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Characterization and Swelling Properties of Copolymer Poly(N, N-dimethyl acrylamide -co-acrylic acid) and Homopolymer Poly(acrylic acid)

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Abstract

This paper investigates the swelling properties of homopolymer and copolymer hydrogels. Copolymeric hydrogels based on N, N-dimethyl acrylamide and acrylic acid (poly(DMA-co-AAc) as well as homopolymer hydrogels based on acrylic acid (polyAAc) were synthesized by radical technique in aqueous solutions using ammonium persulfate as an initiator and N, N-methylene-bis-acrylamide as a crosslinking agent. The properties of hydrogels examined including scanning electron microscopy (SEM) and FT-IR. The results indicate that the poly(DMA-co-AAc) copolymer has a high swelling ability in an aqueous solution. The swelling of hydrogels were achieved a maximum degree and diameter of 270 and 63mm in water, respectively. The swelling behavior of these hydrogels was investigated to determine function of the effect of pH and polymeric compositions.

Keywords: N, N-dimethyl acrylamide; acrylic acid; poly(DMA-co-AAc); polyAAc; Swelling properties;

Introduction

Due to the unique physical-chemical properties, the valuable polymeric materials, hydrogels, are widely used in various industries, such as biotechnology, medicine, etc. While do hydrogels have been widely used in agriculture, such as water retention granules, but they are applied to medical appliances in contact lenses, joint and dental implants, drug delivery, and wound healing as well. All these applications are attributed to their characteristics of retaining large amount of solution and the ability of releasing the solution as it is needed. Copolymers based on DMA monomers are synthesized by various methods and have been used for various biomedical applications, including drug delivery, contact lenses, etc. [1-7]. Addition, swelling properties of the hydrogel are affected by different structural factors, including crosslink density, charge, the concentration of the ionizable group, hydrophilicity, and degree of ionization [8].

Copolymers based on acrylic acid and corresponding acrylates are widely used as unusual polymers because of their strong water absorption capability. Studies have reported modified polymers between acrylic acid or poly acrylic acid with different monomers, such as acrylamide, hydroxypropyl cellulose, Pectin, 2- acrylamide- 2- propane sulfonic acid [9-13]

Swelling properties of the N(-1,1-dimethyl-3-isobutyl) acrylamide (DOBA) and the copolymer of DOBA and Methyl methacrylate (MMA) were measured in distilled water. Maximum water uptake of about 70% was observed for poly(DOBA), while water uptake for copolymer decreased with the increase of MMA content in the polymer chain [14]. However, the swelling of poly(N, N-dimethyl

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acrylamide-co-maleic acid) increased as the content of maleic acid went up in the polymeric matrix and with the increase of pH and the maximum extent was reached at pH 8.7 in all compositions [15]. Significant absorption of water is possible in low crosslink density and vice versa materials. The swelling kinetics of copolymer poly(acrylamide-co-2-acrylamide-2-methyl-propane sulfonic acid) crosslinked with N, N'-methylene bis(acrylamide) to improve the swelling capacity are described in the literature [16]. The copolymers synthesized with N, N'-methylene bis(acrylamide) at a higher pH of the reaction medium present a more considerable swelling degree. The crosslinking density itself can produce this behavior. Murali et al., 2005 investigated the effect of reaction parameters, including concentrations of comonomer sodium methacrylate (NMA), crosslinker, initiator and activator, on the swelling behavior of the copolymer based on acrylamide and sodium methacrylate. The swelling ratio of copolymer rising with the increase of temperature, crosslinker concentration and slain solution [17]. Copolymer based on N, N'-dimethyl acrylamide with NIPAAm and NIPAAm with 2HEA showed the best swelling, antibacterial properties and interpolymeric complex [18-22].

This study synthesized poly(DMA-co-AAc) and polyAAc hydrogels by free-radical copolymerization in aqueous solutions. FTIR and SEM characterized homo and copolymers. In addition, the swelling properties of–poly(DMA-co-AAc) and polyAAc hydrogels under various conditions were investigated.

Experimental

Materials

N, N-dimethyl acrylamide (DMA, 99%), ammonium persulfate (98%, APS, CAS 7727-54-0), and N, N-methylene-bis-acrylamide (99%, CAS 110-26-9) were obtained from Sigma-Aldrich (Heidelberg, Germany). Acrylic acid (AAc) stabilized with hydroquinone with a purity of 99.5% extra pure (CAS 79-10-7) was supplied by Across Organics (Geel, Belgium).

