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Synthesis of pH – Thermosensitive gum arabic based hydrogel and study of its salt-resistant swelling behavior for saline water treatment

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ABSTRACT

An experimental protocol was developed to synthesize *GA-cl-poly(AAm)* hydrogel which was found to be pH as well as temperature sensitive. The polymer was synthesized by optimizing different reaction parameters including initiator, monomer and crosslinker concentration along with the basic reaction conditions like reaction temperature, reaction time, amount of solvent and pH. The graft copolymerization was carried out in the presence of potassium persulphate-hexamethylene tetramine initiator-cross linker system. Characterization of candidate polymer was carried out by FTIR spectroscopy, SEM and TGA/DTA/DTG techniques. Synthesized polymer was studied for its salt-resistant swelling efficiency in different salt solutions: NaCl, $MgCl_2$, $CaCl_2$, $FeCl_3$, $ZnCl_2$ and $BaCl_2$ as a function of salt concentration, temperature and pH. It was observed that optimized polymer exhibits maximum swelling in 1% NaCl solution (1428.32%) at 35°C.

Keywords: Gum arabic; hydrogel; acrylamide; pH-thermosensitive; salt-resistant swelling

1. Introduction

Natural polymers have travelled a long journey since thousand of years and have served mankind in every possible way from food to medicine. Since they face many drawbacks including less stability and difficulty in processing, therefore, they have been successfully modified through graft copolymerization so as to meet out the end usage. Grafting and network formation of the natural polymers with different vinyl monomers and crosslinkers improve their properties and make them potential candidate materials in various fields ranging from food additives [1] to pharmaceuticals [2] to biomedical implants [3].

In addition to this, the sensitivity of these polymeric materials to a large number of physical factors like pH, temperature, salt concentration, electric field and biological agents [4–8] have broaden the versatility of their applications.

The present research proposal deals with the synthesis of pH and thermosensitive *gum arabic* (GA) and acrylamide (AAm) based hydrogels, using potassium persulphate (KPS) as initiator and hexamethylene tetramine (HMTA) as crosslinker. GA is one of the most useful plant gums which is extracted as an amorphous exudate from the stem of *Acacia arabica*, found in tropical and sub-tropical areas of the world. GA is a highly branched polysaccharide consisting of ß-(1→3) galactose backbone (36–42%) having linked branches

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of arabinose (24–29%) and rhamnose (12–14%) with glucuronic acid (16–17%) as terminating units [9,10]. It is available in the form of round lumps, granules, thin flakes or as powder, all of which may be white or slightly yellowish in colour. It is a natural polysaccharide of commercial importance which finds applications in confectionery, flavours, beverages, pharmaceuticals, cosmetics and inks [11] due to its extraordinary adhesive, suspending, stabilizing and emulsifying properties. Grafting and network formation of GA with different monomers and crosslinkers under variable synthetic conditions, is an important method to develop a range of polymers with improved properties and applications [12,13].

Since, very few researchers have worked on GA, so it was thought worthwhile to work on this polysaccharide and synthesize its hydrogels. The synthesis was carried out by free radical polymerization using KPS-HMTA system. The resultant candidate polymer was further characterized using FTIR, SEM and TGA/DTA/DTG techniques and finally evaluated for its application as salt-resistant superabsorbing device which can be used in water treatment industry.

2. Experimental

2.1. Materials and methods

GA, the polymeric backbone, AAm, the monomer, KPS, the initiator and HMTA, the crosslinker, all were obtained from MERCK Pvt. Ltd, which were used without further treatment. Double distilled water was used as solvent through out the experiment.

Weighing was done on electronic balance (LIBROR AEG-220 Shimadzu). The structural characterization of the hydrogels was performed by recording IR spectra of the gels using KBr pellets, on Perkin-Elmer spectrophotometer. SEM of the samples were recorded on a scanning electron micrograph (Jeol Steroscan 150 Microscope) and TGA/DTA studies were carried-out on Perkin Elmer thermal analyzer in air at a heating rate of 10°C/min.

2.1.1. Infrared spectrophotometric studies

The raw backbone and the synthesized hydrogel were mixed separately with KBr and their pellets were prepared with the help of hydraulic press for the FTIR studies.

2.1.2. Scanning electron microscopic studies

Since GA has nonconducting behavior so, it was gold plated to have a conducting effect. Scanning was synchronized with microscopic beam in order to maintain the small size over large distance relative to the specimen. The resulting images had a great depth of the field. A remarkable three-dimensional appearance with high magnification of 1 KX, was obtained. The comparison between SEM results of the raw backbone and the synthesized hydrogel illustrate and magnify the intricacies brought about by graft copolymerization. The scans verify that poly(AAm) has been grafted onto the polymeric backbone and a crosslinked structure was obtained.

2.1.3. Thermogravimetric and differential thermal analysis

The raw backbone and *GA-cl-poly(AAm)* were taken in the alumina crucible for TGA/DTA analysis in air with temperature ranging from 25 to 800°C. The heating rate of the sample was 10°C/min. The combustion of the samples continued for 80 min and the results, weight loss % vs. temperature (°C) in case of TGA and DTA signal (μV) vs. temperature (°C) in case of DTA, were compiled automatically by the software of the thermal analyzer.

