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Synthesis, characterization and rheological behavior of pH sensitive poly(acrylamide-co-acrylic acid) hydrogels

Seddiki Nesrinne, Aliouche Djamel *

Laboratory of Polymers Treatment and Forming, F.S.I., M'Hamed Bougara University, Boumerdes 35000, Algeria

Abstract Poly(acrylamide-co-acrylic acid) poly(AAm-co-AAc) hydrogels were prepared by free radical polymerization initiated by redox initiators of ammonium peroxodisulphate (APS) and N,N,N',N'-tetramethyl ethylene diamine (TEMED); N,N'-methylene bisacrylamide (BIS) was employed as a crosslinking agent. The copolymers were characterized by infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), dynamic rheology and swelling measurements.

Results indicated that the strong interaction in the hydrogels resulted in the formation of a more stable copolymer. The single glass transition temperature (T_g) in sample suggested that the two polymers into the hydrogel have a good miscibility. The elastic modulus (G′) and linear viscoelastic region increased with increase in PAAc concentration. The oscillation time sweep study of the hydrogels exhibited a flat G′ indicating a stable structure and good mechanical strength. In the swelling measurements, the gels exhibited appreciable water uptake and were highly sensitive to pH environment. So the poly(AAm-co-AAc) hydrogel will have promising application in pharmaceutical use and in biomaterials.

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1. Introduction

In recent years considerable research attention has been focused on materials that are able to change their properties in response to external chemical and/or physical stimuli, these materials are called "smart" materials (Zhang and Peppas, 2000; Mahkam and Allahverdipoor, 2004); they are also named as "stimuli-responsive" hydrogels (Scranton et al., 1995).

Stimuli-responsive hydrogels are three-dimensional hydrophilic polymer network, that exhibit volume or phase transition in response to external environmental changes. Because of the presence of certain functional groups along the polymer chains, hydrogels are often sensitive to the conditions of the surrounding environment (Qiu and Park, 2001; Miyata et al., 2002). For example, the swelling ratio of these materials may be sensitive to the temperature, pH, electric field, or ionic strength of the swelling agent.

Hydrogels exhibiting pH-dependent swelling behavior can be swollen from ionic networks. These ionic networks contain either acidic or basic pendant groups. In aqueous media of appropriate pH and ionic strength, the pendant groups can

* Corresponding author. Tel.: +213 552 27 52 86.
E-mail address: aliouche_dj@yahoo.fr (A. Djamel).

ionize developing fixed charges on the gel. As a result of the electrostatic repulsions, the uptake of solvent in the network is increased (Oppermann, 1992; Rubinstein et al., 1996).

In these gels, ionization occurs when the environment pH is above the pK_a of the ionizable group (Brannon-Peppas and Peppas, 1991; Skouri et al., 1995). As the ionization degree increases (increased pH of system), the number of fixed charges increases: resulting in increased electrostatic repulsion between chains. This, in turn, results in increased network hydrophilicity and greater swelling ratios (Ohmine and Tanaka, 1992).

Conversely, cationic hydrogels contain pendent groups such as amines (Schroder and Opperman, 1996; Khare and Peppas, 1995). These groups ionize in media which are at a pH below the pK_b of the ionizable species. Thus, in a low pH environment, ionization increases, causing increased electrostatic repulsion. The hydrogel becomes increasingly hydrophilic and will swell to an increased level.

Such hydrogels have potential applications in drug delivery formulations (Carelli et al., 2000; Lele and Hoffman, 2000), in biomaterials (Chun et al., 2002), and as sensors and actuators (Peppas et al., 2000; Soppimath et al., 2002). For use as drug delivery vehicles, the hydrogel's microstructure needs to be controlled accurately: rheological and volumetric changes of the gels need to be tuned carefully in order to trigger the release of drug molecules under the appropriate physiological environmental conditions (Peppas et al., 2006).

Although characterization of bulk mechanical properties like swelling rate is important, most biomedical applications require a detailed understanding of microstructure and local mechanical properties. Understanding the hydrogel structure and rheology responsiveness to environmental changes is essential for the design of materials with desirable performance, on macroscopic and microscopic length scales. The test conditions should be similar to the physiological environment in which materials will ultimately be used, so that observed structural changes, such as gel formation and break-up, are representatives for ultimate applications (Yu et al., 1997).

It is well-known that poly(acrylic acid) is a typical pH-responsive polyelectrolyte, which has widely been used in the area of drug delivery to specific regions of the gastrointestinal tract (Ramakissoon-Ganorkar et al., 1999). However, high water solubility has limited their use as a drug carrier to a certain extent; because of dissolution before the drug can be delivered (Needleman and Smales, 1995). In order to overcome the above drawback, PAAc is usually copolymerized and crosslinked with organic crosslinkers to form interpenetrating networks (IPNs) and copolymers.

