Tamara Erceg[1], Ivan Ristić[1], Suzana Cakić[2], Jaroslava Budinski-Simendić[1]*

[1]University of Novi Sad, Faculty of Technology Novi Sad, Novi Sad, Serbia, [2]University of Niš, Faculty of Technology Leskovac, Leskovac, Serbia

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The influence of synthesis parameters on swelling behaviour of pH-sensitive acrylate based hydrogels

ABSTRACT

In this work poly(acrylamide-co-acrylic acid) based hydrogels were prepared using the two types of initiators – potassium persulfate (KPS) and ammonium persulfate (APS) and accelerator N,N,N',N'-tetramethylethylenediamine (TEMED). N,N'-methylenebis(acrylamide) (MBAM) was used as crosslinking agent (1 and 3% per total weight of monomers). For the synthesis of hydrogels, acrylic acid (Aac) and acrylamide (Aam) were used in the following mass ratios: 30:70, 50:50, 70:30 and 0:100% Aac/Aam. The swelling behaviour of cross-linked copolymers was characterized in acidic (pH=4.5) and alkaline (pH=10) medium at constant temperature of 37 °C. Lower amount of crosslinking agent has given the hydrogels with greater water absorption capacity. The forming of polymer network has been confirmed by FT-IR method. Thermal properties of obtained hydrogels were analyzed by differential scanning calorimetry (DSC). Obtained results have showed the strong correlation between hydrogels composition and their swelling and thermal properties.

Keywords: *hydrogel, swelling ratio, acrylic acid, acrylamide, monomer ratio.*

1. INTRODUCTION

Conditions of modern life impose the need for application of smart materials, those respond to external stimuli such as temperature, pH, light, stress, electrical and magnetic field. As a result of changes in the external environment, smart materials change some of their properties such as color, viscosity, volume. Stimuli-responsive hydrogels are type of smart materials [1,2]. Hydrogels are network of hydrophilic polymer chains that swell, but do not dissolve in water [3].

Based on the sensitivity to external stimuli, hydrogels are divided into two categories – conventional hydrogels and smart hydrogels. Conventional hydrogels usually do not have any electrical charge located on their cross-linked chains, so they do not show significant sensitivity to environmental changes [2,4]. Smart hydrogels exhibit volume and structural changes as response to specific external stimuli, such as the temperature, pH, electric field, magnetic field, presence of salt, due to the presence of pendant charged functional groups in their structure [5]. Swelling is the most important property of hydrogels. Hydrogel ability to swell depends on polymer nature, polymer-solvent interaction, crosslinking and charge density of polymer network as well as on environmental conditions [6]. Polyelectrolyte hydrogels are charged polymer networks those exhibit pH-depending swelling behavior due to the pendant cationic and anionic groups those ionize at appropriate range of pH values [2]. In hydrogels containing acidic groups ionization occurs in pH domain above the pK_a of ionisable anionic group [6]. Increasing of pH value leads to an increase of ionization degree. Consequently, increased electrostatic repulsion between charged polymer chains results in greater swelling ratio [7]. Cationic groups, such as amines, ionize at pH below their pK_b value, inducing the swelling of polymer network [8].

M.A. Mutar with his associates has investigated the effect of acrylic acid amount on poly(acrylamide -co-acrylic acid) or poly(Aam-co-Aac) hydrogels swelling properties in distilled water at room temperature. They synthesized the series of hydrogel samples by varying the weight of acrylic acid (from 10 to 50% per acryliamide weight), while the type

*Corresponding author: Tamara Erceg
E-mail: tamara.erceg@uns.ac.rs
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and amount of other reaction mixture components were not varied. By monitoring the swelling ratio with time, they have established that swelling rate increases as the amount of acrylic acid in hydrogel increases [9]. The other group of authors [10] synthesized poly(acrylamide-co-acrylic acid) based hydrogels with different Aac/Aam mole ratio (0:100, 40:60 and 60:40). They have investigated the swelling behaviour of gels in deionized water, saline solution and buffer solution at different pH values, at physiological temperature of 37 °C. Polyacrylamide hydrogel have demonstrated the lowest absorption rate and fast saturation in deionized water. On the other hand, the presence of poly(acrylic acid) in hydrogel composition contributes to greater swelling capacity and slower saturation. In the saline solution, the same hydrogels have showed 5 time lower absorption level than in deionized water at the same temperature.

It is the consequence of the presence of ionic species those surround the pendant ionic groups in hydrogel and lead to the decrease of repulsive forces between them. In buffer solution swelling ratio gradually increased in pH range 2.2-7.0. After achieving neutral pH value, swelling ratio gradually decreased with increasing of pH value until 10.

The soft nature and the presence of charge on their chains make those hydrogels suitable for application in tissue engineering for constructing new materials and cell scaffolds. Due to their water absorption capacity, poly(Aam-co-Aac) hydrogels can be used for agriculture purposes, for water supplying of plants [11] and as systems for controlled delivery of fertilizers [9]. Group of authors have demonstrated the possibility of their applications as flocculants in wastewater treatment [12].

Since there is no conjoined data in literature about the influence of initiator type and reaction mixture composition on thermal properties and swelling behaviour of poly(acrylamide-co-acrylic acid) hydrogels in acidic and alkaline medium, the focus of this work is synthesis of those hydrogels and investigation the influence of synthesis parameters on swelling and thermal properties.

2. EXPERIMENTAL

2.1. Materials

Acrylic acid (Aac) (Figure 1a), ammonium persulfate (APS), potassium persulfate (KPS) and N,N,N',N'-tetramethylethylene diamine (TEMED) (Figure 1b) were provided from Fisher Scientific. Acrylamide (Aam) (Figure 1c) and N,N'-methylenebis(acrylamide) (MBAM) (Figure 1d) were supplied from Sigma-Aldrich.