2.2. Synthesis of crosslinked network of poly(AAm)

GA (1.0 g) was taken in a beaker and 15 ml of water was added. Mixture was stirred thoroughly so as to obtain the homogeneity. This was followed by addition of a known amount of KPS (3.69×10^{-2} mol L^{-1}) and AAm (4.69×10^{-1} mol L^{-1}). The reaction was carried out at a specific temperature (70°C) and time (180 min). Various reaction parameters, such as initiator concentration, amount of solvent, reaction time, reaction temperature, vacuum and pH of the reaction medium were optimized so as to get the maximum percent grafting (P_g), which was calculated as per the following equation:

$$P_g = \frac{W_g - W_0}{W_0} \times 100,$$

where W_g and W_o are the weights of grafted and ungrafted samples, respectively.

Crosslinking of *GA-g-poly(AAm)* was carried out using HMTA. The crosslinked polymeric gel so obtained was labeled as *GA-cl-poly(AAm)*. *GA-cl-poly (AAm)* was kept in acetone for 1–2 h and was thoroughly washed with it, following a distilled water wash in order to remove any adhered unreacted monomer, initiator and homopolymer formed during graft copolymerization reaction. Thereafter, optimization of AAm and HMTA concentration was carried out as a function of percent swelling (P_s) in distilled water. P_s was calculated as follows:

$$P_s = \frac{W_s - W_d}{W_d} \times 100,$$

where W_s and W_d are the weights of swelled and dry samples, respectively.

2.3. Salt-resistant swelling behavior

GA-cl-poly(AAm) was subjected for its salt-resistant swelling behavior in different salt solutions: NaCl, $MgCl_2$, $CaCl_2$, $FeCl_3$, $ZnCl_2$ and $BaCl_2$ of varying concentrations (1%, 5%, 10%, 15%, 20%). 100 mg of *GA-cl-poly(AAm)* was immersed in each saline solution for 24 h at 25°C. After every 4 h time interval, the swollen samples were taken out, wiped gently and weighed to get the P_s. After optimization of salt concentration, temperature dependent swelling was optimized for each sample at 15, 25, 35, 45 and 55°C. Similarly, pH was optimized using 0.5N HCl (acidic), distilled water (neutral) and 0.5N NaOH (basic) solutions.

3. Results and discussion

3.1. Scheme of polymerization

The –OH groups present on the backbone polymer act as the active site for the graft copolymerization of poly(AAm) onto it. The mechanism for the same is discussed below [14,15]:

Initiation

$$^{-}O_3S - O - O - SO_3^- \longrightarrow 2SO_4^{-*} \quad (1)$$

$$SO_4^{-*} + H_2O \longrightarrow HSO_4^- + {}^*OH \quad (2)$$

$$GA - OH + SO_4^{-*} \longrightarrow GA - O^* + HSO_4^- \quad (3)$$

$$GA - OH + {}^*OH \longrightarrow GA - O^* + H_2O \quad (4)$$

$$M + {}^*OH^* \longrightarrow M - OH \quad (5)$$

$$M + SO_4^{-*} \longrightarrow {}^*M - SO_4^- \quad (6)$$

Propagation

$$GA - OH + {}^*M - OH \longrightarrow GA - O - M^* + H_2O \quad (7)$$

$$GA - O - M^* + nM \longrightarrow GA - O{-}(M)_n{-}M^* \quad (8)$$

$$GA - O^* + nM \longrightarrow GA - O{-}(M)_{n-1}M^* \quad (9)$$

$$^*M - OH + nM \longrightarrow HO{-}(M)_n{-}M^* \quad (10)$$

Termination

$$GA - O{-}(M)_n{-}M^* + M^*{-}(M)_n{-}O - GA \longrightarrow GA - O{-}(M)_n{-}M_2{-}(M)_n{-}O - GA \quad \text{(Graft copolymer)} \quad (11)$$

$$GA - O{-}(M)_{n-1}M^* + M^*{-}(M)_{n-1}{-}O - GA \longrightarrow GA - O{-}(M)_{n-1}{-}M_2{-}(M)_{n-1}{-}O - GA \quad \text{(Graft copolymer)} \quad (12)$$

$$GA - O{-}(M)_n{-}M^* + {}^*OH \longrightarrow GA - O{-}(M)_{n+1}{-}OH \quad (13)$$

$$HO{-}(M)_n{-}M^* + {}^*M{-}(M)_n{-}OH \longrightarrow HO{-}(M)_n{-}M_2{-}(M)_n{-}OH \quad \text{(Homopolymer)}. \quad (14)$$

where M = AAm, M^* = AAm free radical, GA = Gum arabic, GA-O^* = Gum arabic free radical.

Initially persulphate dissociates to give SO_4^- *which further reacts with water to give *OH. The generated SO_4^- *attacks GA, thereby resulting in the formation of free radical sites on the backbone. *OH attacks the backbone polymer and the monomer (AAm) leading to the generation of free radical sites on both of them. These two generated free radicals react with each other resulting in the formation of graft copolymer and propagation of graft copolymerization reaction takes place. However, termination of the reaction takes place either by the reaction between *OH and a free radical (Eq. (13)) or the reaction between two activated chains (Eqs. (11), (12) and (14)).

