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Water uptake in chemically crosslinked poly(acrylamide-*co*-crotonic acid) hydrogels

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Abstract

The aim of this study was to investigate that swelling capability of acrylamide (AAm) hydrogels by adding hydrophilic co-monomer such as crotonic acid (CA). Superswelling poly(acrylamide/crotonic) acid, poly(AAm-*co*-CA) hydrogels were prepared by free radical polymerization in aqueous solution of AAm with CA. For each copolymerization, four different composition of CA and a concentration of multifunctional crosslinkers such as ethylene glycol dimethacrylate (EGDMA) and *N,N′*-methylenebisacrylamide (NMBA) were used. Equilibrium swelling, some swelling kinetics parameters such as the initial swelling rate, swelling rate constant, theoretical equilibrium swelling and diffusional parameters such as swelling exponent, swelling constant and diffusion coefficients of hydrogels have been determined by swelling studies. At the end of dynamic swelling tests, relative content of CA on the swelling properties were examined. It has seen that, if CA contents were increased, equilibrium swelling of the hydrogels were higher than. Poly (AAm-*co*-CA) hydrogels were swollen in the range 1843–2577% in water, while poly(AAm) hydrogels swelled as 1729–1798%. Equilibrium water content of poly(AAm-*co*-CA) hydrogels were calculated in the range 0.9473–0.9626. Swelling exponents of poly (AAm-*co*-CA) hydrogels has calculated as 0.58–0.69. Water intake of hydrogels followed a *non-Fickian* type diffusion.

Keywords: Types of material; Material science; Characterisation and testing of materials

1. Introduction

Hydrogels are one of the most promising types of polymers being used for new material development and are polymeric materials that do not dissolve in water at a physiological temperature and pH but swell considerably in an aqueous medium. Hydrogels are stimuli responsive materials whose dynamic characteristic is reasonably well understood. Hydrogel transitions (volume changes) occur in response to changing environmental conditions such as temperature, pH, solvent composition and electrical stimuli. These materials have been attracting much attention in medical and mechanical engineering fields. Also, hydrogels have been used in the medical device industry as contact lenses, artificial corneas, dressing as coating for sutures, catheters and electrode sensors. Such a wide range of uses requires easy manipulation of physical properties – attainable by chancing monomers and/or polymerization conditions. Since biocompatibility apparently depends on water content, charaterisation of the amount of imbided water in the swollen gel is essential [1–3].

The increasing importance of hydrogels in areas like for example, the pharmaceutical and food chemistry, medicine and biotechnology, has stimulated theoretical and experimental work on the several properties of hydrogels in aqueous solutions. A lot of work was dedicated to various aspects such as, e.g., the swelling, and

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shrinking of nonionic and ionic gels in aqueous solutions [4–6].

Chemically crosslinked gels can be obtained by radical polymerization of low molar mass monomers in the presence of crosslinking agents. Poly(2-hydroxyethyl methacrylate) (**p**HEMA) and poly acrylamide (**p**AAm) are well known and frequently studied hydrogel system. Using radical polymerization, a great variety of other hydrogel systems has been synthesized. The hydrogel characteristics, among which the swelling, can be modulated by the amount of crosslinker. Moreover stimuli sensitive materials such as pH-sensitive gels and temperature-sensitive gels can be obtained by the addition of special monomers [7,8].

Water-soluble polymers owe to their solubility properties to the presence of functional groups (mainly OH, COOH, NH_2) which can be used for the formation of hydrogels. Covalent linkages between polymer chains can be established by the reaction of functional groups with complementary reactivity, such as an amine, -carboxylic acid or an isocynate-OH/NH_2 reaction [9].

In recent years, considerable research has been done on the characterisation and swelling behaviour of hydrogels prepared by simultaneous free radical copolymerization and crosslinking in the presence of an initiator and a crosslinking agent [10–13]. AAm and their derivatives are known to form three-dimensional network structure when polymerised in aqueous solution by irradiation and other polymerization and crosslinking methods [10–13]. Particularly hydrogels based on polyacrylamide have been investigated by many research groups [14–20]. Many studies about gelation of AAm based hydrogels by free radical polymerization have been reported [14–20].

The aim of this study is to investigate the swelling properties of poly(AAm) hydrogels with addition of an anionic monomer such as CA and some multifunctional crosslinkers such as EGDMA and NMBA. Swelling behaviour of superabsorbent polymers may be characterized by water adsorption. In this study, equilibrium swelling, some swelling kinetics parameters such as the initial swelling rate, swelling rate constant, theoretical equilibrium swelling and diffusional parameters such as swelling exponent and swelling constants of hydrogels can be determined by dynamic swelling studies. These swelling properties will be effected that usability of its as biomaterial in biological, medical, pharmaceutical applications and as an adsorbent in environmental applications.