Synthesis of homo and copolymer-based AAc

AAc based homopolymer and its cross-linked copolymer with DMA were synthesized with composition ratios (M1: 30/70, M3: 50/50, M5: 70/30), (for homopolymer only AAc monomer), by free radical solution (water) polymerization technique with ammonium persulfate ($2x10^{-2}$M) as the initiator and N, N-methylene-bis-acrylamide (0.1 mol. %) as the cross-linking agent. Monomer mixture accounts for 30% of the total volume, and the rest belonged to the water. The total volume of the reaction mixture was maintained at 10 ml for all the compositions. The resulting mixture was poured into the glass ampoule and saturated with argon for 10 minutes to remove oxygen. Then the copolymerization was performed in hermetically sealed glass ampoules at 60 ℃ for 20 min. The obtained hydrogels were washed several times with distilled water for 10 days. The preparation of hydrogel copolymer has been previously described [4].

Instrumentation and methods

Fourier transforms infrared spectrophotometer (FTIR) IR Nicolet 5700 spectrometer were used to analyze chemical structures of poly(DMA-co-AAc) copolymers and its homopolymer in the 400-4000 cm−1 wavenumber range. The dried and grounded (until suitable sized powder) hydrogel samples mixed with standard KBr powder were compressed into a pellet for the test.

The surface morphology of hydrogel was investigated by scanning electron microscopy (SEM), on JSM-6390LV (JEOL, Japan), with an operating voltage of 20 kV. SEM images were obtained from the fractured surface of dried hydrogels.

Hydrogels were taken out after the reaction cleaned by using distilled water for several days from unreacted monomers. The cleaned hydrogels were cut into small pieces of about 0.5 cm in height and dehydrated. Hydrogel samples were dried in a vacuum oven at 25 ℃ until the weight was constant. The cleaned hydrogels were cut into small pieces of about 0.5 cm in height and dehydrated. Hydrogel samples were dried in a vacuum oven at 25 ℃ until the weight was constant.

The equilibrium degree of swelling of each sample was calculated from the formula:

$$\alpha=(m-m_0)/m_0$$

Where m – is the mass of the swollen hydrogel (g); m_0 – is the gel specimens' weight in dried (g); and α is the - degree of swelling.

Gel (**G**) and sol (**S**) fractions yield were calculated according to the formulas:

$$G = m_0/m_s * 100\%$$

$$S=100-G$$

where S is the sol fraction.

m_0 – the weight of the dry sample, g;

m_s – the weight of the synthesized sample, g.

The following formula calculated the cross-linking index (j):

$$J=1/(S+S^{1/2})$$

The weight of dry polymer samples was measured after drying them in a vacuum oven to constant weight.

Results and discussion

FTIR analysis of copolymer polyAAc and poly(DMA-co-AAc)

Fourier transform infrared spectroscopy (FTIR) was used to identify functional groups in synthesized poly(DMA-co-AAc) copolymers and polyAAc. The obtained copolymers were recorded on FTIR spectroscopy in 500-4000cm$^{-1,}$ as shown in Figure 1. As clearly seen, the intensity of C-H groups (stretching, aliphatic) is found at 2931 cm^{-1} and 2670 cm^{-1}, respectively, carbonyl stretching vibration C=O to the carboxyl group gives absorption peak 1723 cm^{-1} of in Polyacrylic acid spectrum. These groups show signals at 2931 cm^{-1} and 1732 cm^{-1} in the copolymer. Meanwhile, other characteristic peaks are: wideband in the area of 3700–3100 cm$^{-1,}$ which corresponds to the O-H stretching vibration of carboxylic groups in AAc and N-H stretching vibration of the copolymer, amide (3435, 3434 and 1606 cm^{-1}) due to N-H bending with a contribution of C-N stretching vibrations, and C-C and C-N stretching vibrations, and peaks at 1449 cm^{-1} and 1360 cm^{-1} are stretching vibration of C-H bond of methyl groups. These signals expressed the structural formula of the poly(DMA-co-AAc).