3.2. Optimization of different reaction parameters

It has been found that graft copolymerization predominates in neutral medium to a greater extent (maximum $P_g = 1.67 \times 10^2$) as compared to acidic and alkaline media (Fig. 1a). The reason for this could be due to the neutralization of OH ions with H^+ ions of the acid (in case of acidic medium), thereby resulting in decrease in production of free radical sites on the backbone. In case of alkaline medium, excess of *OH groups results in early initiation of termination reaction (Eq. (13)). Hence, lesser value of P_g is obtained in this case [14].

P_g was found to increase with increase in time (Fig. 1b) and maximum P_g (1.75×10^2) was observed at 180 min. Further increase in time resulted in decreased P_g. This could be due to the fact that with

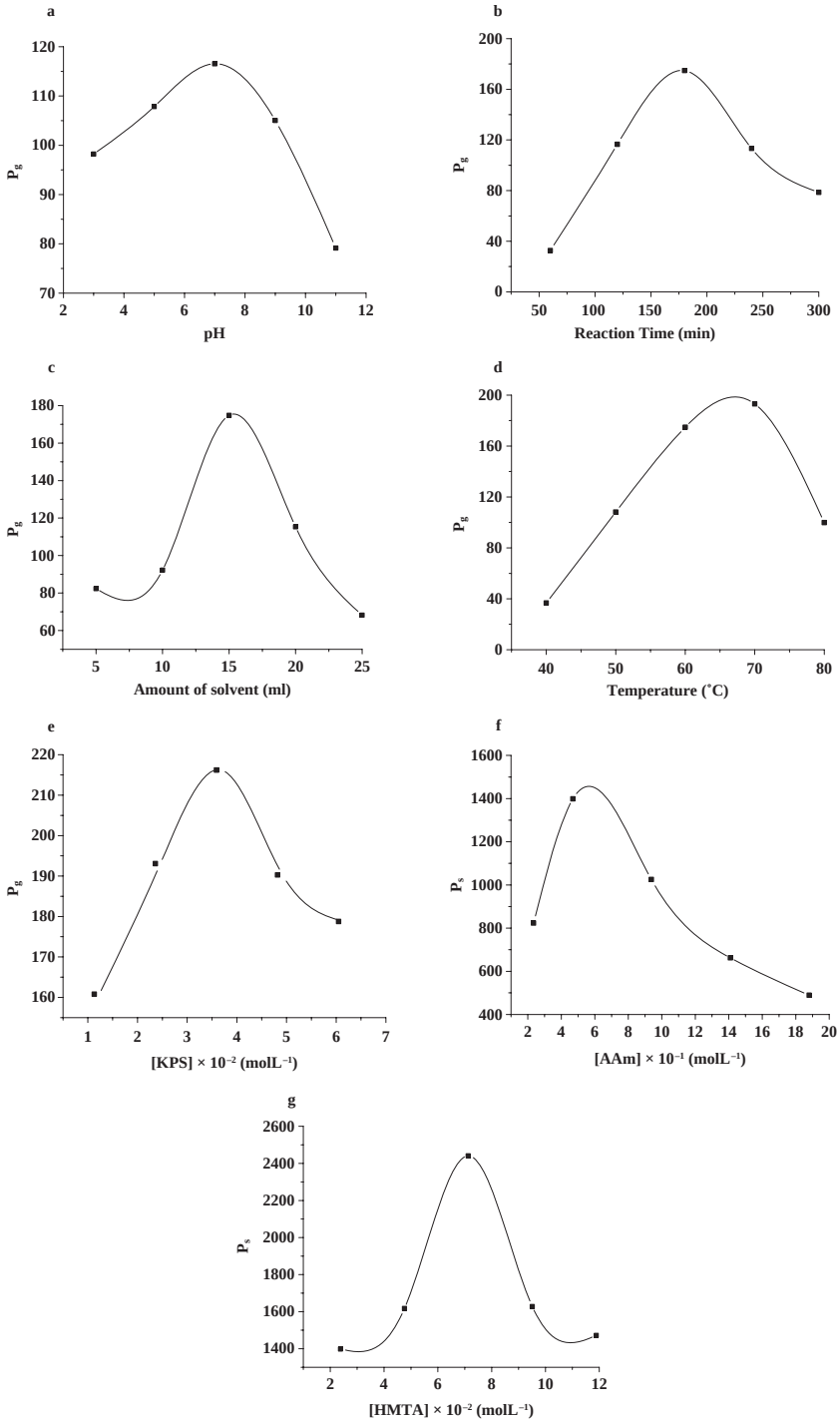

Fig. 1a. Effect of pH onto P_g. ([AAm] = 4.69 × 10^{-1} mol L^{-1}, [KPS] = 2.46 × 10^{-2} mol L^{-1}, reaction time = 120 min, amount of solvent = 15 ml, reaction temperature = 60°C, GA = 1 g). b. Effect of reaction time onto P_g. ([AAm] = 4.69 × 10^{-1} mol L^{-1}, [KPS] = 2.46 × 10^{-2} mol L^{-1}, amount of solvent = 15 ml, reaction temperature = 60°C, GA = 1 g). Effect of amount of solvent onto P_g. ([AAm] = 0.469 mol L^{-1}, [KPS] = 2.46 × 10^{-2} mol L^{-1}, reaction time = 180 min, amount of solvent = 15 ml, reaction temperature = 60°C, GA = 1 g). d. Effect of reaction temperature onto P_g ([AAm] = 0.469 mol L^{-1}, [KPS] = 2.46 × 10^{-2} mol L^{-1}, reaction time = 180 min, amount of solvent = 15 ml, GA = 1 g). e. Effect of [KPS] onto P_g. ([AAm] = 0.469 mol L^{-1}, reaction time = 180 min, amount of solvent =15 ml, reaction temperature = 70°C, GA=1 g). f. Effect of [AAm] onto P_s. ([KPS] = 3.69 × 10^{-2} mol L^{-1}, reaction time = 180 min, amount of solvent = 15 ml, reaction temperature = 70°C,[HMTA] = 4.76 × 10^{-2} mol L^{-1}, GA=1 g). g. Effect of [HMTA] onto P_s. ([AAm] = 0.469 mol L^{-1}, [KPS] = 3.69 × 10^{-2} mol L^{-1}, reaction time = 180 min, amount of solvent = 15 ml, reaction temperature = 70°C, GA = 1 g).

increase in reaction time, the active sites on the backbone and monomer increases, leading to increase in grafting but once the optimum is reached, the concentration of free radicals limits the length of polymeric chain by initiating numerous chains simultaneously which results in decreased P_g [16].

It has been found that amount of solvent plays an important role in graft copolymerization (Fig. 1c). Maximum P_g (1.75×10^2) was found with 15 ml of solvent and further increase in the amount of solvent caused decrease in P_g. This could be explained on the basis of OH^* concentration which initiates the polymerization reaction (Eqs. (4) and (5)) and further propagates it (Eqs. (7)–(10)) and attains maximum P_g. After attaining the maximum value, P_g starts declining which happens as a result of termination reaction in response to increased concentration of OH^* (Eq. (13)) [16].

P_g has been found to be temperature dependent (Fig. 1d) and maximum P_g (1.93×10^2) has been found at 70°C. The increase is due to the generation of more free radical sites on the backbone polymer and easy accessibility of monomer radical moieties to the active sites of backbone. But further increase in temperature resulted in decreased P_g.

