Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2014, 5(5):19-26

ISSN: 0976-8505
CODEN (USA) CSHIA5

Preparation of hydrogels via cross-linking of partially hydrolyzed polyacrylamides with potassium persulfate at moderate temperatures

Mehrdad Ghazinezhad[1], Yauheni V. Hryniuk[2] and Leonid P. Krul[1]

[1]Department of Macromolecular Compounds, Faculty of Chemistry, Belarusian State University, Address: No.14, Leningradskaya St, Minsk, Republic of Belarus
[2]Department of Radiation Chemistry and Chemical-Pharmaceutical Technology, Faculty of Chemistry, Belarusian State University, No.14, Leningradskaya St, Minsk, Republic of Belarus

---

ABSTRACT

A series of hydrogels were prepared by cross- linking of a low molecular weight partially hydrolyzed polyacrylamide (HPAM) in aqueous solutions, with potassium persulfate (KPS) as cross linker at moderate temperatures between 60-80 ℃.The minimum concentration of polymer solution for consistent gel formation is 1.5wt%, and the time to obtain the stronger gel decreases with increasing the KPS/HPAM ratio and concentration of HPAM. Increasing the concentration of polymer solutions shifts the onset of gel formation to the lower KPS/HPAM ratios. Increasing the KPS/HPAM ratio at constant weight percent of HPAM decreases the water absorbency, and increasing the polymer content at any KPS/HPAM ratio increases the water absorption .Gel fraction increases with increasing the weight percent of polymer. Increasing the KPS/HPAM ratio has the similar effect on variations of the gel fraction. A gel, prepared at 60°C based on the 2 wt% copolymer solution and cross-linker/copolymer ratio of 1/3 is an optimum gel in terms of gel strength, water absorbency and gel fraction. The Proposed mechanism of gel formation is cross-linking through macroradical combination. FTIR analysis confirms the absence of imidization during gel formation .The Conversion time of gelant solutions to consistent gel is decreased 2 times for every 10°C increase of temperature. Fluctuations in the water absorbency of hydrogels which prepared at different temperatures can be explained with competition between degradation and radical combination. Hydrogels prepared at different temperatures and similar KPS/HPAM ratio, have no significant difference in gel fraction.

Keywords: Hydrogel, Consistency, Viscosity, Water absorbency, Gel fraction

---

INTRODUCTION

Superabsorbent Polymers (SAPs) are “slightly” cross-linked networks of hydrophilic polymers that can absorb and retain a lot of aqueous fluids. Chemically speaking, SAPs are cross-linked polyelectrolytes which start to swell upon contact with water or aqueous solutions resulting in the formation of a hydogel [1,2]. The ability of SAPs to absorb water and aqueous solutions, as high as 10 to 1,500 g/g [2,3], as a function of their environment is one of the most notable properties of these materials. The most efficient water absorbents are polymer networks containing dissociated ionic functional groups. Their affinity for water makes them useful, especially for personal hygiene products, industrial absorbents, medicine, cosmetics, agriculture and horticulture [4].The most common SAPs are synthetic hydrogels based on hydrophilic monomers containing double bonds, such as acrylic acid, acrylamide, hydroxyethylmethacrylate,2-acrylamido-2-methylpropanesulfonic acid, and its sodium salt, which can be polymerized and form chemical bonds with the aid of double bond-containing cross-linkers [5].