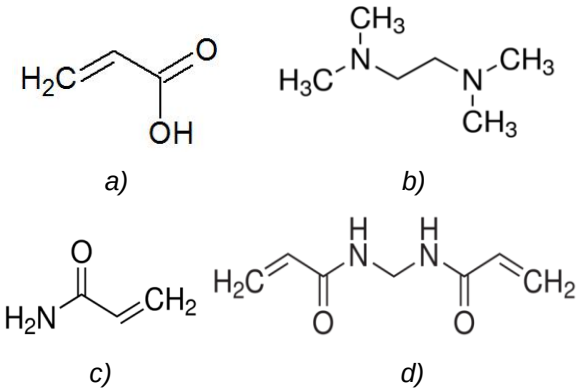

Figure 1. a) Structural formula of acrylic acid, b) N,N,N',N'-tetramethylethylenediamine, c) acrylamide, d) N,N'-methylenebis(acrylamide)

Slika 1. a) Strukturna formula akrilne kiseline, b) N,N,N',N'- tetrametiletilendiamina, c) akrilamida, d) N,N'-metilenbis(akrilamida)

2.2. Methods

2.2.1. Synthesis of hydrogels

Poly(acrylamide-co-acrylic acid) (poly(Aam-co-Aac)) based hydrogels were synthesized by free-radical polymerization in aqueous medium in the one-step procedure, using the two types of initiators - APS and KPS, TEMED as accelerator and MBAM as crosslinking agent. In order to investigate the influence of hydrogels composition on their swelling behaviour and thermal properties, the monomers feed ratio was varied as it is showed in Table 1. Two series of samples with the same monomers feed ratio were prepared - one using the APS and the other one using the KPS, with the goal to determine the effect of initiator type on hydrogels properties. The amount of crosslinking agent (1 and 3% per total weight of monomers) were varied within each series prepared using the same initiator type in order to get hydrogels with different degree of crosslinking and, consequently, different swelling capacity. Synthesis of copolymer and their crosslinking using the MBAM were carried out simultaneously in distilled water at temperature of 60-70 °C, for 3h. When the polymerization had completed, the prepared hydrogels were removed from the vials to Petri plates and put in dryer, where those were being dried on 50 °C to constant mass.

Table 1. The ratio of monomers weights in formulation of poly(acrylamide-co-acrylic acid) hydrogels

Tabela 1. Maseni odnos monomera u formulaciji hidrogelova na bazi poli(akrilamid-ko-akrilne kiseline)

Monomers	Mass ratio (%)			
Aac	0	30	50	70
Aam	100	70	50	30

2.2.2. Characterization

Chemical structures of obtained samples were confirmed by Fourier transform infrared spectroscopy (FTIR spectrophotometer Bomem Hartmann & Braun, MB-series) in solid state, using KBr pellet.

Swelling behaviour of crosslinked copolymers were investigated by swelling measurements in alkaline medium (pH=10), physiological pH of 7.4 and acidic medium (pH=4.5 and 2.2) at constant temperature of 37 °C.

Obtained pre-weighed xerogel samples were immersed in aqueous solution with a certain pH value (10, 7.4, 4.5 and 2.2), at temperature of 37 °C.

The swollen gels were being taken out in regular time intervals (on 30 minutes), wiped superficially using a filter paper, weighed, and then placed in the same bath. The swelling ratio was determined using the following equation:

$$Swelling\ ratio = (M_t - M_0)/M_0 \qquad (1)$$

where M_o is the initial weight in grams and M_t is a weight of swollen hydrogel in grams at different time intervals.

Thermal properties of poly(Aam-co-Aac) hydrogels were investigated using a differential scanning calorimeter (TA Instruments Q20) undergo nitrogen atmosphere in temperature regime from 25 to 180 °C, at heating rate of 10 °C/min.

3. RESULTS AND DISCUSSION

3.1. FT-IR spectral analysis of hydrogel samples

The IR spectra of hydrogels poly(Aam-co-Aac) 50:50 and poly(Aam) were depicted in Figure 2. The broad bands at 3436 and 3425 cm^{-1} in hydrogels correspond to N-H stretching of amide group from acrylamide unit. The corresponding peaks appear at 3352 and 3180 cm^{-1} in IR spectra of pure acrylamide. The broad region at 3276 cm^{-1} in hydrogel 50:50 can be allocated to the OH group of carboxyl group. In IR spectrum of monomer Aac, OH stretching appears at 3650 cm^{-1}. This shifting is a proof of H-bonding in polymer. The peaks at 2973 and 2930 cm^{-1} in two hydrogels correspond to C-H stretching of polymer backbone; at 1719 cm^{-1} and 1652 cm^{-1} to stretching of C=O group from acrylic acid and acrylamide units, respectively. In IR spectrums of acrylic acid and acrylamide, those bands appear at 1705 and 1690 cm^{-1}, respectively. Characteristic peaks due to C=C vibrations appear at 1648 cm^{-1} in acrylamide and around 1630 cm^{-1} in acrylic acid. The absence of those vibrations in IR spectra of observed hydrogels is the proof of complete polymerization. Two close lower intensive peaks at 1451 and 1407 cm^{-1} in hydrogel 50:50 and at 1455 and 1409 cm^{-1} in poly(Aam) hydrogel are allocated to C-N stretching originated from MBAM backbone. Sharper peak in acrylamide IR spectrum at 1426 cm^{-1} corresponds to C-N vibrations. In poly(Aam) hydrogel, the same vibrations are manifested as two small peaks at 1349 and 1320 cm^{-1}.