The present work focuses on the hydrogel synthesis of poly(acrylamide) and copolymers based on poly(acrylic acid) at various concentrations, N,N'-methylene bisacrylamide was used as crosslinker. The swelling properties of the hydrogels, in different solutions (water, NaCl) and different pH were systematically studied. The copolymer hydrogels synthesized were characterized through infrared spectroscopy and thermal analysis; rheological behavior of these hydrogel systems was evaluated.

2. Experimental

2.1. Materials

Acrylamide (AAm) and acrylic acid (AAc) monomers used in this study were obtained from Aldrich Chemical Co. Acrylamide was purified by recrystallization from methanol and dried in vacuum desiccator over silica gel; acrylic acid was purified by vacuum distillation.

The crosslinker N,N'-methylene bisacrylamide (BIS), the activator N,N,N',N'-tetramethyl ethylene diamine (TEMED) and the initiator ammonium peroxodisulphate (APS) were all analytical grade and purchased from Panreac Monplet & Esteban, S.A., Spain. All reagents were used without further purification. Deionized water was used throughout the experiments in the preparation of hydrogels, of buffer solutions and in the swelling experiments. Physiological saline solution (0.9% NaCl) was used for swelling measurements. Physiological solution is usually used to characterize the absorption of hygienic products (Herrmann, 1996).

2.2. Methods

2.2.1. Synthesis of hydrogels

Hydrogels were prepared by free radical crosslinking copolymerization procedure (Rintoul and Wandrey, 2005; Bajpai and Johnson, 2005) in deionized water, which is the solvent for all components of the feed mixture.

First, the hydrophilic AAm monomer was used as a base monomer in the synthesis of hydrogel copolymers; the comonomer was AAc carrying acid group. Aqueous solutions of AAm were prepared in deionized water. Different amounts of AAc were added to AAm solution (AAm/AAc mole ratios, 100:0, 60:40, and 40:60); Table 1 describes the different formulations used in this work.

After nitrogen bubbling for 15 min, free radical copolymerization of hydrogels was carried in glass tubes of 10 mm inner diameter at room temperature for 2 h, using APS and TEMED as redox initiator. Subsequently, the crosslinking of PAAm hydrogels was carried out by BIS.

After polymerization, crosslinked copolymers were removed from tubes and the hydrogels obtained in long cylindrical shapes were cut into pieces of approximately 1 cm length. Polymer samples were immersed in distilled water at room temperature for 48 h and the water was refreshed every several hours in order to allow the unreacted chemicals to leach out. Finally extracted gels were dried in a vacuum oven at 30 °C.

Table 1 Compositions of the PAAm-co-PAAc copolymer hydrogels.

Sample	AAm (g)	AAc (g)	APS (g)	BIS (g)	TEMED (ml)
PAAm (100%)	5	0	0.08	0.25	0.48
PAAm-co-PAAc (60–40%)	3	2	0.08	0.25	0.48
PAAm-co-PAAc (40–60%)	2	3	0.08	0.25	0.48

2.2.2. Characterization

- The spectroscopy characterization of PAAm and PAAm-co-PAAc hydrogels was performed by Infrared Spectroscopy and Fourier Transform (FT-IR) in solid state using KBr pellet. Dried hydrogels were analyzed through a Shimadzu M850 Model FT-IR Spectrophotometer with 40 scans in the range of 4000–400 cm^{-1}, with a 2 cm^{-1} resolution (Aouada et al., 2009; Mandal et al., 2009).
- DSC characterized thermal behaviors of PAAm and PAAm-co-PAAc hydrogels on dry samples of 5 ± 0.5 mg. The DSC analysis was carried out using a NETZSCH DSC 204 F1 Phoenix thermal apparatus by scanning in the temperature range of ambient to 200 °C at a rate of 20 °C/min under a nitrogen atmosphere, flow rate 10 mL min^{-1}, the DSC was calibrated with an indium standard (Leung et al., 1985; Bouwstra et al., 1995; Alves et al., 2011). The heat flow (DSC curve) was recorded simultaneously as a function of temperature.