There are numerous studies that show the practical applications of hydrogels in the agricultural and horticultural fields. Superabsorbent hydrogels for use in soil to promote plant growth has been reviewed by Kazanskii et al.[6].Several methods of modification have been proposed for enhancing the absorption and controlled release properties of synthetic hydrogels. Study of radiation synthesis of hydrogels and superabsorbent polymers is frequently seen in literatures[7-11].Preparation of hydrogels through copolymerization of carbohydrates and acrylamide/acrylic acid is another trend in recent years [9,12-13].It is reported that clay composites of poly(acrylic acid) can provide controlled. release of urea and nitrogen fertilizers[14,15].In most of the above-mentioned cases, using expensive monomers/modifiers/processes for improving water absorbency and controlled release will result in increased cost, making the resulting SAP economically unsuitable. Singhal et al.[16] tried to prepare cheap SAP based on acrylamide-acrylic acid copolymers via optimization of different parameters such as initiator (potassium persulfate) and cross-linker (N,Ń-methylenebisacrylamide).In general, ammonium persulfate and potassium persulfate (KPS) are water soluble thermal initiators which are used frequently in both solution and inverse-suspension polymerization processes of hydrogels synthesis [3].Preparation of cross-linked poly (Vinyl pyrolidon)/poly (Vinyl alcohol) hydrogels (PVP/PVA) in aqueous solution at 80°C in presence of KPS as cross-linker has been reported [17]. Kurenkov V.F. et al.[18] studied the thermal degradation of acrylamide- sodium acrylate copolymers in presence of KPS as residual initiator of polymerization and observed the increasing of molecular weight at 60-80°C. But application of persulfates as cross-linking agent for acrylamide polymers less investigated up to now.

The aim of current work is to prepare hydrogels based on a low molecular weight partially hydrolyzed polyacrylamide (HPAM) ,using KPS as a free radical cross-linking agent, at temperatures between 60-80°C. An alphabetical coding method is applied to determine the strength of gels and kinetics of gel formation, using bottle test and viscometric results .Gel fraction (δ) and equilibrium water absorption(A) are measured using gravimetric method. FTIR spectroscopy is applied to characterize chemical structure of obtained networks. Mechanism of gel formation will be discussed, based on experimental results, evidences and comparison with other works. Finally, the effect of preparation temperature on kinetics of gel formation, water absorbency and gel fraction will be investigated.

MATERIALS AND METHODS

Materials

HPAM with an average molecular weight of 500,000 Dalton, degree of hydrolysis not more than 5% and water content, less than 10 wt% was provided by BASF under the trade name of Alcoflood 254S in powder form. KPS was the product of Applichem (P.A. grade) and used in solid form (after recrystallization). Distilled water which was prepared in situ, was used as a solvent to prepare gelant solutions.

Samples Preparation and Characterization

The polymer gels were prepared according to the following two steps :(1) HPAM solutions at different concentrations were prepared by adding distilled water to polymer powder by gentle stirring for 2 hours. Then, they were held without stirring overnight until a homogeneous solution was obtained. (2) Potassium persulfate as cross-linker was mixed in required amounts with polymer solutions at room temperature using a magnetic stirrer (Griffin & George Minimag stirrer SWT-180-010K (UK)) for 10 min to obtain gelant solutions (mixture of copolymer and cross-linker). The obtained gelant solutions were poured into wide mouth glass bottles (70 mL). Then, the bottles were kept in an oven at 60, 70 and 80°C as long as it was required. The gel formation process was monitored based on the Sydansk's gel strength code [19] by observing the appearance of the gel structure on the wall of the bottle when the bottle is inverted. A comprehensive series of bottle tests were conducted at 60-80°C in order to select suitable reactants concentration for the polymer gel treatment. The final objective of these screening tests was to determine the limit of concentration of gel components which leads to gel formation [20].Based on the screening work, suitable systems were selected for extensive investigations of gel fraction and degree of swelling.

Bottle Test

There are different methods presented in literature for determination of polymer gel properties including bottle test (sealed tube) [19], dynamic shear (rheometer)[20] and steady shear viscometry method (viscometer)[21].In this work, the bottle test method was used to evaluate qualitatively the gel formation process over an extensive range of cross-linker concentrations ,copolymer concentrations using the Sydansk's strength code[19].Generally, the bottle test method is an experimental technique which provides a semi-quantitative measurement of gel formation rate and gel strength. Also, it can be considered as a fast and inexpensive method to study the gel formation kinetics[20]. Bottle test is conducted at 60-80°C using laboratory bottles. The bottles are filled with 40g of the gelant, and the cross-linking process is monitored as a function of time, starting from the point that the gelant is put into the bottle. The bottles were inverted periodically to check the sample-flow behavior under the influence of gravity and each was assigned by a strength code as defined in Table 1.