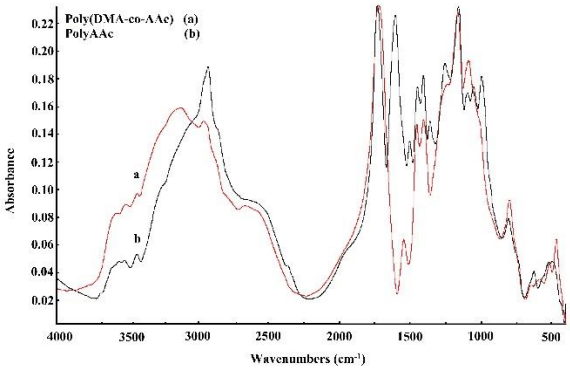


Figure 1: FTIR signals of PolyAAc and poly(DMA-co-AAc) hydrogels

Swelling Characteristics of hydrogels

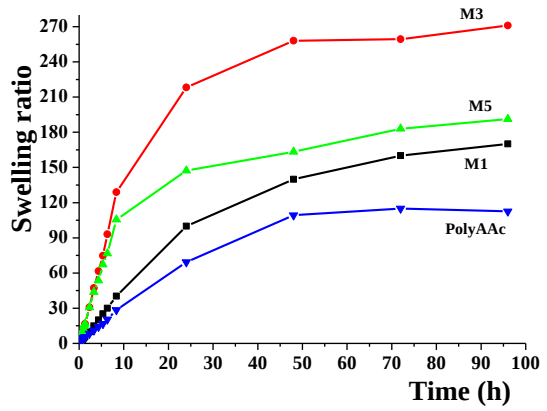
AAc based homo hydrogel and its cross-linked copolymer with DMA were synthesized in a water media. The crucial criteria for the synthesized copolymers were the ability to absorb water and the external characteristics after the complete swelling of the gel (hard or soft). These criteria were mainly influenced by the association between the ratio of the initial monomer mixture and water. If the water content is high (during the synthesis of 90% of the total volume), a soft gel will be obtained, which creates inconvenience for further research. In contrast, with low water content, difficulties arise with the dissolution of solid monomers, initiators, crosslinking agents, etc. Therefore, the hydrogels were obtained during the synthesis with a water content of 90% to 50% in the reaction environment, and 70% was chosen as the optimal amount of water. The main regularities of three-dimensional copolymerization were investigated by sol-gel analysis and gravimetric methods. Table 1 shows the yield of gel-sol fraction, degree of crosslinking and swelling of the homopolymer based AAc and its copolymer with DMA. Herein it can be seen that the yield of the gel-sol fraction and the degree of crosslinking for the copolymer and homopolymer are the same, indicating that the parameters of the copolymer are the same (amount of crosslinking agent added, synthesis time and the synthesis regularities).

The properties of the equilibrium swelling of hydrogels were investigated by measuring the degree of swelling with time. Figure 2 shows swelling degree as a function of time for homo hydrogel polyAAc-and its copolymeric hydrogels with different DMA and AAc monomer ratios. After 2 days, water absorption of the gel slowed down, with the gels further saturated and striving for balance. The swelling ability of poly(DMA-co-AAc) hydrogels is based on the feed of copolymer composition. Thus, this process increased with decreasing the ratio of AAc in the hydrogel. The hydrogel showed the highest degree of swelling while AAc and DMA monomers were in the same proportion in the copolymer.

Although these hydrogels were synthesized under the same conditions, they showed different degrees of swelling, depending on the nature of the monomers. The degree of swelling of polyacrylic acid is lower than ~~the~~ its own copolymer. Comparing models M1 and M5, the degree of swelling decreased due to the increase in the proportion of AAc in the polymer, suggesting. That their swelling properties tend to be homopolymeric (polyAAc). The diameter of the hydrogel poly(DMA-co-AAc) hydrogel) showed the highest degree of swelling, which was 8 mm when in dried condition and further increased to 63 mm while swollen (Figure 3).