The glass transition temperature (T_g) was determined as the temperature at the midpoint of the endothermic rise, measured from the extension of the post-transition baselines (Song et al., 2007). Three measurements were thus taken for each sample and the average reported as the glass transition temperature

- The rheological measurements of aqueous suspensions of PAAm and PAAm-co-PAAc copolymers were carried out in controlled stress AR-2000 Advanced Rheometer (T.A. Instruments) under the oscillatory shear. The flow of dilute hydrogel suspensions under shear was studied in Couette geometry, using a pair of coaxial cylinders with 15 mm of external diameter and gap of 1 mm. Silicone oil was added to the surface of the sample to prevent evaporation during measurements (Mihranyana et al., 2007; Yen and Yang, 2003).

The suspensions of gel particles swollen to different extents were prepared by simply mixing dry gel powder with a certain amount of deionized water. The size of the dry gel particles is about 0.1–0.2 mm with a maximal degree of swelling in water of about 250 g/g.

The rheological behavior of polymer suspensions of 0.1 wt.% concentrations was studied at room temperature. The fluid is sheared for 10 min at a shear rate which varies from 0 to 4000 s^{-1} in the linear mode; each shear rate is maintained for a level of 0.1s. Rotor speed was variable, it enabled rheograms (shear stress versus shear rate diagram) to be constructed (Shevchenko et al., 2004; Yang, 2001).

In oscillatory mode, the experiments were done at 6.2 Hz. The gel properties were described in terms of two dynamic mechanical properties: the elastic modulus G′ (also known as dynamic rigidity), reflecting the reversibly stored energy of the system, and the viscous modulus G″, reflecting the irreversible energy loss (Calvet et al., 2004; Okay and Oppermann, 2007).

- Swelling measurements: For several applications, in particular in the medical and pharmaceutical fields, it is significant to know the behavior of absorbing materials in the physiological solution, usually simulated by aqueous

0.9% NaCl solution. The swelling behavior of the gels was investigated in deionized water and saline solution at the physiological temperature 37 °C. The effect of pH of the swelling medium on the equilibrium water uptake of the hydrogel samples was determined in buffer media of varying pH, ranging from 2.2 to 10.0, with ionic strength maintained at 0.1 mol/l. by adding definite amount of NaCl into the buffer solutions.

Completely dried pre-weighed hydrogel samples were placed in 500 ml of buffer solution at 37 °C. The swollen gels were taken out at regular time-intervals, wiped superficially with filter paper to remove surface-bound water, weighed and then placed in the same bath. The percent mass swelling was determined using the following expression (Gudeman and Peppas, 1995; Wan et al., 2000):

$$\% \text{ Swelling} = \frac{M_t - M_0}{M_0} \times 100 \qquad (1)$$

where M_0 and M_t are the initial mass and mass at different time-intervals, respectively. All the experiments were carried out in triplicate and the average values have been reported in the data.

3. Results and discussion

3.1. FT-IR spectral analysis of copolymer samples

It is well understood that PAAc has carboxylic acid groups which could develop different intermolecular interactions like electrostatic interaction, hydrogen bonds, and dipole-ion with other polymers. Many investigations have shown that there are strong interactions between PAAc and ionic polymers in aqueous solutions. There is a great potential for utilizing these interactions in pharmaceutical preparations, particularly in drug delivery systems.

Intermolecular interactions affect the vibration of groups on polymer segments, this information can be obtained by FTIR analysis. Fig. 1 presents the FTIR spectra of poly(AAm) (a) and poly(AAm-co-AAc) (b) hydrogels with 60/40% ratio.
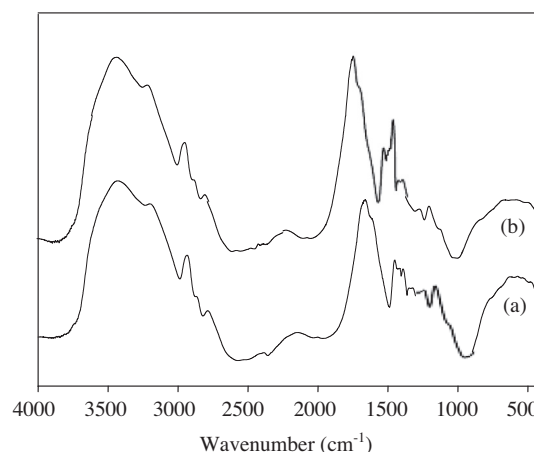

Figure 1 FT-IR spectra of the poly(AAm) (a) and poly(AAm-co-AAc) (b) hydrogel samples.