The reason for this could be due to the dissolution of water soluble components of backbone polymer and predominance of homo-polymerization over graft copolymerization [17]. Initiator concentration has a remarkable effect onto P_g (Fig. 1e). P_g was found to increase up to 3.69×10^{-2} mol L^{-1} of KPS ($P_g = 2.16 \times 10^2$). The reason for this increase is the generation of free radical sites on the backbone as well as on the monomer, facilitating in the graft copolymerization. After the optimum value, most of the active sites become inactive resulting in side chain reactions and finally chain termination takes place. Secondly, at higher initiator concentration homopolymerization predominates copolymerization resulting in decreased P_g [14].

It was found that with increase in monomer concentration, there was increase in percent swelling (1.40×10^3) upto 4.69×10^{-1} mol L^{-1} (Fig. 1f) and further increase in AAm concentration resulted in decreased P_s. The initial increase in the P_s is due to the reason that there is greater availability of monomer molecules in the vicinity of the chain propagating sites of backbone molecule which goes on increasing till the optimum value is reached, after which it starts decreasing. The decrease in P_s after attaining maximum P_s is due to the reason that homo-polymerization predominates over graft copolymerization and an increase in the viscosity of the medium hinders the movement of free radicals and monomer molecules [18].

From Fig. 1g, it has been found that maximum percent swelling (2.44×10^3) occurred with 7.13×10^{-2} mol L^{-1} of HMTA and further increase in HMTA concentration resulted in declined P_s. The initial increase in P_s is due to the reason that there are small spaces in between the grafted polymeric chain which could easily accommodate the crosslinker molecules in it, till the formation of the three-dimensional polymeric network of the AAm-grafted polymeric backbone with the crosslinker, after which P_s decreases. The reason for this decrease is attributed to the fact that with increasing crosslinker concentration the pore size decreases, resulting lesser solvent molecules to approach the matrix [17].

3.3. FTIR spectroscopy

IR spectrum of GA (Fig. 2a) exhibited broad peaks at 3.37×10^3 cm^{-1} (O–H stretching of carbohydrates), 2.93×10^3 cm^{-1} (CH_2 asymmetric stretching), 1.42×10^3 cm^{-1} and 1.38×10^3 cm^{-1} (CH, CH_2 and OH in-plane bending in carbohydrates), 1.15×10^3 cm^{-1}, 1.08×10^3 cm^{-1}, 1.04×10^3 cm^{-1} (C–O stretching region as complex bands, resulting from C–O and C–O–C stretching vibrations) and 8.93×10^2 cm^{-1} (pyranose rings), whereas, IR spectrum of *GA-cl-poly(AAm)* (Fig. 2b) showed peaks at 3.39×10^3 cm^{-1} (N–H stretching in amides), 1.73×10^3 cm^{-1} (C=O stretching in acids), 1.67×10^3 cm^{-1} (C=O stretching in amides), 1.25×10^3 cm^{-1} (C–N stretching vibrations) and 6.03×10^2 cm^{-1} (OCN deformation in amides) in addition to peaks obtained with that of GA.