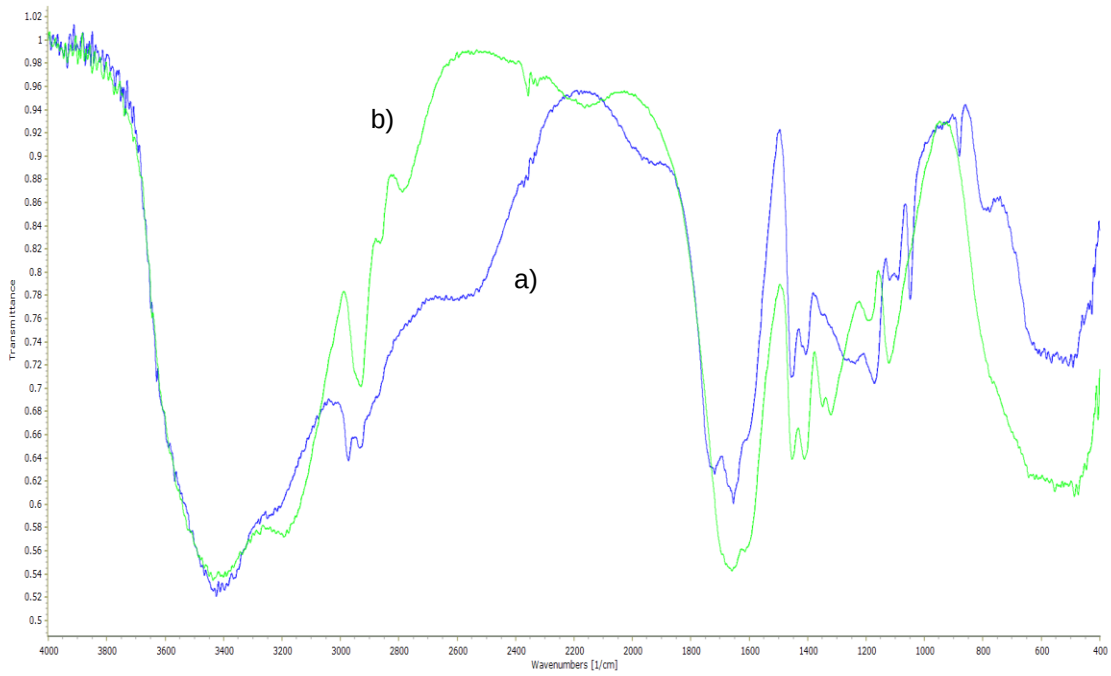

Figure 2. FT-IR spetra of poly(Aam-co-Aac) 50:50 hydrogel (a line) and poly(Aam) hydrogel (b line)
Slika 2. FT-IR spektri hidrogela na bazi poli(akrilamid-ko-akrilne kiseline) sa odnosom monomera 50:50 (a linija) i poliakrilamidnog hidrogela (b linija)

3.2. Swelling behaviour of hydrogel samples

Swelling behaviour of synthesized hydrogels are affected by monomer ratio, type of initiator, amount of crosslinking agent and environmental pH value. Swelling measurements were carried out at 37 °C, what is below the glass transition temperature of poly(Aam-co-Aac) hydrogels, so the swelling kinetics are diffusion-controlled (Fickian) [13]. In alkaline solution (pH=10) water absorption increases with increasing of acrylic acid amount in hydrogels synthesized using the APS as initiator (Figure 3 and Table 2). The highest value of equilibrium swelling ratio is 2965%, observed for hydrogel 70:30. It is the consequence of higher concentration of carboxylic groups (-COOH) in copolymer structure those are in ionized form ($-COO^-$) in high pH values domain.

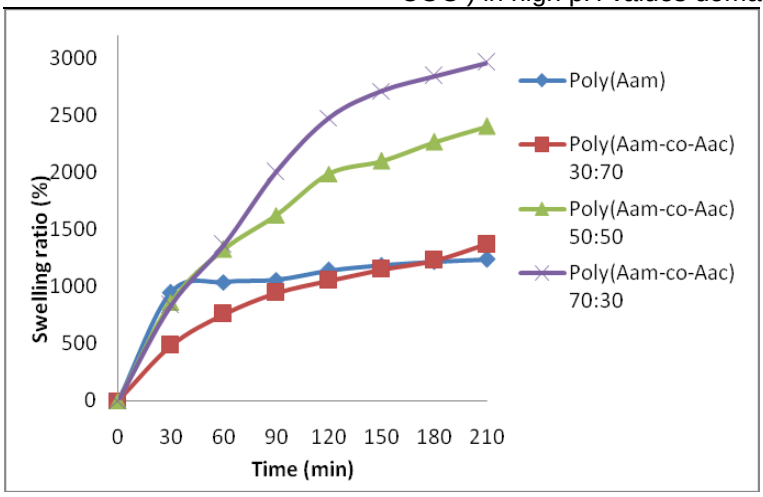

Figure 3. Swelling behaviour of APS initiated poly(acrylamide-co-acrylic acid) hydrogels with 3% crosslinking agent in alkaline medium (pH=10).

Slika 3. Bubrenje hidrogelova na bazi poli(akrilamid-ko-akrilne kiseline) sa 3% umreživača u alkalnoj sredini (pH=10, inicijator APS)

Table 2. Swelling ratio of APS initiated poly(acrylamide-co-acrylic acid) hydrogels with 3% crosslinking agent in alkaline medium (pH=10)

Tabela 2. Stepen bubrenja hidrogelova na bazi poli(akrilamida-ko-akrilne kiseline) sa 3% umreživača u alkalnoj sredini (pH=10, inicijator APS)

Hydrogel sample (Aac:Aam) (mass%)	70:30	50:50	30:70	0:100	Time (min)
Swelling ratio (%)	0	0	0	0	0
	836	862	483	947	30
	1365	1328	757	1039	60
	2006	1626	946	1056	90
	2479	1989	1054	114	120
	2714	2102	1148	118	150
	2844	2268	1230	1219	180
	2965	2407	1368	1237	210

KPS initiated hydrogels have shown the same pattern of swelling behaviour in alkaline medium, but significantly greater equilibrium swelling ratio than corresponding hydrogels synthesized using the APS as initiator (Figure 4 and Table 3). The maximum value of swelling ratio (5179%) is almost two times greater than for the hydrogel with the same composition (70:30 Aac/Aam, 3% MBAM) but synthesized using the APS as initiator. It can be the consequence of more flexible structure and greater segmental mobility of hydrogels synthesized using the KPS as initiator.