Table 1.Strength coding for gel formation

Gel strength code	Gel description
A	No detectable gel formed: the gel appears to have the same viscosity as the original polymer solution.
B	Highly flowing gel: the gel appears to be only slightly more viscous than the initial polymer solution.
C	Flowing gel: most of the gel flows to the bottle cap by gravity upon inversion.
D	Moderately flowing gel: only a small portion (5—l0%) of the gel does not readily flow to the bottle cap by gravity upon inversion (usually characterized as a tonguing gel).
E	Barely flowing gel: the gel can barely flow to the bottle cap and/or a significant portion (> 15%) of the gel does not flow by gravity upon inversion.
F	Highly deformable non flowing gel: the gel does not flow to the bottle cap by gravity upon inversion.
G	Moderately deformable non flowing gel: the gel deforms About half way down the bottle by gravity upon inversion.
H	Slightly deformable non flowing gel: only the gel surface slightly deforms by gravity upon inversion.
I	Rigid gel: there is no gel surface deformation by gravity upon inversion.
J	Ringing rigid gel: a tuning fork-like mechanical vibration can be felt upon tapping the bottle.

Viscosity Measurements

To represent the degradation of non gel-forming samples in a quantitative manner, some viscosity measurements were conducted using Rheotest (Germany), a coaxial viscometer with the spindle of N and S1, according to instruction manual of it. Viscosity of the prepared gelants was measured in a shear rate domain of 10 to 1000 s^{-1}.

Equilibrium water absorbency and gel fraction

After obtaining gels with strength codes higher than H, they were vacuum dried at moderate temperature (40°C) in order to avoid thermal decomposition, until constant weight. Then approximately 40 mg of each hydrogel was immersed into 500 mL distilled water for 48 hours to reach the equilibrium swelling at room temperature. Then excess liquid was filtered through acrylic/polyester gauze with fine mesh. Swollen gel was weighed after 15 minutes remaining on filter and removing the water on the surface with tissue paper, and the water absorbency (A) was calculated using equation (1):

$$A = (W - W_0) / W_0 \qquad (1)$$

Where, W and W_0 are the weights of the water–swollen gel and dry absorbents, respectively. Absorbency is expressed in grams of water retained in the gel by one gram of dried gel. The tabulated results are the arithmetic mean of 3 experiments. The method's precision has been determined to be around ±3.5%[3].Drained gels were held in oven at 70°C until constant weight (W_1),and the gel fraction(δ) was calculated using equation(2):

$$\delta = (W_1 / W_0) \times 100 \qquad (2)$$

FTIR spectroscopy

Transmission FTIR spectra were recorded on a Bruker ALPHA spectrometer, equipped with measuring module of diamond crystal. Samples were thin films of hydrogels, vacuum-dried at 40°C.

RESULTS AND DISCUSSION

Commercial HPAM copolymers at 40-80°C undergo thermal degradation, caused by decomposition of residual initiator to free radicals [18].We also presented that ,at dilute polymer solutions, and up to KPS/HPAM ratio of 25%, viscosity decreases during thermal treatment (see Figure1 for example).Decrease of viscosity confirms thermal degradation of such samples.