3.4. SEM studies of the gels

SEM studies were conducted to differentiate the morphological differences on the surface of the backbone polymer and the synthesized polymer (Figs. 3a and 3b). SEM studies clearly differentiate between the homogeneous surface of GA and uneven and crosslinked structure in case of *GA-cl-poly(AAm)*.

3.5. Thermal behavior of gels

TGA/DTA and DTG studies of both the backbone and functionalized polymer were performed as a function of percent weight loss vs. temperature (Figs. 4a and 4b). In both the cases, two-stage decomposition has been observed. GA showed initial decomposition temperature (IDT) at 227°C and final decomposition temperature (FDT) at 517°C. In case of DTA, GA showed exothermic peaks at 292°C (30 μV), corresponding to the first decomposition stage in case of TGA (227–296°C) and 470°C (131 μV) and 513°C (212 μV) corresponding to the second decomposition stage in case of TGA (296–517°C). Weight loss rate of 1.025 and 0.636 mg/min has been obtained from DTG curve

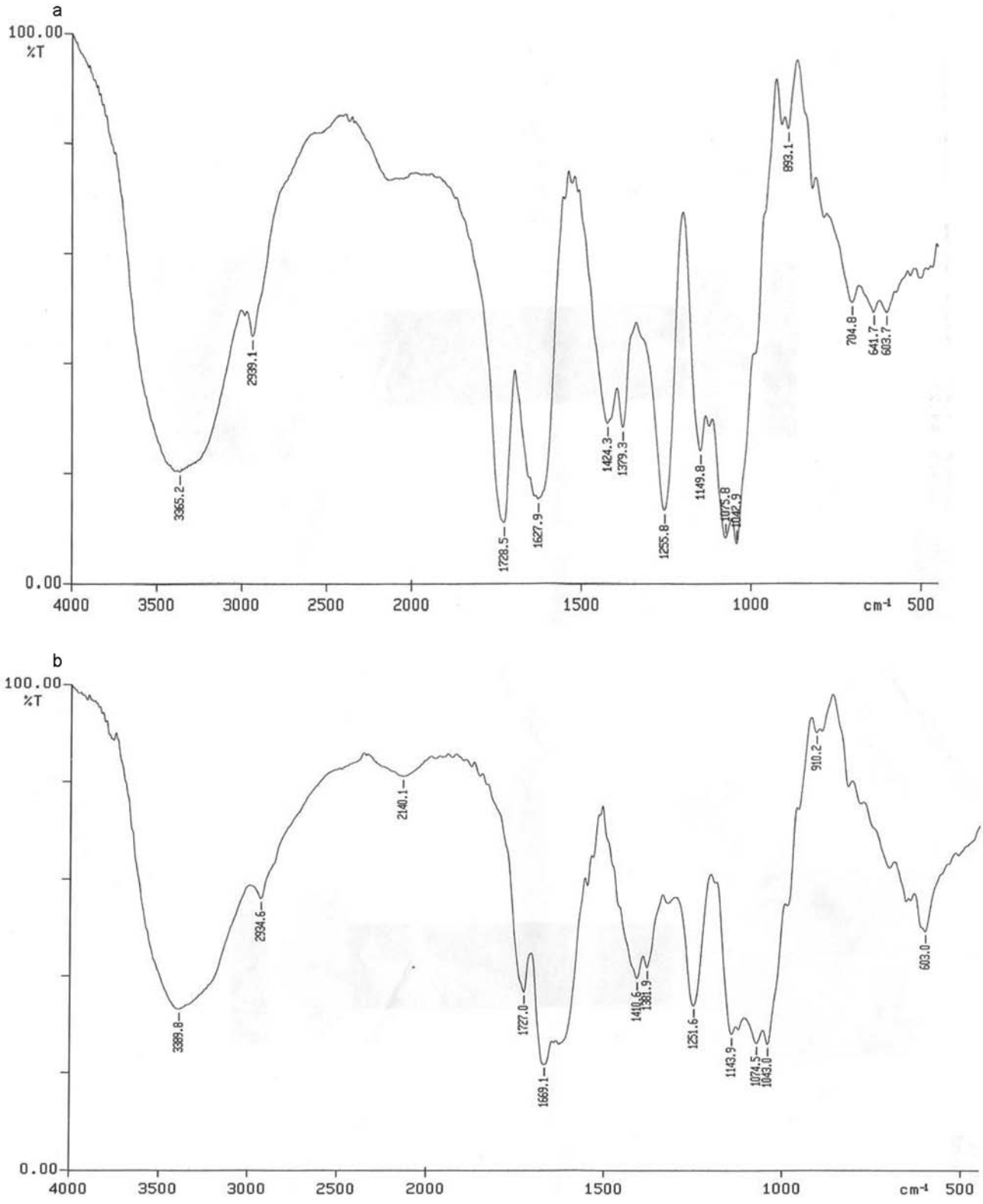

Fig. 2a. FTIR of GA. b. FTIR of *GA-cl-poly*(*AAm*).