The IR spectra confirm the formation of co-polymer of Acrylamide and acrylic acid as is evident from bands that appeared in the range of 3100–3500 cm^{-1} (O–H and N–H stretching), in poly(AAm) and poly(AAm-co-AAc) hydrogel. Asymmetrical and symmetrical stretching of C–H are found at 2900 and 2740 cm^{-1}, respectively, carbonyl stretching vibration C=O connected to the carboxyl group gives an absorption peak at 1742 cm^{-1} in poly(AAm-co-AAc), this peak C=O group connected to the amide group gives absorption peak at 1670 cm^{-1} in poly(AAm). Symmetric and asymmetric stretching of COO$^-$ are found at 1448 cm^{-1} and 1580 cm^{-1}, respectively in poly(AAm-co-AAc) spectra. These results indicate that the carboxylic groups of PAAc are dissociated into COO$^-$, which complexes with the cationic groups of PAAm through electrostatic interaction to form the co-polymer complexes during the polymerization procedure (Solpan et al., 2003). The spectra also show a weak band at 2186 cm^{-1}, which is due to the presence of –C–N group of crosslinking agent (N-N′-methylene bisacrylamide) and Acrylamide.

3.2. Thermal analysis of copolymer samples

The glass transition temperature is arguably one of the most important parameters for characterizing polymeric materials. The measurement of the glass transition temperature (T_g) of a copolymer hydrogel is often used as a criterion to determine its miscibility. The miscible copolymer hydrogel would exhibit a single transition. With increasing immiscibility there is a broadening of the transition, whereas an incompatible system would be marked by separate transitions of the polymer components in the hydrogel (Biliaderis et al., 1999).

In order to demonstrate that the presence of a single transition in the hydrogels is the result of interactions between the two polymers, thermal analysis was performed on poly(AAm-co-AAc) mixtures prepared. The typical scan thermograms corresponding to this sample is reported in Fig. 2, together with those corresponding to PAAm pure sample.

The DSC curves of the three hydrogels have similar events, because they present two endothermic reactions. The first endothermic peak can be attributed to the loss of water; the
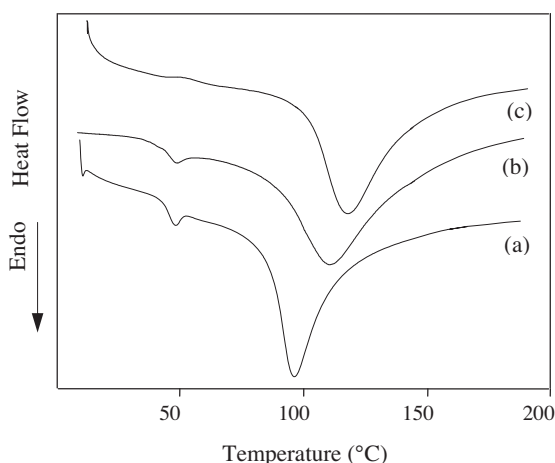

Figure 2   DSC thermograms of the poly(AAm) (a), poly(AAm-co-AAc) (60/40) (b) and poly(AAm-co-AAc) (40/60) (c) hydrogel samples.

second peak corresponds to the glass transition temperature of the polymers. For pure PAAm, the glass transition temperature is observed around 97 °C, T_g of pure PAAc is about 123 °C (Maurer et al., 1987; Huang et al., 2007) the random co-polymer systems poly(AAm-co-AAc) exhibit only one T_g, which has a value between the T_g of the individual homopolymers. Addition of AAc shifts the glass transition temperature slightly to 110 °C for 60/40 poly(AAm-co-AAc) and 119 °C for 40/60 poly(AAm-co-AAc) polymers resulting in a more stable co-polymer because the connections of hydrogen bonds between the polymers are stronger (Xia et al., 2005). There is no apparent phase separation in the hydrogels. Painter et al. (1991) have discussed that this behavior is often found in blends of polymers where there are H-bonding interactions.

Thermal analysis by differential scanning calorimetry shows that all blends have a single T_g for the two compositions tested. The occurrence of a single T_g in the blends is a strong indication of miscibility between PAAm and PAAc, a fact that has been reported in the literature for PAAc systems (Daniliuc et al., 1992; Vasquez-Torres et al., 1993). The miscibility between PAAm and PAAc has been attributed to the capacity of these polymers to form intermolecular H-bonding. However it is clear that hydrogel samples are quite stable and its stability shall not be affected at the physiological temperature 37 °C.