2. Experimental

Acrylamide(AAm) supplied by from Merck (Darmstad, Germany) and the anionic comonomer, crotonic acid (CA) supplied by from Aldrich Chemical Co. (Milwaukee, US), The initiator, ammonium persulfate (APS) and the activator *N,N,N′,N′*-tetramethylethylenediamine (TEMED) supplied from Merck(Darmstad, Germany) and were used as the redox initiator pair. The multifunctional crosslinkers, ethylene glycol dimethacrylate (EGDMA) and *N,N′*-methylenebisacrylamide (NMBA) were purchased from Merck (Darmstad, Germany). AII chemicals were used as received. Doubly distilled water were used in the copolymerizations and swelling studies. Chemical structure of used monomers, initiator, activator and crosslinkers tabulated in Table 1.

For preparation of poly(AAm-*co*-CA) hydrogel systems, first, 1 g of AAm was dissolved in 1 mL distilled water and then 00, 20, 40 and 60 mg CA were added to the aqueous, solutions of AAm. For investigation of the effect of crosslinkers on preparation of poly-(AAm-*co*-CA) hydrogel systems, 0.25 mL of 1% concentration of EGDMA, or 0.25 mL of 1% concentration of NMBA was added to the aqueous solutions of poly-(AAm) or poly(AAm-*co*-CA) hydrogel. Then 0.2 mL of APS (5 g/100 mL water) was added this solution as initiator, and finally, 0.25 mL of TEMED (1 mL/100 mL water) was added onto solution.

These solutions mentioned above were placed in poly(vinyl chloride) straws (as the polimerization reactors) of 3 mm diameter. The polymerization was conducted at room temperature (25°C) for 24 h. Fresh hydrogels obtained in long cylindrical shapes were cut into pieces of 3–4 mm length. These were dried in air and then under vacuum, and stored for swelling studies.

The swelling behaviours of dried poly(AAm-*co*-CA) hydrogels were carried out by immersion in doubly distilled water at 25 ± 0.1 °C in a water bath. The water absorbed was determined by weighing the samples, after

Table 1
Used monomers and crosslinkers in the preparation of hydrogel systems

	Formula	Abbreviations
Acrylamide (Propen amid)	$H_2C{=}CHCONH_2$	AAm
Crotonic acid	$CH_3CH{=}CHCOOH$	CA
Ammonium persulfate	$(NH_4)_2S_2O_8$	APS
N,N,N′, N′-Tetramethylethylenediamine	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	TEMED
Ethylene glycol dimethacrylate	$[H_2C{=}CCH_3COOCH_{\ 2}]_2$	EGDMA
N,N′-Methylenebisacrylamide	$(H_2C{=}CHCONH)_2CH_2$	NMBA

wiping, at various time intervals. Swollen gels weighed by an electronic balance (SARTORIUS, BP 210S, $d = 0.1$ mg).

3. Results and discussion

3.1. Preparation of crosslinked copolymers

In this study, poly(AAm-*co*-CA) hydrogels were prepared by free radical polymerization in aqueous solutions of AAm, CA and crosslinkers such as EGDMA and NMBA. In the polymerization, first step is a reaction between APS and TEMED in which the TEMED molecule is left with an unpaired valance electron. The activated TEMED molecule can combine with an AAm and anionic comonomer such as CA and crosslinker molecules, in the process the unpaired electron is transferred to the monomeric units, so that they in turn become reactive. Another monomer or comonomers can therefore be attached and activated in the same way. The polymer, poly(AAm) or copolymer poly(AAm-*co*-CA) hydrogel can continue growing indefinitely, with the active center being continually shifted to the free end of the chain. Crosslinker molecules can be incorporated into chains simultaneously and forms a permanent link between them [10]. Polymerization and crosslinking process has been taken an hour in poly(AAm-*co*-CA) gelation. But, for all hydrogels, it has been waited for 24 h for good gelation.

3.2. Swelling measurements

The percentage swelling (%S) is the most important parameter about swelling studies. %S was calculated from the following equation:

$$\%S = \frac{M_t - M_0}{M_0} \times 100, \quad (1)$$

where M_t is the mass of the swollen gel at time t, and M_0 is the mass of the dry gel at time 0.