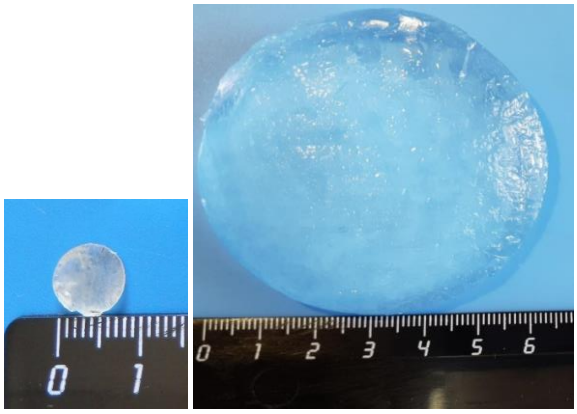
Table 1: Composition, the sol-gel fraction (G and S), degree of swelling (α) and degree of crosslinking (J) for poly(DMA-co-AAc) copolymers and polyAAc

№	Copolymer	G	S	J	α (in water)
M1	30/70	32	68	2.295	165
M3	50/50	34	67	2.311	270
M5	70/30	33	67	2.311	180
polyAAc	100	34	66	2.33	105



poly(DMA-co-AAc) 30/70 (M1); 50/50 (M3); 70/30 (M5); and polyAAc)

Figure 2: Time-dependent swelling of poly (DMA-co-AAc) and polyAAc hydrogels



Dry hydrogels (A); d=8мм

Swollen hydrogel (B); d=63мм

Figure 3: Photograph depicting (A) dry and (B) swollen poly (DMA-co-AAc) hydrogels

The kinetics of swelling of the copolymer in various buffer solutions were investigated. Figure 4 shows the kinetics of swelling of hydrogels in solutions with different pH (4; 6.6 and 9.18). A hydrogel (M5) was used here, which showed the highest swelling of the copolymer hydrogel in water. Herein that hydrogels showed better-swelling properties in acidic media than in base media. Hydrogels containing acidic groups swell well in a weakly alkaline medium and they can shrink in an acidic environment [16]. According to this concept, polyAAc indicated a high degree of swelling in the base medium. poly(DMA-co-AAc) hydrogels have fewer acid groups than homopolymer polyAAc. Consequently, in an acidic environment (pH = 4 and 6.86), the hydrogels changed slightly compared to the initial volume. The basic environment (pH = 9.18) was lower than the homopolymer, although it showed a high degree of swelling.

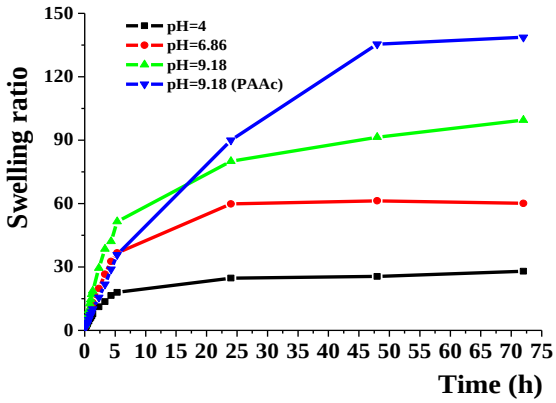


Figure 4: Time-dependent in different pH solution swelling of poly (DMA-co-AAc) and polyAAc hydrogels

In addition, the kinetics of edema in poly(DMA-co-AAc) hydrogel solution at pH 10 was studied (Figure 5). The sample with 50% AAc monomer (M3) in the hydrogel showed the highest degree of swelling. The remaining poly(DMA-co-AAc) absorbs well the solution in hydrogels (M1 and M5). Sample M5 absorbs solution better than sample M1, and ~~This~~ is due to the presence of more acidic groups.

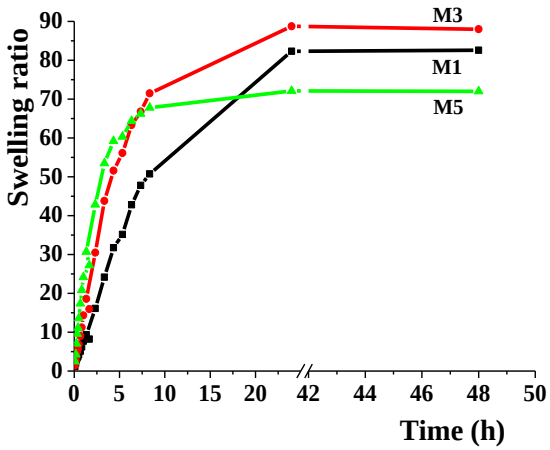


Figure 5: Time-dependent in pH (10) solution swelling poly(DMA-co-AAc) hydrogels

Scanning Electron Microscopy (SEM)