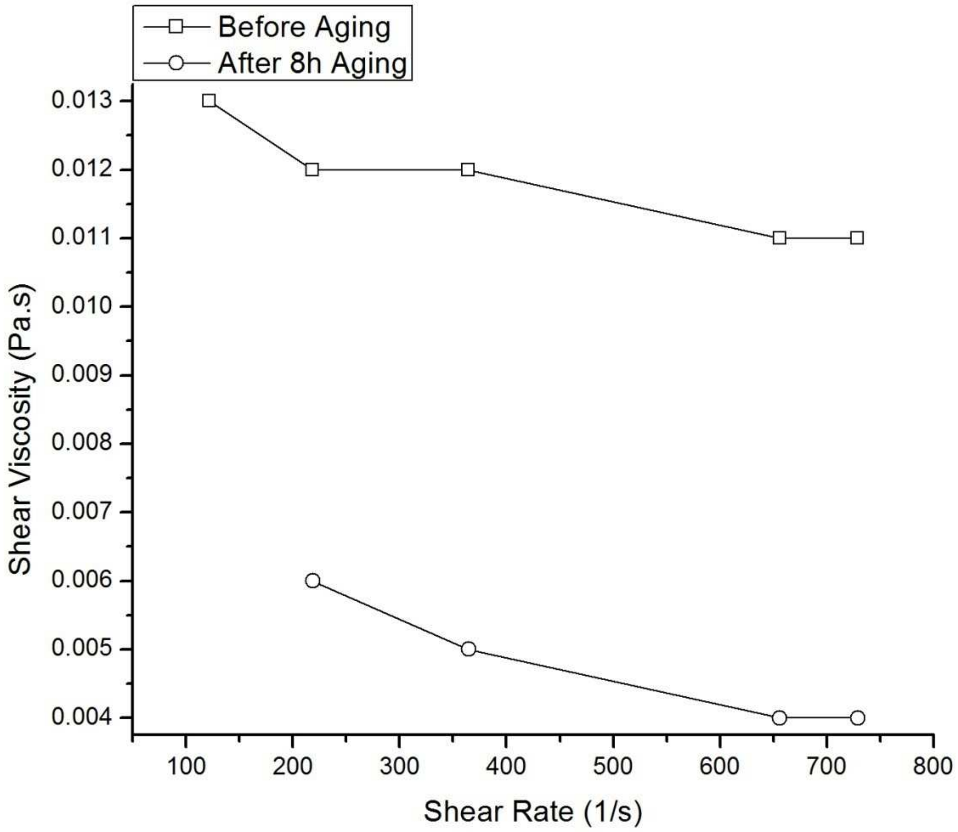

Figure 1.Effect of cross-linker/polymer ratio of 15%,on thermal degradation of HPAM in 1.5wt% aqueous solution at 60^{0}C

Table 2 is a typical qualitative scheme of kinetics of gel formation process in this study. It is clearly observed that the onset and rate of gel formation depends on concentration of polymer solution and KPS/HPAM ratio. The minimum concentration of polymer solution for consistent gel formation is 1.5wt%. At constant weight percent of polymer, increasing the amount of KPS decreases the time to obtain stronger gel. Also, at constant KPS/HPAM ratio, higher concentration of polymer leads to similar effect.

Table 2 Effect of HPAM and KPS concentrations on gel strength at 60^{0}C

Copolymer concentration(wt%)	**1.0**	**1.0**	**1.0**	**1.5**	**1.5**	**1.5**	**2.0**	**2.0**	**2.0**
KPS/copolymer(%)	25	30	35	25	30	35	25	30	35
Aging time(h)	Gel strength code								
1	B	B	C	C	D	E	E	F	F
2	B	B	C	D	E	F-G	F	H	H-I
3	B	B	C	E	F-G	G	F-G	H	H-I
4	B	C	D	F	G	G-H	G	H	H-I
5	C	C	D	F-G	G-H	H	G-H	H	H-I
6	C	C	D	G-H	H	H	H	H-I	H-I
7	C	D	E	G-H	H	H	H-I	H-I	H-I
8	C	E	F	H	H	H	H-I	H-I	H-I

Results of bottle tests (Table 2*)* and viscometry suggest that, increasing the concentration of polymer solutions shifts the threshold of gel formation to the lower KPS/HPAM ratios. As is shown in Figure 2, the ratio of 3% at 6 wt% copolymer concentration leads to thermal degradation of polymer. But the KPS/HPAM ratio of 5% increases shear viscosity after the thermal treatment .Thus, ratio of 3-5% is the onset of gel formation at this polymer concentration .No doubt that, higher polymer concentration increases the probability of effective collisions between polymer chains and cross-linker. Thus, threshold of gel formation is shifted to the lower cross-linker concentrations.