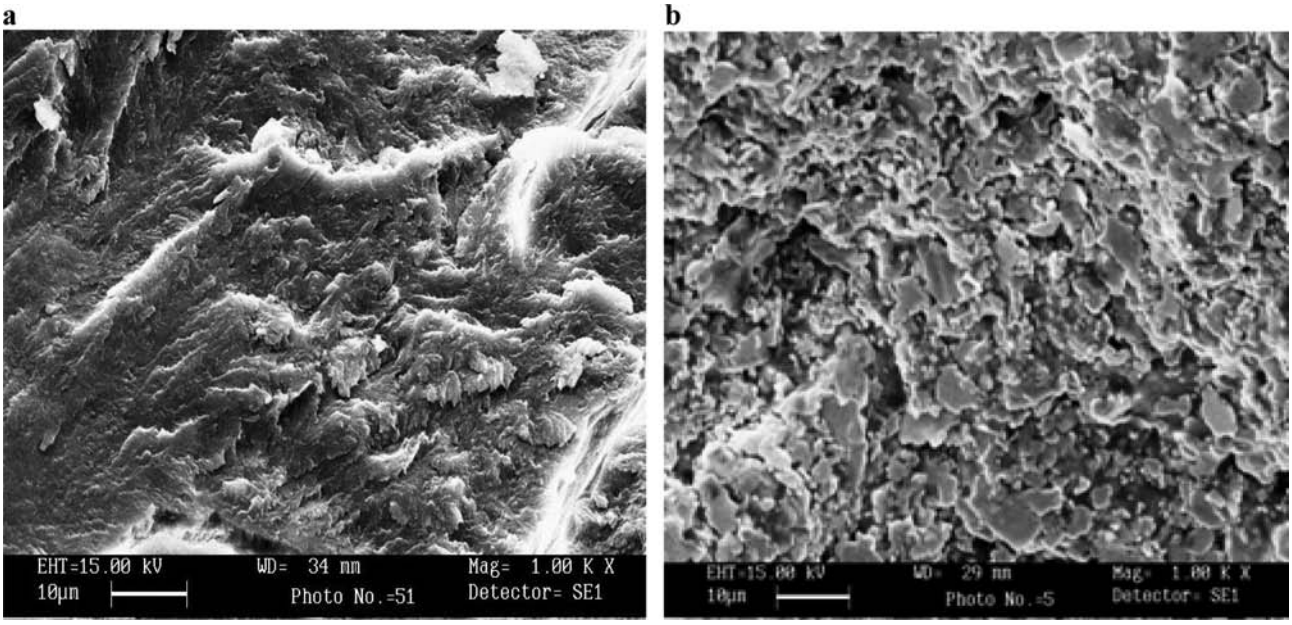

Fig. 3a. SEM of GA. b. SEM of *GA-cl-poly*(*AAm*).

which corresponds to temperature range of 227–296°C of TGA, whereas, in the temperature range of 296–517°C of TGA, weight loss of 0.488 mg/min at 463°C, 0.665 mg/min at 500°C and 0.676 mg/min at 509°C has been observed. In case of *GA-cl-poly*(*AAm*), IDT and FDT have been found to be 209 and 550°C, respectively, in case of TGA. The lower value of IDT of the synthesized hydrogel as compared to GA appears due to the initial disturbance during grafting which disturbed its basic structure, whereas, FDT of resultant product is higher than the backbone polymer which shows that on crosslinking of GA with AAm-HMTA, its thermal stability increases. Two-stage decomposition has been observed from 209–274°C and 274–550°C. DTA studies revealed two minor exothermic peaks at 206°C (15 µV) and 263°C (23 µV) and a major peak at 460°C (180 µV). DTG curve showed weight loss rate of 1.024 mg/min at 251°C and 0.652 mg/min at 448°C corresponding to the first and second decomposition stages of TGA. DTA and DTG results support the TGA results which accounts for more thermal stability of the synthesized hydrogel.

3.6. Salt-resistant swelling studies

3.6.1. Effect of concentration of salt onto P_s

From Fig. 5a, it has been found that P_s decreases with increase in salt concentration which was varied from 1% to 20%. The reason for this type of behavior could be due to the fact that swelling of hydrogels decreases with the increase in ionic strength of the solution [19]. However, maximum swelling has been found at 1% salt concentration for each of the salt solutions.

3.6.2. Effect of temperature onto P_s

The temperature range selected for the swelling studies was 15–55°C (Fig. 5b). It has been observed that P_s increases with increase in temperature and attains the maximum value (1.20×10^3) at 35°C. However, further increase in temperature resulted in decreased P_s [15]. The temperature sensitivity of the synthesized hydrogel is predicted from the observation that on further increasing the temperature, the P_s goes on decreasing which could be due to desorption at higher temperature.

3.6.3. Effect of pH onto P_s

Further salt-resistant water absorbing capacity of the hydrogel was investigated in different media using 0.5N HCl, distilled water and 0.5N NaOH and it has been found that the hydrogel swells to very less extent in acidic and basic media but showed appreciable swelling in distilled water (Fig. 5c). The reason for this could be that the disintegration of *GA-cl-poly*(*AAm*) occurs both in acidic and basic media and is quite stable in neutral medium. This study also supports the pH-sensitivity of the synthesized hydrogel.