A physiological pH value of 7.4 is above pK_a value of carboxylic groups and below the pK_b value of amine groups, which implies that both types of functional groups are in ionizated form and in such state they both should contribute to water uptake. The highest swelling rates are observed for hydrogels with greater amounts of Aac - 70:30 and 50:50 (Aac/Aam) and the lowest for poly(Aam) hydrogel, considering the swelling behaviour of both hydrogels series (synthesized using the APS and KPS) (Figure 5). Water uptake increases with increasing of Aac amount in hydrogel composition and the swelling pattern is very similar to one established for the hydrogels in alkaline medium (pH=10). Therefore, disociated carboxylic groups have a greater contribution to swelling capacity at physiological pH than protonated amine groups. That can be the consequence of higher ionization degree of carboxyilic groups in those conditions and the fact that carboxylic groups tighter hold molecules of water due to the hydrogen bonds.

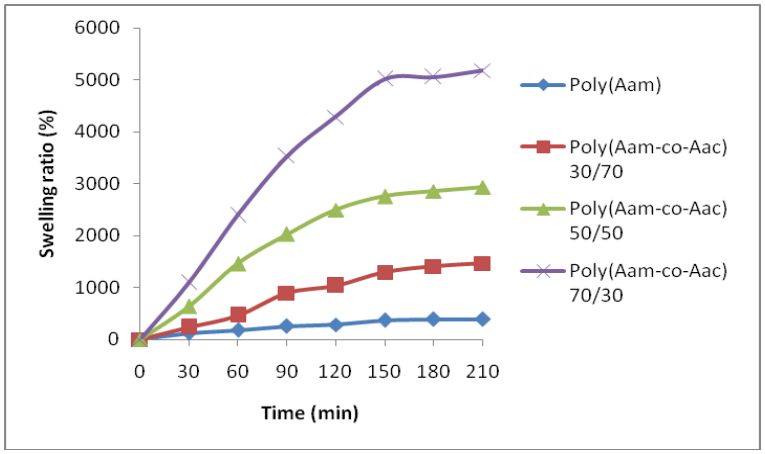

Figure 4. Swelling behaviour of KPS initiated poly(acrylamide-co-acrylic acid) hydrogels with 3% crosslinking agent in alkaline medium (pH=10)

Slika 4. Bubrenje hidrogelova na bazi poli(akrilamid-ko-akrilne kiseline) sa 3% umreživača u alkalnoj sredini (pH=10, inicijator KPS)

Table 3. Swelling ratio of KPS initiated poly(acrylamide-co-acrylic acid) hydrogels with 3% crosslinking agent in alkaline medium (pH=10)

Tabela 3. Stepen bubrenja hidrogelova na bazi poli(akrilamida-ko-akrilne kiseline) sa 3% umreživača u alkalnoj sredini (pH=10, inicijator KPS)

Hydrogel sample (Aac:Aam) (mass%)	70:30	50:50	30:70	0:100	Time (min)
Swelling ratio (%)	0	0	0	0	0
	1091	634	237	124	30
	2394	1460	460	183	60
	3535	2028	891	253	90
	4285	2491	1039	284	120
	5017	2756	1293	369	150
	5055	2853	1406	384	180
	5179	2933	1463	390	210

A physiological pH value of 7.4 is above pK_a value of carboxylic groups and below the pK_b value of amine groups, which implies that both types of functional groups are in ionizated form and in such state they both should contribute to water uptake. The highest swelling rates are observed for hydrogels with greater amounts of Aac - 70:30 and 50:50 (Aac/Aam) and the lowest for poly(Aam) hydrogel, considering the swelling behaviour of both hydrogels series (synthesized using the APS and KPS) (Figure 5). Water uptake increases with increasing of Aac amount in hydrogel composition and the swelling pattern is very similar to one established for the hydrogels in alkaline medium (pH=10). Therefore, disociated carboxylic groups have a greater contribution to swelling capacity at physiological pH than protonated amine groups. That can be the consequence of higher ionization degree of carboxyilic groups in those conditions and the fact that carboxylic groups tighter hold molecules of water due to the hydrogen bonds.

At pH=7.4, there is no significant difference between two types of initiators, considering the swelling behaviour of synthesized hydrogels, which is confirmed by the measurements of swelling ratio values (Figure 6). KPS initiated hydrogels have a little higher values of maximum swelling ratios than corresponding APS initiated hydrogels.

At pH 4.5, the APS initiated hydrogels have shown inverse swelling bahaviour in regards to alkaline medium (Figure 7 and Table 4). Swelling capacity in acidic medium (pH=4.5) decreases with increasing of acrylic acid amount. Poly(acrylamide) hydrogel has demonstrated the greatest swelling capacity in acidic solution because the pendant amine groups in acrylamide units are protonated in acidic solution (pH=4.5). Electrostatic repulsion between them results in greater water uptake. The pK_a value of acrylic acid based copolymer is between 4.5 and 5, therefore carboxylic groups originated from acrylic acid are mostly deprotonated and do not contribute to increasing of swelling capacity at applied pH value. In alkaline medium, above their pK_a value, carboxylic groups tend to dissociate and refuse each other, what leads to increasing of osmotic pressure inside the polymer network and greater water uptake, which originates from a higher concentration of COO^- groups. Ionization of amine groups takes place below their pK_b value which is in the range between 8.5 and 9. That results in icreased number of fixed positive charges, greater osmotic pressure inside the polymer network and consequently greater water uptake [14].