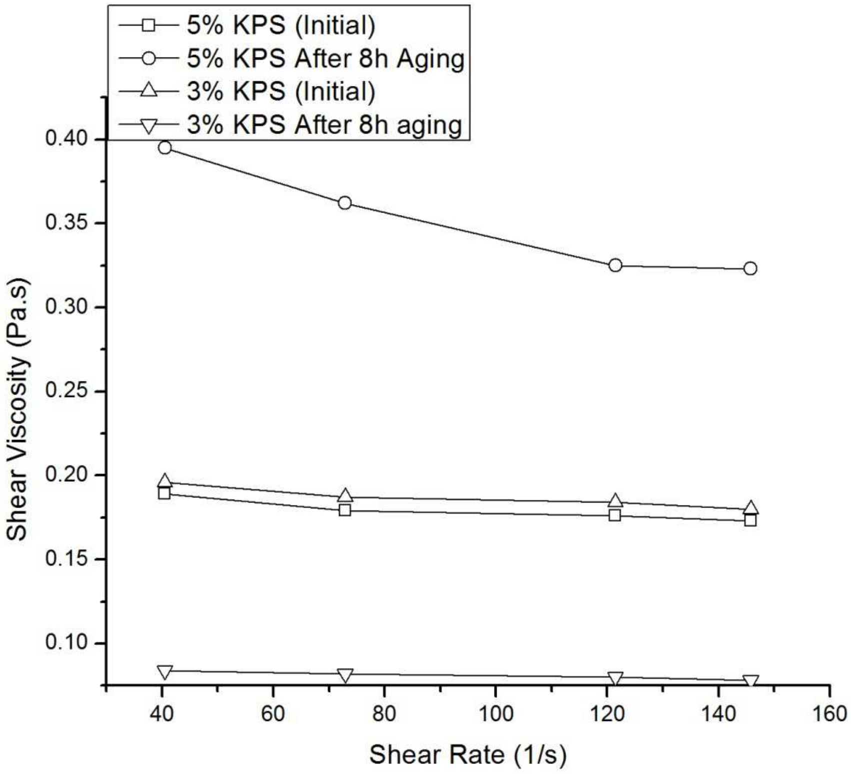

Figure 2.Viscosity behavior of 6wt% aqueous solutions of HPAM , containing different KPS/HPAM ratios (60°C)

Effect of HPAM concentration and KPS/HPAM ratio on water absorption (A) and gel fraction(δ) is shown in table 3. It is clear that the value of (A) decreases with increasing the KPS/HPAM ratio. At constant KPS/HPAM ratio, increasing the HPAM concentration increases the value of (A). Gel fraction increases with increasing the KPS/HPAM ratio. Pattern of changes in values of A and δ versus KPS concentration (as cross-linker) is in accordance with well-known patterns[3].Similar behavior was reported for effect of KPS concentration on A and δ of PVA/PVP based hydrogels [17].It seems that 2.0 wt% of Alcoflood 254S and KPS/HPAM ratio of 30% provides optimum values of water absorption and gel fraction in this study.