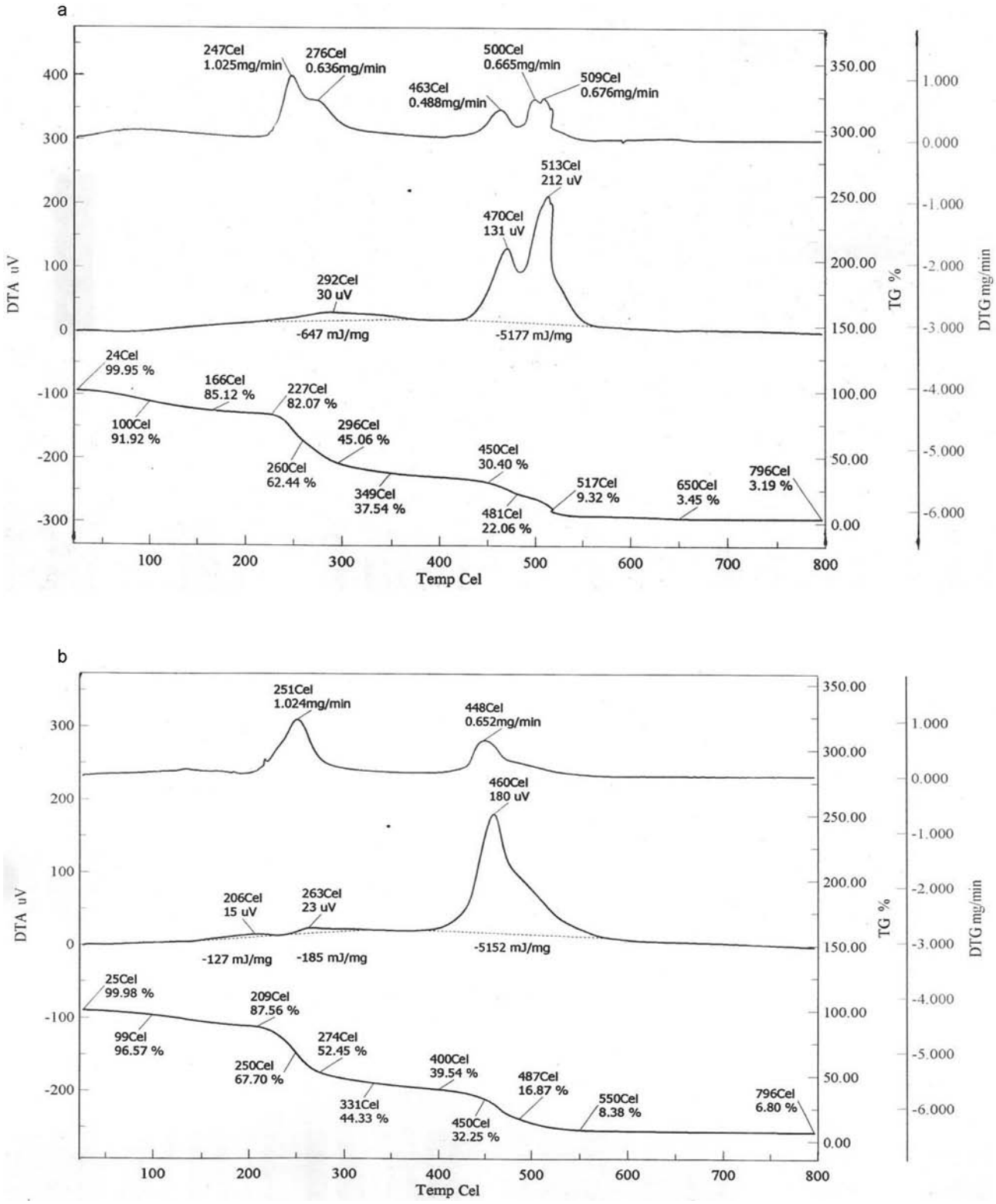

Fig. 4a. TGA-DTA-DTG curves of GA. b. TGA-DTA-DTG curves of *GA-cl-poly*(*AAm*).