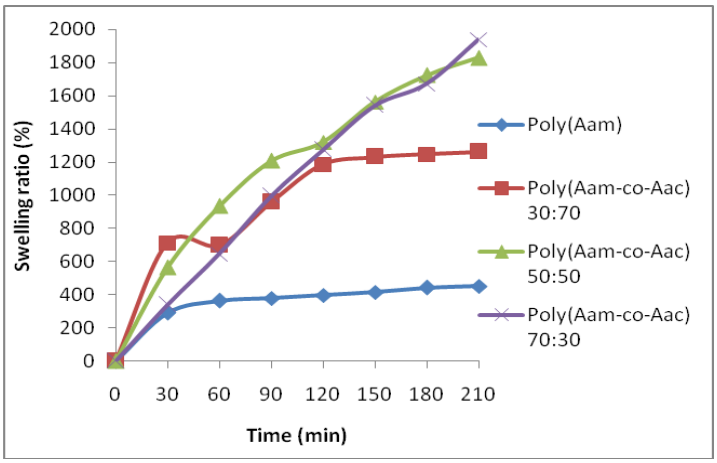

Figure 5. Swelling behaviour of APS initiated poly(acrylamide-co-acrylic acid) hydrogels with 3% crosslinking agent at physiological pH=7.4

Slika 5. Bubrenje hidrogelova na bazi poli(akrilami-ko-akrilne kiseline) sa 3% umreživača na fiziološkom pH 7.4 (inicijator APS)

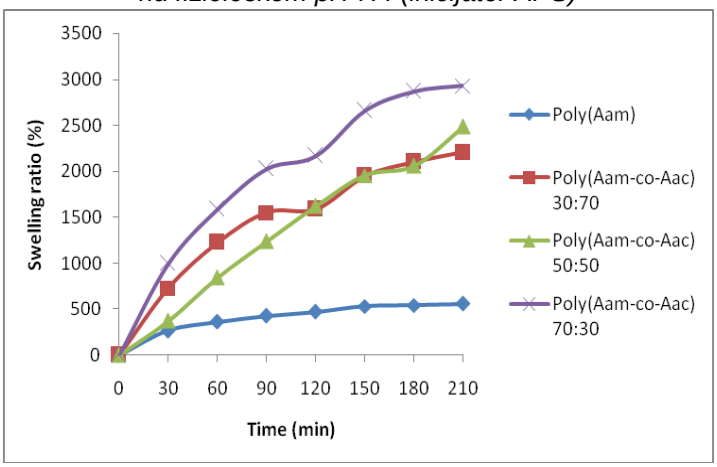

Figure 6. Swelling behaviour of KPS initiated poly(acrylamide-co-acrylic acid) hydrogels with 3% crosslinking agent at physiological pH=7.4

Slika 6. Bubrenje hidrogelova na bazi poli(akrilami-ko-akrilne kiseline) sa 3% umreživača na fiziološkom pH 7.4 (inicijator KPS)

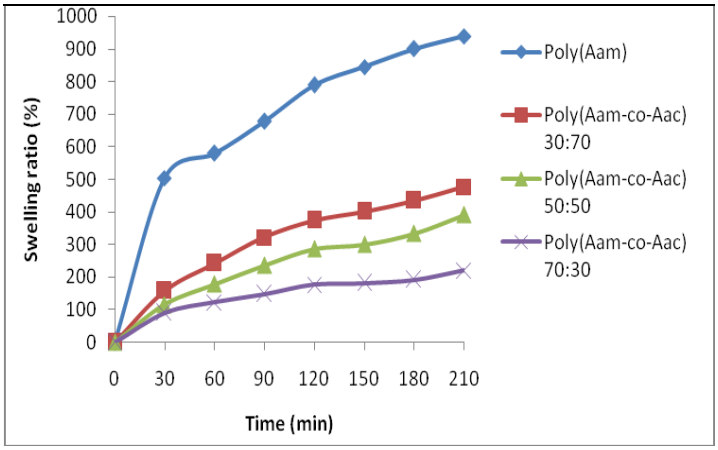

Figure 7. Swelling behaviour of APS initiated poly(acrylamide-co-acrylic acid) hydrogels with 3% crosslinking agent in acidic medium (pH=4.5)

Slika 7. Bubrenje hidrogelova na bazi poli(akrilamid-ko-akrilne kiseline) sa 3% umreživača u kiseloj sredini (pH=4.5, inicijator APS)

Table 4. Swelling ratio of APS initiated poly(acrylamide-co-acrylic acid) hydrogels with 3% crosslinking agent in acidic medium (pH=4.5)

Tabela 4. Stepen bubrenja hidrogelova na bazi poli(akrilamida-ko-akrilne kiseline) sa 3% umreživača u kiseloj sredini (pH=4.5, inicijator APS)

Hydrogel sample (Aac: Aam) ass%)	70:30	50:50	30:70	0:100	Time (min)
Swelling ratio (%)	0	0	0	0	0
	90	115	158	503	30
	123	178	241	579	60
	148	236	321	677	90
	176	285	374	789	120
	181	300	401	844	150
	192	334	434	900	180
	221	390	476	939	210

The orderliness in correlation between swelling ratio and hydrogel composition was also established at KPS initiated hydrogels in acidic medium (Figure 8 and Table 5). In acidic medium, initiator type does not affect significantly the swelling ratio. The lowest values of swelling ratio are noticed for hydrogel 70:30, in the range between 79 and 176%.

Hydrogel with the same composition, synthesized using the APS does not have significantly higher values of swelling ratio (range from 90 to 221).