Table 3 . Effect of HPAM and KPS concentrations on water absorption and gel fraction (gels formed at 60°C)

Copolymer concentration(wt%)	**1.5**	**1.5**	**1.5**	**2.0**	**2.0**	**2.0**
KPS/copolymer(%)	25	30	35	25	30	35
Water absorbency (g $_{H2O}$/g $_{hydrogel}$)	250.9	173.6	142.1	469.5	449.2	310.7
Gel fraction (%)	61.5	61.6	69.2	53.8	64.3	66.1

FTIR spectrum of a typical hydrogel sample is presented in Figure 3. These spectra clearly mark a stretching vibration of amide C=O at 1651 cm^{-1}, and of carboxylate groups at 1603 cm^{-1} due to partial hydrolysis of acrylamide groups, and vibration of methylene at 1420 cm^{-1}.The spectra also contains characteristic C-O-C bonds with stretching vibration at 1094 and 1250 cm^{-1} due to cross-linking of the chains. As mentioned in[22],presence of a broad peak between 1640-1750 cm^{-1} in our work could be interpreted to presence of imide formation. An imide structure has been proposed to be an intermediate in the low pH hydrolysis of poly(acrylamide), yielding short blocks of carboxyl groups distributed along the polymer chain[23].Dominance of imide formation in acidic hydrolysis of polyacrylamide aqueous solutions is confirmed in [24] too. In neutral and basic pH, both hydrolysis to acrylate and imide formation do occur, but hydrolysis is favored [25]. Kurenkov V.F.et al.[18] showed that increase in the molecular weight of HPAM copolymers at 60-80°C,in presence of residual initiator (KPS) can be attributed to intermolecular imidization of HPAM chains. But in our study, absence of any peak after 1650 cm^{-1} confirms the absence of intramolecular or intermolecular imidization and dominance of free radical cross-linking via KPS decomposition, formation of macroradicals and combination of them. An absorbance is seen at 1044 cm^{-1}, which is characteristic of SO groups. HPAM, applied in this study is considered non-ionic, because of its low degree of hydrolysis. Introduction of SO groups to such a polymer can result in higher water absorbency. Thus, decrease of *A* with increasing the KPS/HPAM ratio may be an evidence to very low conversion of KPS to SO groups during gel formation.

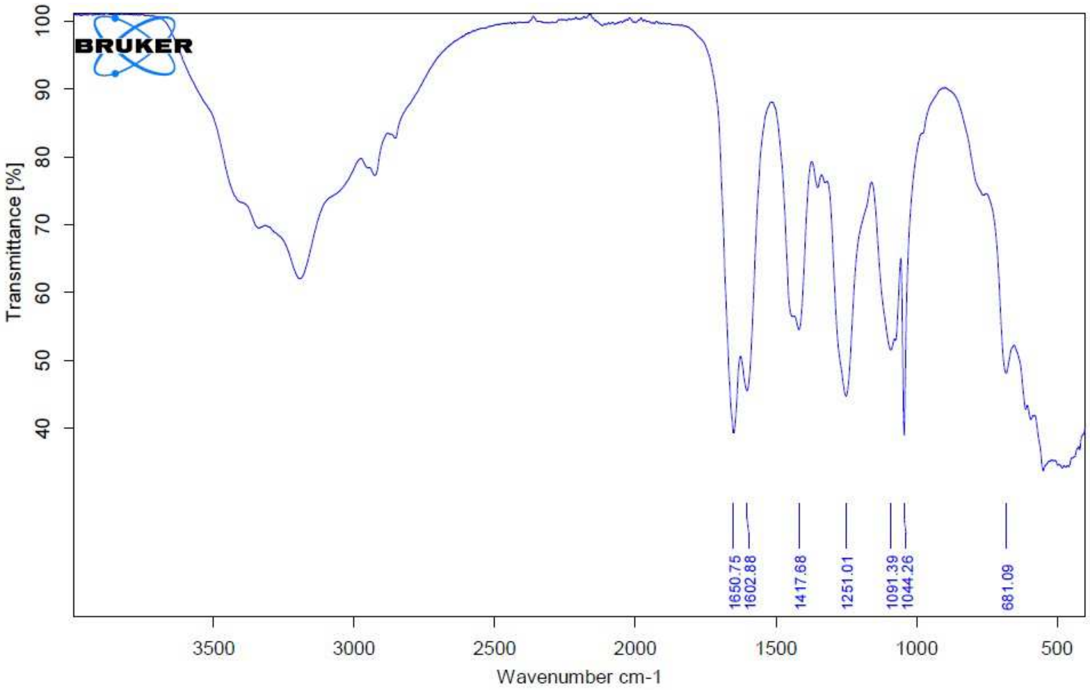

Figure 3.FTIR spectra of hydrogel , based on 1.5wt% solution of HPAM and KPS/HPAM ratio of 35%,cross-linked at 70°C