The water intake of initially dry hydrogels was followed for a long time. Swelling isotherms of poly(AAm-*co*-CA) hydrogel crosslinked by EGDMA are plotted and shown in Fig. 1. It can be seen that %S increases with time until a certain point, when it becomes constant (Fig. 1). This value of %S may be named "equilibrium" swelling (%S_{eq}). The values of %S_{eq} of hydrogels are used for the calculation of some characterisation parameters (Table 2). The values of %S_{eq} of AAm are 1729% and 1798%, but the values of %S_{eq} of poly (AAm-*co*-CA) hydrogel vary between 1843% and 2577%. It is well known that the swelling of hydrogel is induced by the electrostatic repulsion of the ionic charges of its network. The ionic charge content is important. CA contains many hydrophilic units (–COOH) and the swelling increase is due to an increase of the hydrophilic units. The hydrophilic group numbers of poly(AAm-*co*-CA) copolymers are more than these of poly(AAm), so, the swelling of poly(AAm-*co*-CA) hydrogel is more than that of poly(AAm) hydrogels [12,13,20].

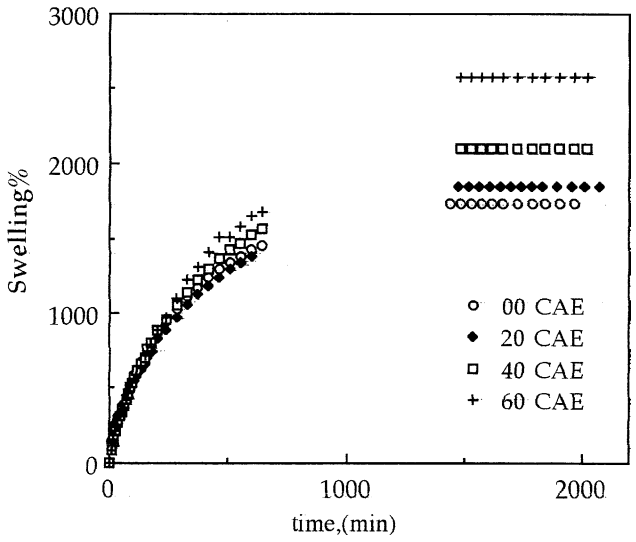

Fig. 1. Swelling isotherms of poly(AAm-*co*-CA) hydrogels crosslinked by EGDMA.

Table 2
Equilibrium swelling values of poly(AAm-*co*-CA) hydrogels

	CA (mg)			
	00	20	40	60
Equilibrium swelling (%S_{eq})				
EGDMA	1729	1843	2100	2577
NMBA	1798	1946	2048	2246

The effect of crosslinkers are important to preparing of AAm-based hydrogels [12]. %S_{eq} of poly (AAm-*co*-CA) hydrogels are similar to each other. The reason of this behaviour may be molecular structure of crosslinkers. That is why EGDMA and NMBA are tetrafunctional crosslinkers. Swelling degree of poly(AAm-*co*-CA) hydrogel are parallel to each others. But, with the increasing of concentration of CA, %S of the hydrogels may be increased.

3.3. Equilibrium water content

The water absorbed by poly(AAm-*co*-CA) hydrogels is quantitatively represented by the equilibrium water content (EWC) [21], where

$$\text{Equilibrium water content} = \frac{M_S - M_0}{M_S}. \quad (2)$$

Here, M_S is the mass of the swollen gel at time t (equilibrium), and M_0 is the mass of the dry gel at time 0. EWCs of all hydrogels were calculated and the values

Table 3
Equilibrium water contents of poly(AAm-*co*-CA) hydrogels

	CA (mg)			
	00	20	40	60
Equilibrium water contents (EWC)				
EGDMA	0.9543	0.9485	0.9545	0.9626
NMBA	0.9473	0.9511	0.9534	0.9573

of EWC are tabulated in Table 3. AII EWC values of the hydrogels (0.9473–0.9626) were greater than the percent water content values of the body about 0.60 (or 60%). Thus, the hydrogels were exhibit similarity of the fluid contents with those of living tissues. It can be said that poly (AAm-*co*-CA) hydrogel crosslinked EGDMA and NMBA used as a new material as a biomaterial in medicine, pharmacy or veterinary.

3.4. Swelling kinetics studies

For swelling of polymers, following second-order kinetics relation can be used [12]:

$$\frac{t}{S} = A + Bt, \tag{3}$$

where $B = 1/S_{eq}$ is the inverse of the maximum or equilibrium swelling, $A = 1/k_S\ S_{eq}{}^2$ is the reciprocal of the initial swelling rate $[(dS/dt)_0]$ of the hydrogel, and k_S is swelling rate constant.