3.3. Rheological behavior of copolymer samples

Suspension of swollen-in-water hydrogel particles is a complex rheological fluid; one of the main problems for using such fluids is that the particles are settling with gravity, reducing their rheological properties. There are three different concentrations that must be recognized in these swollen hydrogel suspensions: the first is the total polymer concentration in the suspension, the second is the polymer concentration in the gel particle (100 wt.% for dry gel), and third concentration is the gel particle concentration in the suspension, it can vary from 0 (no gel in the suspension) to the maximum packing density which is close to 100% for soft deformable gel particles. The variation of the total polymer concentration in the hydrogel suspension either changes the polymer concentration and keeps those of the particle constant when the gel degree of swelling is lower than the maximal; or changes C particle and keeps C polymer constant when the gel is swollen at its maximum. With the increase of total polymer concentration, the gel particles become more and more "hard" since there is less and less water in the system. This also increases the flow stress by limiting the layer of water between the particles, and probably preventing particles to accommodate the deformation (Budtova and Navard, 2001). This is the phenomenon of dilatancy, also known as shear thickening which becomes progressively larger as the volume concentration of solid particles increases.

In the first part the flow of the gel suspensions under shear will be reported. Fig. 3 shows the experimental results of shear stress (τ) versus shear rate (γ). Typical shear stress–shear rate data for the aqueous polymer suspensions of different compositions are presented in the curves. Swollen-in-water hydrogel suspensions are structured fluids, they do not obey a simple linear relationship between applied stress and flow (Newtonian fluid behavior), with increasing volume fraction in water. The data were analyzed by using conventional flow equations such as Bingham, Casson, and Ostwald as well as the Herschel–Bulkley
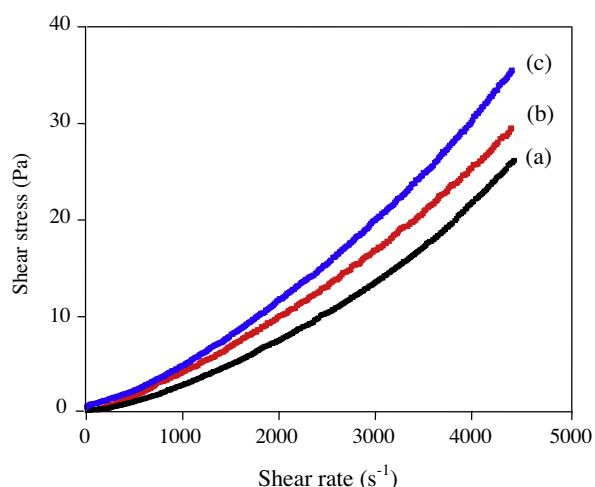
Figure 3 Shear stress as a function of the shear rate for the poly(AAm) (a), poly(AAm-co-AAc) (60/40) (b) and poly(AAm-co-AAc) (40/60) (c) hydrogel particles.

equations known as the model describing the flow behavior of the hydrogel polymers very well. Ostwald and especially Herschel–Bulkley ($R^2 = 0.995$–0.998) models were more satisfactory to describe the flow behavior while the Bingham and Casson models were digressed from the actual flow curves.

The viscosity of the liquid phase in suspensions usually plays an important role on the flow properties of the material. Suspensions have wide variations in performance depending on particle size, shape, concentration, and affinity with the continuous phase in which they are suspended. The flow properties with shear rate for hydrogel suspensions are illustrated in Fig. 4. In this study the concentration was 0.1%, Figure curves show that the swollen-in-water suspensions are responding as quasi-solid bodies, with a viscosity almost proportional to shear rate. This reflects the fact that the dissipated energy is due to the friction of the quasi-solid suspension on the wall of the rheometer, 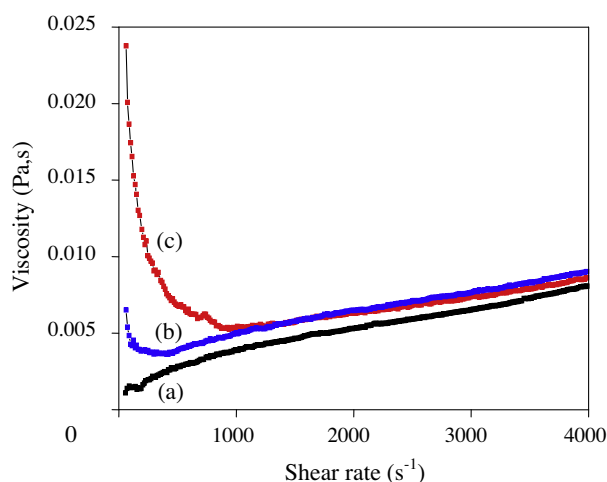due to the difficulty of one gel particle to pass around another one. The higher is the concentration, the harder are the particles and the smaller is the amount of water that can be used for lubricating.

It can be observed that the aqueous copolymer suspension firstly showed an initial remarkable shear-thinning behavior with a large decrease of apparent viscosity at about $60\ s^{-1}$ shear rate. When the particles are fully swollen the shear-thinning characteristic will disappear and then the copolymer suspension will thicken gradually with shear. In this case, the increase in viscosity means that all the space is filled by the particles, which are then changing the fluid into a quasi-solid one.