Effect of temperature on kinetic of gel formation is presented in Table 4.As is shown, conversion time of gelant solutions to consistent gel is decreased 2 times for every 10°C of temperature increase .Preparation temperature also affects on water absorbency ,as is seen in table 5.It is obvious that increasing the preparation temperature at KPS concentrations of 25 and 30% reduces the water absorbency. At higher concentrations like 35%,change in preparation temperature from 60°C to 70°C results in higher polymer or gel destruction and consequently, formation of less consistent (looser) hydrogel with higher water absorbency. Gel degradation maybe caused by ions and ultraviolet irradiation that result in complexation and breaking of cross-links [5].Increase in preparation temperature from 70°C to 80°C results in higher degree of cross-linking and consequently, formation of more consistent (tighter) hydrogel with lower water absorbency. Absence of any imide group in spectra, even at 80°C, proves that network formation takes place via macroradical combination. At 60°C with any KPS concentration, macroradical combination plays dominant role in competition between destruction and macroradical combination .With increasing the KPS concentration at 70 and 80°C,absorbency first decreases due to higher degree of macroradical combination. Then more KPS concentration results in more degradation and more water absorption. As is seen Table 6, hydrogels prepared at different temperatures and the same KPS/HPAM ratio (except higher limit of temperature and KPS concentration that causes extensive destruction) have no significant difference in gel fraction.

Table 4.Effect of temperature and concentration of cross-linker on conversion time of 1.5% HPAM solution to consistent gel

KPS/copolymer(%)	Consistent gel formation time at 60°C (h)	Consistent gel formation time at 70°C (h)	Consistent gel formation time at 80°C (h)
25	8	4	2
30	6	3	1.5
35	4	2	1

Table 5.Effect of temperature and KPS concentration on water absorbency (A) of hydrogels, based on 1.5% aqueous solutions of HPAM,cross-linked at different temperatures

KPS/copolymer(%)	A (g $_{H_2O}$/g $_{hydrogel}$) at 60°C	A (g $_{H_2O}$/g $_{hydrogel}$) at 70°C	A (g $_{H_2O}$/g $_{hydrogel}$) at 80°C
25	250.9	225.5	193
30	173.6	147.4	96.6
35	142.1	190.8	104.5

Table 6.Effect of temperature and KPS concentration on gel fraction (δ) of hydrogels, based on 1.5% aqueous solutions of HPAM, cross-linked at different temperatures

KPS/copolymer(%)	δ(%) at 60°C	δ(%) at 70°C	δ(%) at 80°C
25	61.5	66.1	64.8
30	61.6	61.8	61.9
35	69.2	70.3	55.8

CONCLUSION

KPS can be used as a cross-linker for preparing super absorbent hydrogels based on aqueous solutions of relatively low molecular weight HPAM copolymers at moderate temperatures. Onset of gel formation, consistency of obtained gels, time to obtain the stronger gel, water absorbency and gel fraction depend on concentration of aqueous polymer solution and amount of cross-linker. Gel formation proceeds via competition between free radical cross-linking and free radical polymer degradation Water absorbency and degradability of these hydrogels beside thermal insulation of water and polymer as their main components, makes them appropriate compounds that may facilitate early plantation and optimize the efficiency of agriculture in cold regions. In order to optimize the stability and swelling properties of these hydrogels, studying the effects of pH, and concentration of different ions can be the next steps of present study .