Fig. 2 shows the linear regression of the swelling curves obtained by means of Eq. (3) for the poly(AAm) and poly(AAm-*co*-CA) hydrogels crosslinked by NMBA. The initial swelling rate, the swelling rate constant and the values of theoretical equilibrium swelling of the all hydrogels are calculated from the slope and the intersection of the lines, respectively (Table 4). The

Table 4
Swelling kinetic parameters of poly (AAm-*co*-CA) hydrogels

	CA (mg)			
	00	20	40	60
The initial swelling rate, $r(dS/dt)_0$; g_{water}/g_{gel} min				
EGDMA	8.74	7.58	7.48	7.65
NMBA	8.77	8.32	9.92	5.98
The swelling rate constant, $k_s \times 10^{6}$; g_{gel}/g_{water} min				
EGDMA	2.29	1.68	1.21	0.75
NMBA	2.10	1.66	1.84	0.75
The theoretical equilibrium swelling, S_{max}; g_{water}/g_{gel}				
EGDMA	1950	2123	2479	3180
NMBA	2041	2233	2321	2811

values of theoretical equilibrium, swelling of the hydrogels are parallel to the results of swelling of the gels (Tables 2 and 4).

3.5. Diffusion of water

The following equation was used to determine the nature of diffusion of water into hydrogels [22,23]:

$$F = \frac{M_t}{M_S} = kt^n, \tag{4}$$

where F denotes the amount of solvent fraction at time t, k is a constant related to the structure of the network and the exponential n is a number indicative of the type of diffusion. This equation is applied to the 60% of swelling curves, the nature of diffusion of water into hydrogels can be evaluated. Plots of $\ln F$ versus $\ln t$ are shown in Fig. 3. The exponents are calculated from the slope of the lines and, are presented in Table 5.

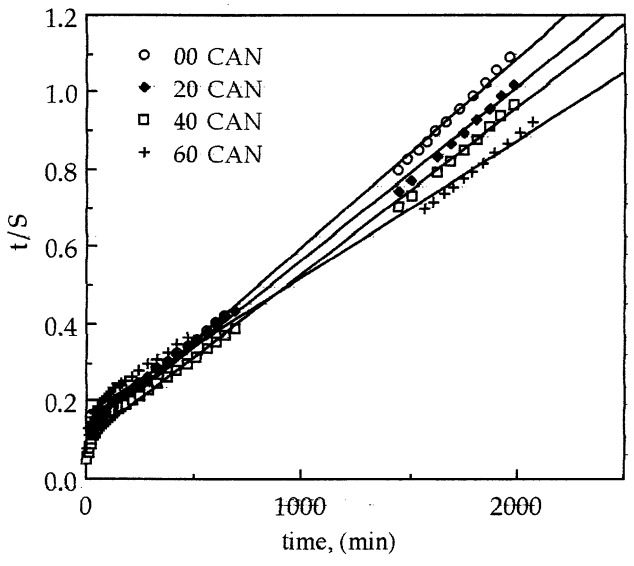

Fig. 2. Swelling rate curves of poly(AAm-*co*-CA) hydrogels crosslinked by NMBA.

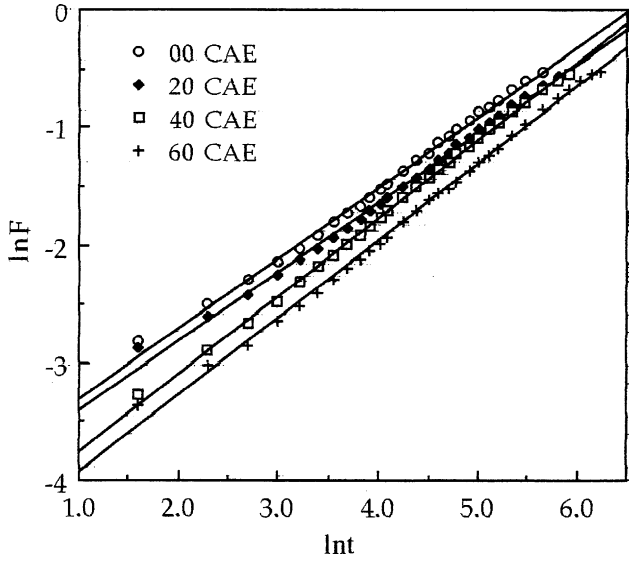

Fig. 3. Swelling kinetics curves of poly (AAm-*co*-CA) hydrogels crosslinked by EGDMA.