In the second part dynamic response of the hydrogel suspensions will be reported. Oscillatory rheometry provide information on the gel strength expressed as viscosity or elasticity and the relation of this strength with the gel composition and its stability.

The gel properties were described in terms of two dynamic mechanical properties: the elastic modulus G′ (also known as dynamic rigidity), reflecting the reversibly stored energy of the system, and the viscous modulus G″, reflecting the irreversible energy loss. The effect of the copolymer composition on the elastic and viscous properties of the hydrogels is shown on Fig. 5. Here, G′ and G″ are shown as a function of the shearing time.

When plotted against time, a pronounced plateau is present in the G′ modulus spectrum for true gel structures, while the G″ modulus should be considerably smaller than G′ in the plateau region. This indicates that the elastic response of the material is stronger than the viscous response. The present hydrogel system displays a predominantly solid-like behavior; this type of dynamic response is a characteristic of gel-like materials (Almdal et al., 1993; Rossmurphy and McEvoy, 1986).

As known, the storage modulus can be considered as a measure of the extent of gel network formation; the higher G′ value
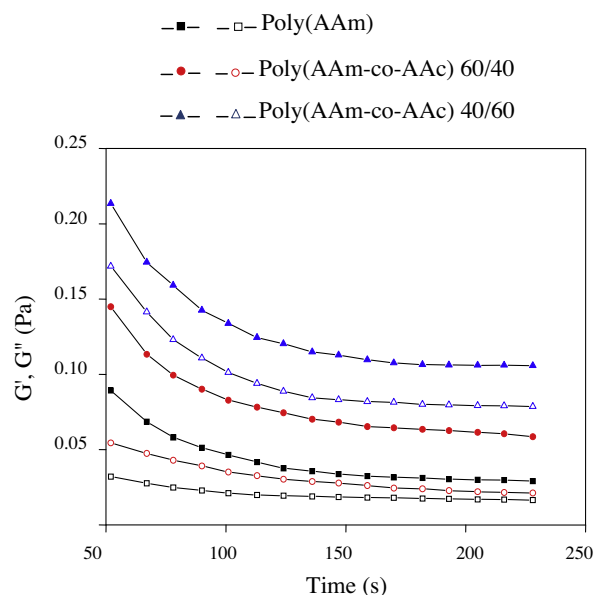

Figure 4 Flow curves of the suspensions of the poly(AAm) (a), poly(AAm-co-AAc) (60/40) (b) and poly(AAm-co-AAc) (40/60) (c) hydrogel particles.

Figure 5 Time dependence of the elastic modulus G′ (filled symbols) and the viscous modulus G″ (open symbols) of the hydrogel particle suspensions.

of the gel means the stronger gel intensity. Poly(acrylic acid), was chosen as a thickener to study the rheological behavior of copolymer hydrogels, PAAc polymers as an anionic hydrogel are widely used to improve the rheological properties of thickening systems. Those cover a wide range of applications from cosmetics to pharmaceutical uses for emulsification, stabilization and rheological control.

The elastic modulus (G') of a gel system correlates with the rigidity (stiffness) of the network where G' is independent of the shearing time. Thus, we expect that more rigid structures were formed with increasing PAAc concentrations as shown in Figs. 4 and 5. G' was always larger than G'', i.e., elastic component is dominant over viscous component. The copolymer gels exhibited a time-independent elastic modulus G' that is about one order of magnitude higher than the G'' over the entire shearing time. This behavior is beneficial to the improved toughness of hydrogels based on the energy dissipation mechanism (Abdurrahmanoglu et al., 2009).

3.4. Swelling behavior of copolymer samples

The swelling kinetics of polymer hydrogels can be classified as diffusion-controlled (Fickian) and relaxation-controlled (non-Fickian) swelling. The phenomenon of water sorption by hydrogel depends mechanistically on the diffusion of water molecules into the gel matrix and subsequent relaxation of macromolecular chains of the hydrogel. When water diffusion into polymer occurs much faster than the relaxation of the polymer chains, the swelling kinetics is diffusion-controlled (Peppas and Colombo, 1997). The swelling behavior of our co-polymeric hydrogels also depends upon the composition of the gels, particularly when at least one constituent monomer contains ionizable groups. In this case, the increase in ionic monomer within the polymer matrix causes an enhancement in its swelling capacity due to increased chain relaxation as well as osmotic swelling pressure. In the present study, as the monomer acrylic acid is ionic, variation in its concentration in the hydrogel may influence the swelling capacity or water

uptake of hydrogel. Almost, the swelling of hydrogel samples was assessed by the measurement of liquid amount absorbed by the material as a function of time until saturation. As an example, the behavior of the hydrogel samples is shown in Fig. 6 for swelling in water and Fig. 7 for swelling in saline solution.