REFERENCES

[1]Buchholz FL,Graham AT(Eds.),*Modern Superabsorbent Polymer Technology*,Wiley-VCH,New York,**1998**,pp251.
[2]Mechtcherine V,Reinhardt HW(Eds.),*Application of superabsorbent polymers (SAP) in concrete construction*,Springer,Dordrecht Heidelberg London New York,2012,pp13
[3]Zohuriaan-Mehr MJ, Kabiri K, *Iran Polym J*, **2008**,17(6),451-477.
[4]El-Sherif H,El-Masry M,*Polym Bull*,**2011**,66,721-734.
[5]Omidian H,Park K,In:Ottenbrite R.M et al. (Eds.), *Biomedical Applications of Hydrogels Handbook*,Springer Science & Business Media, LLC, **2010**,pp1.
[6]Kazanskii K.S,Dubrovski S.A,*Adv Polym Sci*,**1992**,104, 97-133.
[7]Abd El-Rehim HA,Hegazy ESA,Abd El-Mohdy HL,*J Appl Polym Sci*,**2004**,93(3),1360-1371.
[8]Chen P,Zhang WA, Luo W,Fang Y,*J Appl Polym Sci*,**2004**,93(4),1748-1755.
[9]Luo W, Zhang WA,Chen P,Fang Y,*J Appl Polym Sci*,**2005**,96(4),1341-1346.
[10]Abd El-Rehim HA,*Radiat Phys Chem*,**2005**,74(2),111-117.
[11]El-Rehim HAA,Hegazy ES, El-Mohdy HLA,*J Appl Polym Sci*,**2006**,101(6),3955-3962.
[12]Ibrahim SM,El Salmawi KM,Zahran AH,*J Appl Polym Sci*,**2007**,104(3),2003-2008.
[13]Guilherme MR ,Reis AV,Takahashi SH, Rubira AF, Feitosa JPA,Muniz EC, *Carbohydr Polym*,**2005**,61(4), 464-471.
[14]Liang R,Liu MZ,*Ind Eng Chem Res*,**2006**,45(25),8610-8616.
[15]Liang R,Liu MZ,*J Appl Polym Sci*,**2007**,106(5),3007-3015.
[16]Singhal R,Tomar R.S,Nagpal A.K,*Int J Plast Technol*,**2009**,13(1),22-37.
[17]Mansour Lakouraj M,Tajbakhsh M,Mokhtary M,*Iran Polym J*,**2005**,14(12),1022-1030.
[18]Kurenkov V.F,Trofimov P.V,Kurenkov A.V,Khartan Kh.G,Lobanov F.I,*Russian Journal of Applied Chemistry*,**2005**,78(6),995-999.
[19] Sydansk R.A,Argabright P.A,(Marathon oil company),*US Patent 4,683,949*,**1987**.
[20]Dadvand Koohi A,Vafaie Seftie M,Zarrin Ghalam A,Mousavi Moghadam A,Zanjani Sabet S,*Iran Polym J*,**2010**,19(10),757-770.
[21] Shevchenko T.V,Ul'rikh E.V, Yakovchenko M.A, Pirogov A.N,Smirnov O.E,*Colloid J* ,**2004**,66,756-759.

[22]Zil'berman E.N, Radina I.A, Spasskaya R.I,*Vysokomol Soedin ,Ser.A*,**1978**,20(6),1240-1245.
[23]Mark H.F(Ed.),*Encyclopedia of polymer science and technology,Vol.1*,John Wiley & Sons Inc,**2005**,pp41.
[24]Shepitka J.S,Case C.E,Donaruma L.G,Hatch M.J,Kilmer N.H,Khune G.D,Martin F.D,Ward J.S, Wilson K.V,*J Appl Polym Sci*,**1983**,28(12),3611-3617.
[25] Swift G,Carraher Jr. C.E, Bowman C.N(Eds.),*Polymer modification*,Plenum press,New York,**1997**,pp79