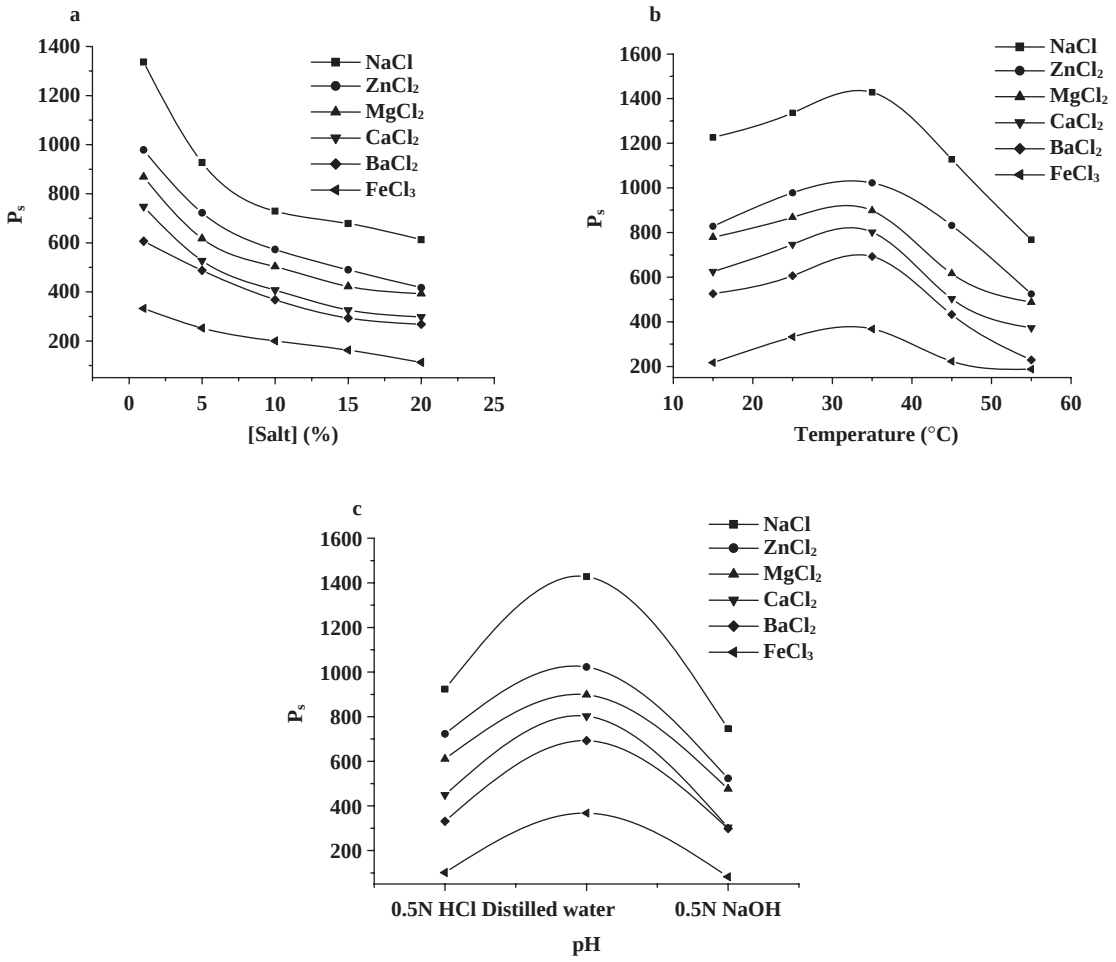

Fig. 5a. Effect of salt concentration onto P_s of *GA-cl-poly*(*AAm*) in different salt solutions. ([AAm] = 4.69×10^{-1} mol L^{-1}, [HMTA] = 7.13×10^{-2} mol L^{-1}). b. Effect of temperature onto P_s of *GA-cl-poly*(*AAm*) in different salt solutions. ([AAm] = 4.69×10^{-1} mol L^{-1}, [HMTA] = 7.13×10^{-2} mol L^{-1}). c. Effect of pH onto P_s of *GA-cl-poly*(*AAm*) in different salt solutions. ([AAm] = 4.69×10^{-1} mol L^{-1}, [HMTA] = 7.13×10^{-2} mol L^{-1}).

3.6.4. Effect of charge of cation onto P_s

It has been found that the swelling capacity of the hydrogel in saline solution appreciably decreased as compared with the values measured in distilled water. The swelling capacity decreased with increasing charge of the cation of the salt. It may be explained by charge screening effect of additional cations causing non-perfect anion–anion electrostatic repulsion, leading to decreased osmotic pressure (ionic pressure) difference between the polymer network and the external solution [18] (Figs. 5a–c). Therefore, the swelling capacity would be in the order: $Na^+ > (Zn^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}) > Fe^{3+}$.

3.6.5. Effect of size of cation onto P_s

Further it was found that among the same valent ions, lesser the size of cation, more the swelling capacity, i.e., swelling capacity would be in the order: $Zn^{2+} > Mg^{2+} > Ca^{2+} > Ba^{2+}$. Therefore, keeping in view the aspects of cation charge and size, the trend in the percent swelling would be: $Na^+ > Zn^{2+} > Mg^{2+} > Ca^{2+} > Ba^{2+} > Fe^{3+}$ (Figs. 5a–c).

4. Conclusions

It is concluded from the foregone discussion that a crosslinked hydrogel, *GA-cl-poly*(*AAm*) has been synthesized by grafting AAm onto GA by free radical graft copolymerization in presence of KPS-HMTA as initiator-crosslinker system. Swelling capacity of the hydrogel was found to be affected by monomer and crosslinker concentrations. The swelling of hydrogels exhibited high sensitivity towards temperature and pH. So, the synthesized gel is temperature as well as pH sensitive and can be put to a variety of applications

including drug delivery – a much talked about topic these days. Secondly, the hydrogel has been found to show salt-resistant swelling behavior which makes its way directly to the water purifying industry. The desalinated water becomes fit for its desired end-use for industrial and medical processes. One such use is returning water that has been used back into the natural environment without adverse ecological impact.

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