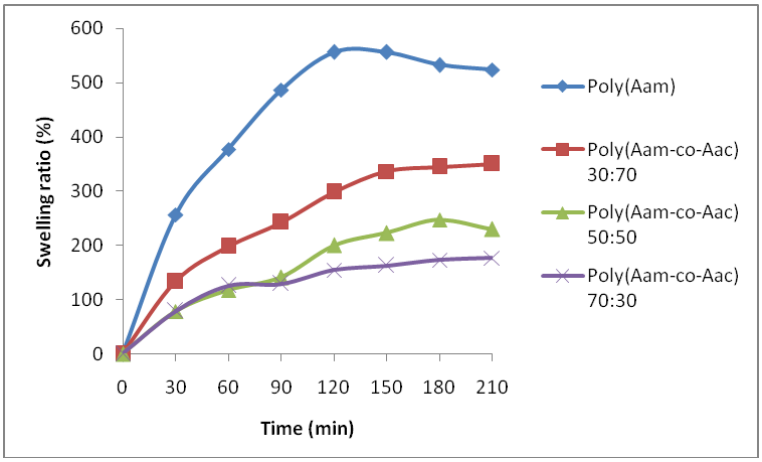

Figure 8. Swelling behaviour of KPS initiated poly(acrylamide-co-acrylic acid) hydrogels with 3% crosslinking agent in acidic medium (pH=4.5)

Slika 8. Bubrenje hidrogelova na bazi poli(akrilamid-ko-akrilne kiseline) sa 3% umreživača u kiseloj sredini (pH=4.5, inicijator KPS)

Table 5. Swelling ratio of KPS initiated poly(acrylamide-co-acrylic acid) hydrogels with 3% crosslinking agent in acidic medium (pH=4.5)

Tabela 5. Stepen bubrenja hidrogelova na bazi poli(akrilamida-ko-akrilne kiseline) sa 3% umreživača u kiseloj sredini (pH=4.5) (inicijator KPS)

Hydrogel sample (Aac:Aam) (mass%)	70:30	50:50	30:70	0:100	Time (min)
Swelling ratio (%)	0	0	0	0	0
	79	78	133	256	30
	125	117	197	377	60
	129	141	242	486	90
	154	200	298	556	120
	162	222	336	556	150
	172	247	344	532	180
	176	229	350	523	210

Below the pK_a and pK_b of poly(Aam-co-Aac), at pH 2.2, amine groups are in protonated form and carboxylic groups are not ionizated. Therefore, the swelling ratio of hydrogels at that pH value is affected by acrylamide content in hydrogel composition. In very acidic medium, at pH 2.2, according to the theory of the influence of pH on swelling rate, it is expected that poly(Aam) hydrogel will have the highest value of maximum swelling ratio. However, the swelling pattern of APS initiated hydrogels with 3% of MBAM does not show theoretically predicted colerration between swelling ratio and Aam amount (Figure 9). The highest equilibrium swelling ratio value (770%) is observed for hydrogel 50:50. The other three samples have similar swelling rates and equilibrium swelling ratio values. The reason probably lies in the influence of Aam content on rigidity of polymer network. Aam simultaneously with crosslinking agent contributes to higher density of polymer network, what is expressed for higher amounts of

crosslinking agent (3 wt%). Therefore, the value of equilibrium swelling ratio increases with decreasing of Aam amount. The sample 50:50, with higher swelling rate, deviates from this pattern. The explanation shoud be sought in the balance between contribution of Aac to decreasing of network rigidity and contribution of Aam to increasing of water uptake in acidic medium.

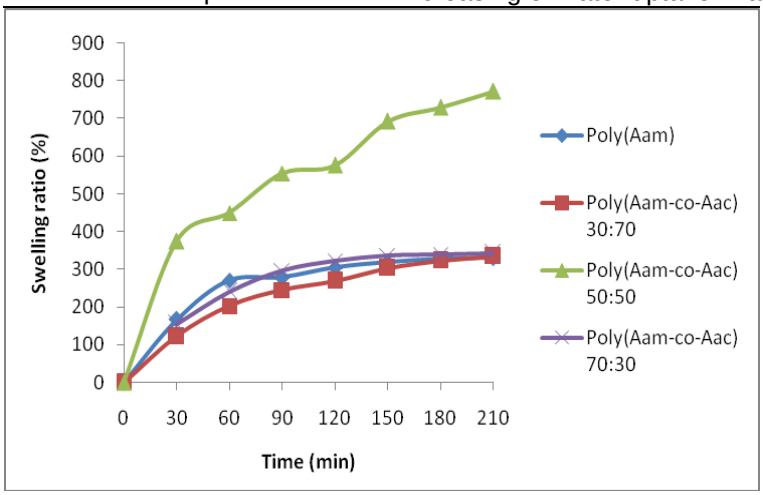

Figure 9. Swelling behaviour of APS initiated poly(acrylamide-co-acrylic acid) hydrogels with 3% crosslinking agent in acidic medium (pH=2.2)

Slika 9. Bubrenje hidrogelova na bazi poli(akrilamid-ko-akrilne kiseline) sa 3% umreživača u kiseloj sredini (pH=2.2, inicijator APS)

The orderliness between Aam amount and swelling ratio values is confirmed by investigation of swelling behaviour of KPS initiated hydrogels with 3% MBAM, where with increasing of Aam amount (and concentration of amine groups) in hydrogel composition increases a equilibrium swelling ratio value (Figure 10). The swelling ratio values are close regardless of the significant difference in Aam amounts in hydrogels composition. That is the consequence of distinction in flexibility of copolymer chains influenced by monomers ratio.

Swelling measurements in alkaline and acidic medium have shown similarities between two types of initiators used for the hydrogels synthesis. By monitoring the swelling ratio of hydrogels with the time, the only deviation is established for swelling behavior of APS initiated hydrogels at pH 2.2, where the difference in network density influenced by initiator type, comes to expression. It can be the consequence of difference in degradation rate between APS and KPS.