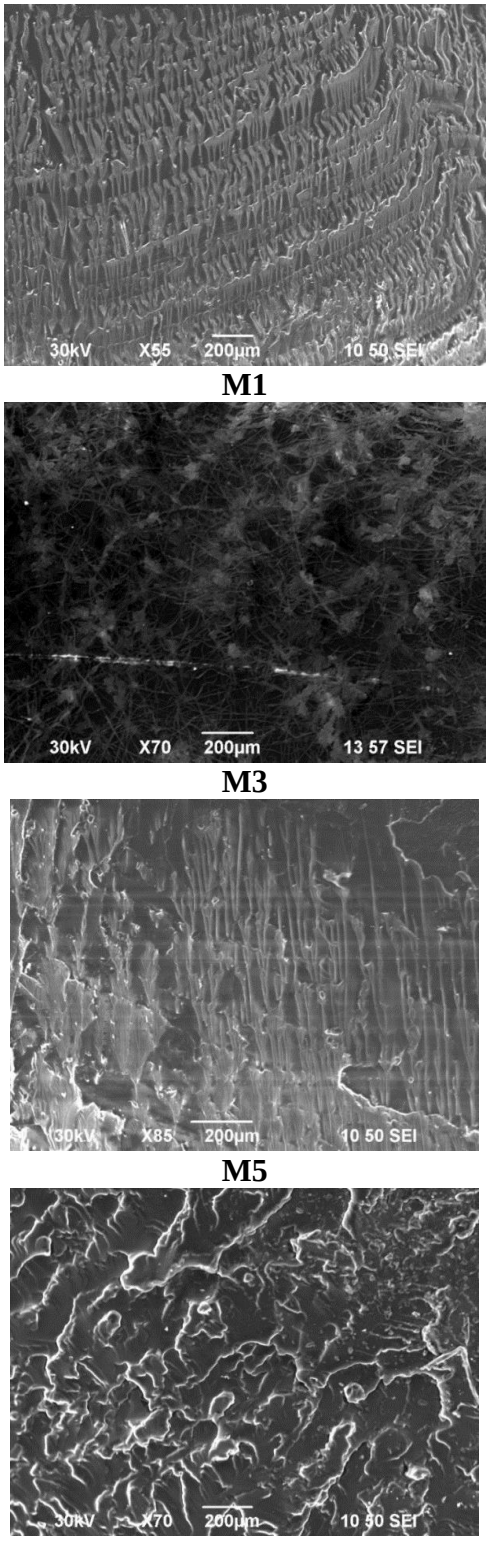


Figure 6: SEM Micrographs of Poly(DMA-co-AAc) and polyAAc hydrogels

The SEM micrographs of polyAAc, poly(DMA-co-AAc) composition ratios (30/70 (M1), 50/50 (M3), and 70/30 (M5) are presented in Figure 6. The complete difference in the surface morphologies between homopolymer and co-polymers hydrogels is shown in Figure 6. All hydrogel formulations revealed uniform porous networks, but the difference in structure and space between porous was observed (17, 18). M1 showed the relatively small space between porous. However, with the decreasing ratio ratio of AA in the copolymer hydrogels, the space between porous increased. polyAAc showed the largest space between porous ~~as~~ compared to copolymer hydrogels, which was attributed to AAc enhancing the crosslinking of the copolymer hydrogel (19, 20). Moreover, the AAc improved the swelling properties of copolymer hydrogel by increasing the water uptake capacity of the hydrogel. SEM showed the mesh- structure for M3, and fibrillary net-like structure was observed for M1, M5 and polyAAc.

Conclusion.

Hydrogels based N, N-dimethyl acrylamide and acrylic acid and homopolymer hydrogels based acrylic acid were synthesized through free radical copolymerization. The synthesis regularities of the hydrogels have been studied. Scanning electron microscopy (SEM) and FT-IR spectroscopy performed the surface characteristics of crosslinked homo and copolymers, and their structure was performed by scanning electron microscopy (SEM) and FT-IR spectroscopy. It was found that the poly(DMA-co-AAc) copolymer in an aqueous solution has a high swelling ability. Their swelling degree and increase diameter in water achieved a maximum of 270 and 63mm. The swelling behaviour of these hydrogels was investigated as a function of the effect of pH and polymeric compositions. The swelling of polymers was significantly affected by the pH and ratio of monomers.

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Conflict of interest.

Authors declare no conflict of interest.

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