In aqueous solutions, acrylic polymers are capable of forming hydrogen bonds and rigid frameworks, which explains why these suspensions usually occur in a gel-like state.

The interaction of acrylic polymers with water involves several stages. First, water intensively diffuses into the polymer bulk and produces active hydration of the macromolecules, which is followed by their relaxation and the formation of a polymer solution. In the final stage, the solution exhibits structurization (Lee, 1985).

The plotted curves show a weak tendency to swelling for the PAAm sample, which shows a low absorption rate with a rather fast saturation. On the other hand, the relatively slower saturation of PAAm–PAAc samples occurs on a distinctly higher level of swelling.

The observed increase in the equilibrium water uptake with initial increase in the PAAc content may be attributed to the fact as the concentration of acrylic acid increases, the number of $-COO^-$ groups along the macromolecular chains also increases along with increase in number of free H^+ ions (counter ions) within the gel phase. This causes an enhancement in the chain relaxation owing to the repulsion among similarly charged $-COO^-$ groups. Moreover, higher concentration of free or mobile counter ions in the gel phase also increases the osmotic swelling pressure. These two factors ultimately result in higher water uptake of gels.

Hydrogels do not swell appreciably in the presence of electrolyte salts due to ex-osmosis and even the swollen hydrogels shrink dramatically in the presence of salts. Hydrogels shriveling results from the loss of hydrophilic–hydrophobic balance of the networks in the presence of electrolyte salts. Thus, the pre-swollen gels shrink quickly and regain their original shape and weight
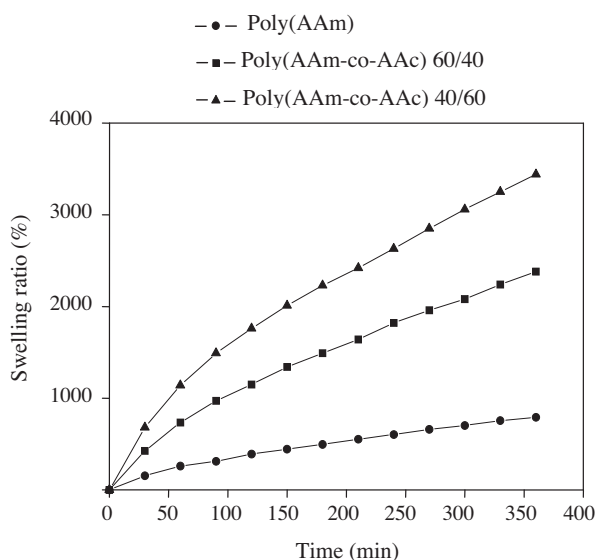

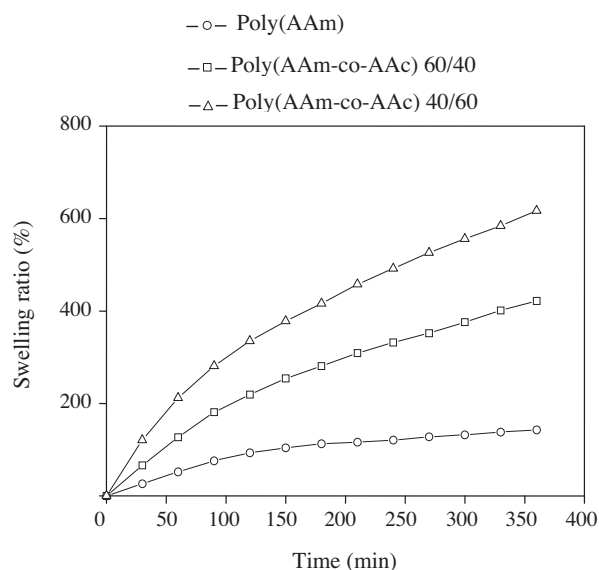**Figure 6** Swelling behavior of the poly(AAm)-co-poly(AAc) hydrogels in deionized water.

Figure 7 Swelling behavior of the poly(AAm)-co-poly(AAc) hydrogels in saline solution.

by de-swelling when they are subjected to electrolyte salt solutions (Kim et al., 2004).

For all samples, the absorption level of deionized water was about 5 times greater than those of saline solution. This phenomenon results from the counter ion effect of Na$^+$ around the polymer, which induces a collapse of its internal network. The concentration of counter ions (i.e., Na$^+$ ions in the present study) becomes so high that they condense around the fixed –COO$^-$ charges thus causing a decrease in repulsive forces among –COO$^-$ groups along polymeric segments and hence the swelling will begin to decrease.