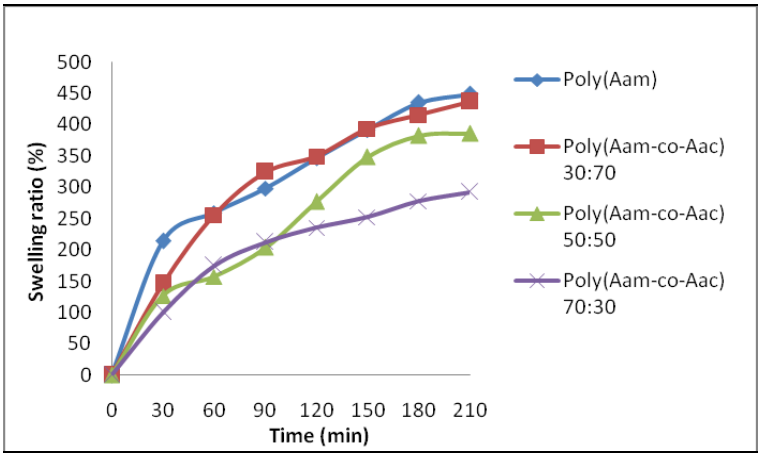

Figure 10. Swelling behaviour of KPS initiated poly(acrylamide-co-acrylic acid) hydrogels with 3% crosslinking agent in acidic medium (pH=2.2)

Slika 10. Bubrenje hidrogelova na bazi poli(akrilamid-ko-akrilne kiseline) sa 3% umreživača u kiseloj sredini (pH=2.2, inicijator KPS)

Figure 11 demonstrates the influence of different amounts of crosslinking agent on swelling ratio of two hydrogels with the same monomers ratio, in alkaline environment. Reducing the amount of

crosslinking agent leads to an increasing of water uptake, because hydrogels with greater crosslinking density have less flexible structure and ability to deform themselves [2]. Hydrogel with the same composition, but 3 times lower amount of crosslinking agent has about 5 times higher swelling ratio values in alkaline medium.

Variation in initiator type has imposed a conclusion that using a KPS as initiator results in obtaining the hydrogels with greater swelling capacity in alkaline medium. Hydrogels synthesized using the APS have demonstrated lower ability to absorb water at pH=10. The reason lies in different degree of crosslinking, what is the consequence of using of different initiator type.

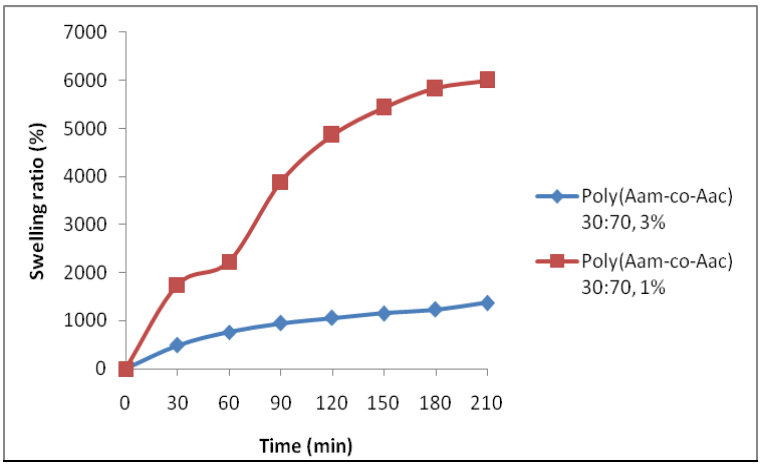

Figure 11. Comparison the swelling bahaviour of APS initiated hydrogels with the same copolymer composition, but different amount of crosslinking agent in alkaline medium (pH=10)

Slika 11. Poređenje svojstava bubrenja hidrogelova u alkalnoj sredini (pH=10) sa istim kopolimernim sastavom, ali drugačijim udelima umreživača (inicijator APS)

3.3. Thermal analysis of hydrogel samples

DCS thermograms of hydrogel samples with different amounts of acrylamide are shown in Figure 12. Hydrogels with 30, 50 and 70 wt% of acrylamide have similar glass transition temperature (T_g) values, implying the fact that an increasing of acrylamide amount in that range does not affect significantly the T_g value of copolymer hydrogel. Hydrogel based on pure acrylamide has higher T_g value in comparison with other samples. That indicates a reduction in segmental mobility due to the stronger inter-molecular reaction contributed by amide groups.

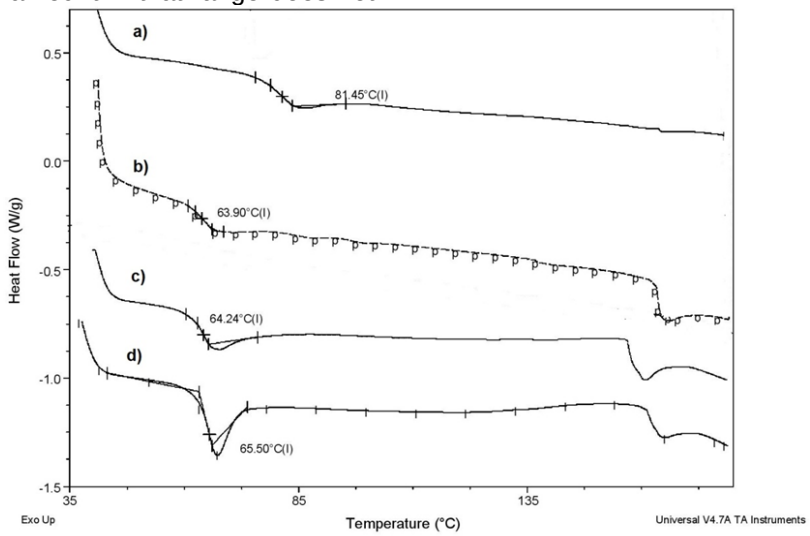

Figure 12. DCS thermograms of different hydrogels with 1% of crosslinking agent synthesized using the KPS as initiator: a) poly(Aam) hydrogel, b) poly(Aam-co-Aac) hydrogel, 30:70, c) poly(Aam-co-Aac) hydrogel 50:50, d) poly(Aam-co-Aac) hydrogel 70:30

