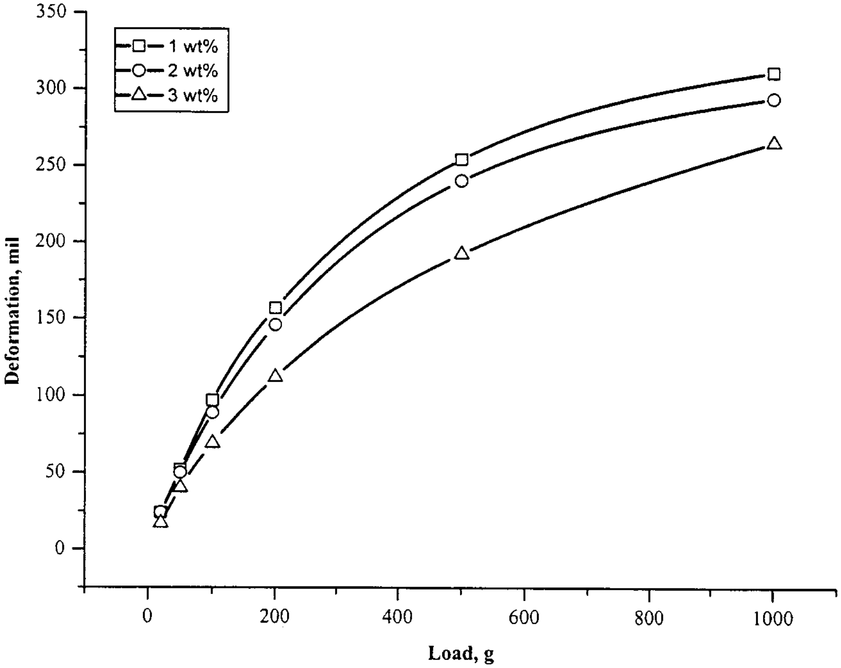

Figure 4. Load–deformation behavior of hydrogels in terms of crosslinker concentration.

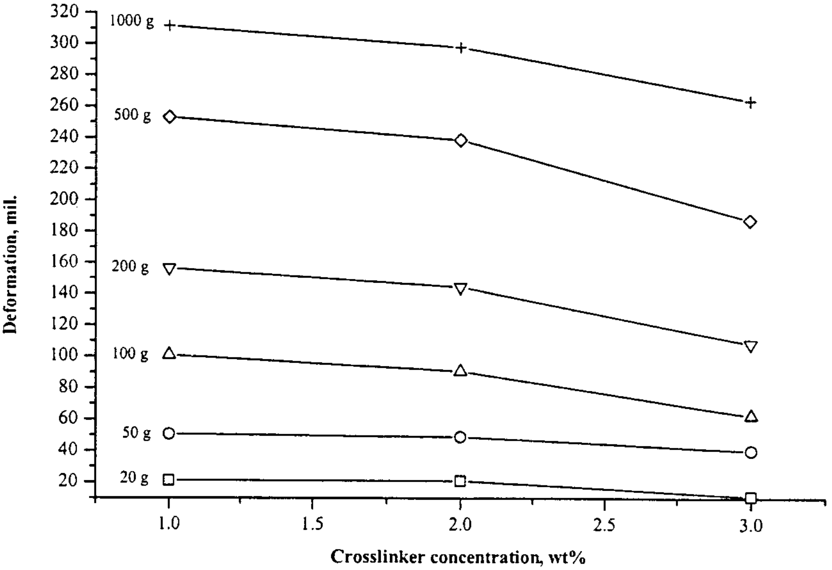

Figure 5. Deformation dependence on crosslinker concentration under different loads.

CONCLUSION

An experimental design, based on L-18 Taguchi matrix for superporous hydrogels, was used to evaluate the influence of starting materials on the final properties of PAAm-based hydrogel networks. Variables such as different concentrations showed definite effects on the gelation features of hydrogel formulations. Features, such as inhibition period, exothermic period and temperature rise, were found to be critically dependent on the type and concentrations of the materials within the hydrogel formulation. This correlation was used to design a simple formulation in order to make a strong superporous hydrogel network. Among the variables studied, the dilution with water (monomer concentration) and comonomer concentration showed the strongest influence on the gelation properties. A relationship was found between the strength properties of the hydrogel and gelation features. Tough or very tough hydrogels were attainable under conditions that minimum inhibition and exothermic periods and maximum temperature rises (during gelation) are favored. Based on the experimental observations and the results from using the Taguchi matrix, a hydrogel formulation was designed and examined for a superporous hydrogel preparation.

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