A unique feature of acrylic polymers is the dependence of their properties on the pH of the medium. Environmental pH value has a large effect on the swelling behavior of the acrylic hydrogels. It is observed that percent swelling changes smartly with change of pH of the swelling medium (Tanaka, 1979).

The influence of pH values of the buffer solution on the equilibrium swelling behavior of hydrogels at 37 °C is shown in Fig. 8.

From the plot, it was obviously observed a gradual increase in swelling ratios from pH 2.2–7.0, and then a sharp transition is observed from pH 7.0–10.0 with a slight decrease in water uptake. Because the pK_a of carboxylic acid containing in the copolymer is about 4.5, and carboxyl groups of hydrogels tend to dissociate at a pH > 4, the osmotic pressure inside the hydrogels increases resulting in a higher swelling. In the range of pH 7.0–10.0, the system has a basic pH and the concentration of basic cations in the outer solution also increases. As a consequence, the mobile ion concentration increases more rapidly than in the outer solution. Thus, a sharp transition was observed in this pH range. The decrease in swelling above pH 7.0 can be explained in that the –COOH groups may dissociate and further increase in the amount of mobile ions leads to a decrease in osmotic pressure.
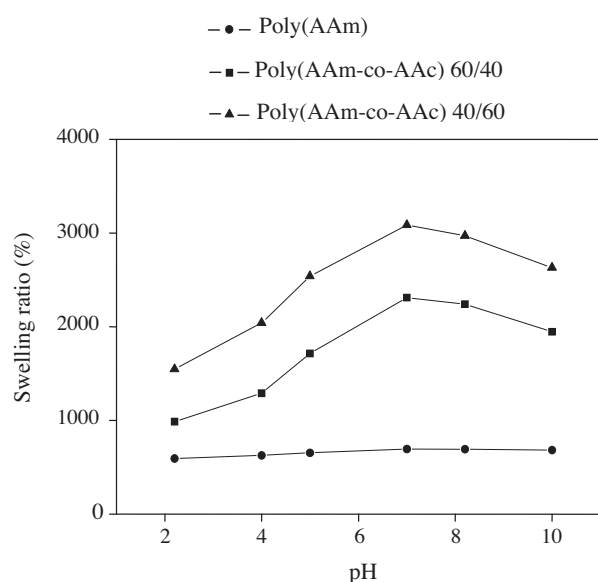
4. Conclusion

Poly(AAm-co-AAc) hydrogels were prepared through free radical polymerization using APS as initiator, TEMED as activator and BIS as crosslinking agent. The copolymer hydrogels were well characterized through FTIR, DSC, rheology and swelling measurements.

The results indicated that the strong electrostatic interaction existed in the hydrogels, which resulted in the formation of a more stable co-polymer. In the DSC analyses, the single T_g in the samples suggested that the two polymers in the hydrogel have good miscibility. Their miscibility, assessed by DSC measurements, indicates that the blends as prepared are miscible in all compositions; this behavior was attributed to the ability of these polymers to form H-bonding as has been observed for other polymers with the same characteristics.

The aqueous poly(AAm-co-AAc) polymer gel systems were investigated by static and dynamic rheometry. In static rheometry the flow behavior of the swollen-in-water suspension particles follows a Herschel–Bulkley model and firstly shows an initial shear-thinning with a large decrease of apparent viscosity. When the particles are fully swollen the shear-thinning characteristic will disappear and then the co-polymer suspension will thicken gradually with shear. Viscoelastic properties have been investigated using oscillatory deformation tests. It was observed that all the measured viscoelastic properties, including G' and G'', are not influenced by the oscillation time sweeps. The poly(AAm-co-AAc) hydrogels with increased concentration of AAc exhibited an enhancement in elastic modulus G' compared to the pure PAAm hydrogel, indicating that adding AAc not only reinforced but also toughened PAAm hydrogels.

Equilibrium swelling measurements were carried out in deionized water, 0.9% NaCl saline solution and in various buffers. The hydrogels display interesting swelling results indicating that it was highly sensitive to the pH environment. It is concluded that the swelling of polymeric networks is affected by composition of the polymer i.e. AAc concentration, and nature of swelling media such as pH: swelling rate increased with increased pH and AAc content in hydrogel. Swelling of the hydrogels abruptly changes by changing the swelling media from distilled water to the solution of high pH indicating the intelligent nature of the polymers.

Figure 8 Influence of pH on the water uptake of the poly(AAm)-co-poly(AAc) hydrogels.

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