Table 5
The values of n and k of poly(AAm-*co*-CA) hydrogels

	CA (mg)			
	00	20	40	60
Swelling exponent, n				
EGDMA	0.59	0.58	0.66	0.65
NMBA	0.65	0.65	0.64	0.69
Swelling constant, $k \times 10^2$				
EGDMA	2.02	1.87	1.21	1.03
NMBA	1.53	1.41	1.58	0.83

In Table 5, it is shown that the values of swelling exponent range between 0.58 and 0.69. For the hydrogels studied here the n values indicating the type of diffusion is found to be over 0.5. Hence the diffusion of water into the hydrogels was taken to be a *non-Fickian* characteristic [22,23]. This is generally explained as a consequence of slow relaxation rate of the polymer matrix.

The study of diffusion phenomena in hydrogels and water is of value in that it clarifies polymer behaviour. The complete swelling-time curves for hydrogels in water are used to calculated diffusion coefficient. Diffusion coefficients of hydrogels can be calculated by various methods. One of these methods is 'the short time approximation method' [23]. The short time approximation is valid only for the first 60% of the swelling. The diffusion coefficients of the cylindrical poly(AAm) and poly(AAm-*co*-CA) hydrogels are calculated from the following relations:

$$F = 4\left[\frac{Dt}{\pi r^2}\right]^{1/2} - \pi\left[\frac{Dt}{\pi r^2}\right] - \frac{\pi}{3}\left[\frac{Dt}{\pi r^2}\right]^{3/2} + \cdots, \quad (5)$$

Where D in $cm^2\ s^{-1}$, t in seconds and r is the radius of cylindrical polymer sample (cm). A graphical compactions of related equations shows the semi-empirical Eq. (5) with $n = 0.5$ and $k = 4(D/\pi r^2)^{1/2}$. For the hydrogels, F versus $t^{1/2}$ plots were plotted and some representative results are shown in Fig. 4. The diffusion coefficients were calculated from the slope of the lines. The values of diffusion coefficient determined for the hydrogels are listed in Table 6. It is shown that the values of D of the hydrogels varied from 62.24×10^{-6} to 104.45×10^{-6} $cm^2\ s^{-1}$. The diffusion of the water to poly(AAm-*co*-GA) hydrogels content 40 mg CA is faster than others.

Table 6
The values of D of poly (AAm-*co*-CA) hydrogels

	CA (mg)			
	00	20	40	60
Diffusion coefficients, $D \times 10^6$ $cm^2\ s^{-1}$				
EGDMA	82.18	63.99	62.24	84.38
NMBA	73.70	87.13	104.45	63.81

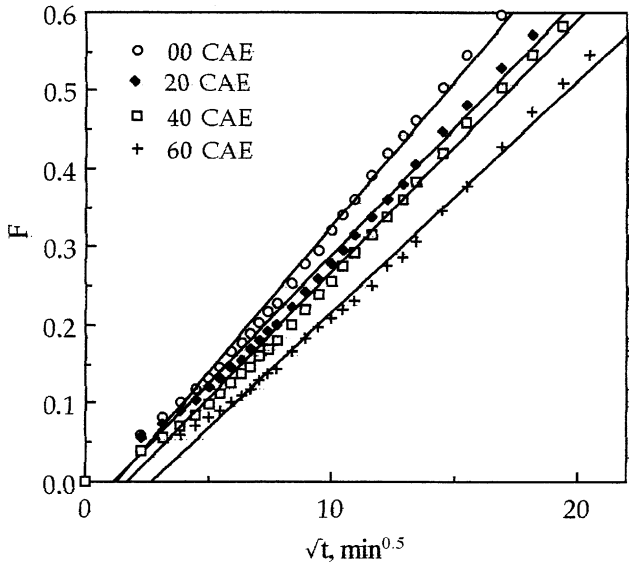

Fig. 4. Diffusion curves of poly (AAm-*co*-CA) hydrogels crosslinked by EGDMA.

4. Conclusion

In this study, poly(AAm-*co*-GA) hydrogels were prepared by free radical polymerization. Some multifunctional crosslinker such as EGDMA and NMBA used at polimerizatien. Hydrogels were prepared in water, and swollen to equilibrium in water. Hydrogel systems swelled in the range 1729–2577%. EWCs were calculated to the range 0.9473–0.9626. This result showed that poly (AAm-*co*-CA) hydrogels would be used as a biomaterial on some biomedical applications, because equilibrium water contents was bigger than the percent water content value of the body about 0.60. The diffusion type of hydrogels was a *non-fickian* diffusion character. Swelling exponents of poly (AAm-*co*-CA) hydrogels are changed between 0.58 and 0.69. It was seen that swelling of poly(AAm-*co*-CA) hydrogels increased with the increasing of content of CA. As a result, poly (AAm-*co*-CA) hydrogels can be used as a super water retainer for carrying of some substances in aquatic fields in pharmaceutical, agricultural, environmental and biomedical applications, or in the applications of immobilised biologically active molecules.

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