Slika 12. DSC termogrami za različite hidrogelove sa 1% umreživača sintetisane primenom KPS-a kao inicijatora: a) poli(akrilamidni) hidrogel, b) hidrogel na bazi poli(akrilamid-ko akrilne kiseline) sa odnosom monomera 30:70, c) hidrogel na bazi poli(akrilamid-ko akrilne kiseline) sa odnosom monomera 50:50, d) hidrogel na bazi poli(akrilamid-ko akrilne kiseline) sa odnosom monomera 70:30

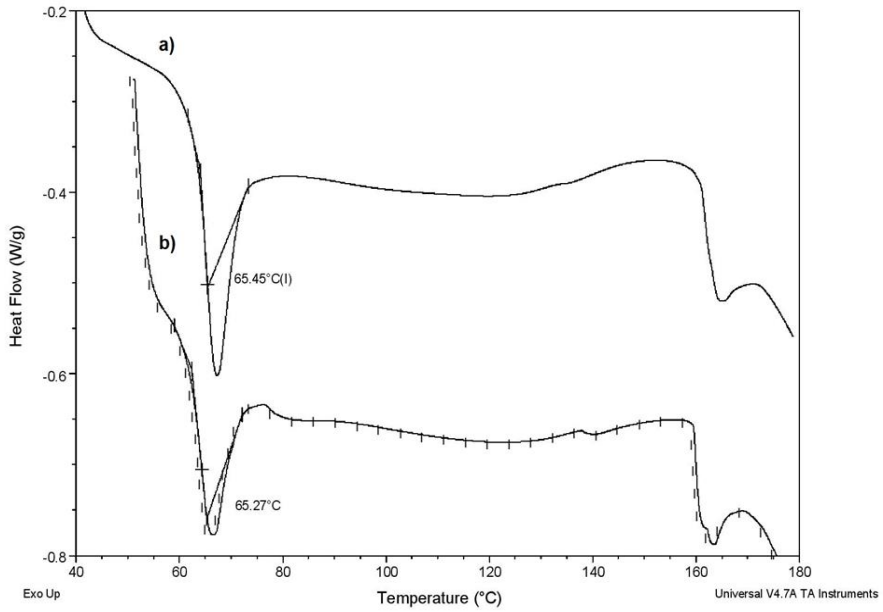

Figure 13. DSC thermograms of poly(Aam-co-Aac) hydrogel 70:30 (Aac:Aam) with 1% of crosslinking agent synthesized using the: a) APS, b) KPS as initiator

Slika 13. DSC termogrami od hidrogela na bazi poli(akrilamid-ko-akrilne kiseline) sa odnosom monomer 70:30 sa 1 % umreživača sintetisani primenom: a) APS-a, b) KPS-a kao inicijatora

Based on similar curves trends and close T_g values of two samples with the same composition, synthesized using the different type of initiators, it can be concluded that there is no difference between APS and KPS in terms of thermal properties of obtained hydrogels (Figure 13). Increasing of crosslinking agent amount and, consequently crosslinking density, lead to the decreasing of free volume in polymer material, reduced segmental mobility and increasing of T_g value. That is demonstrated by DSC curves recorded for the two samples with the same monomers ratio and different amounts of crosslinking agent (Figure 14).

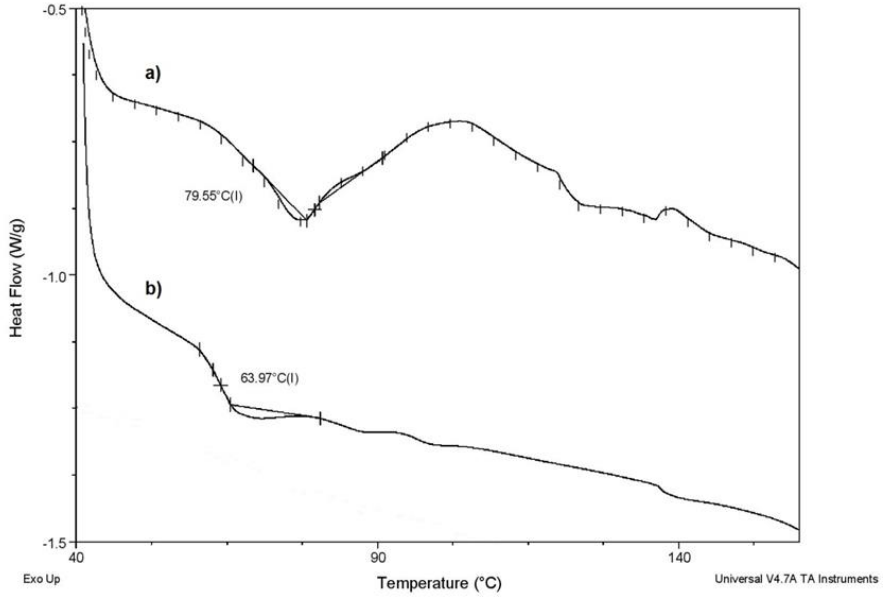

Figure 14. DSC thermograms of poly(Aam-co-Aac) hydrogel 30:70 synthesized using the one type of initiator (KPS) and different amounts of crosslinking agent: a) 3%, b) 1% of crosslinking agent

Slika 14. DSC termogrami hidrogelova na bazi poli(akrilamida-ko-akrilne kiseline) sa odnosom monomer 30:70, sintetisanih primenom jednog tipa inicijatora (KPS) i različitih udela umreživača: a) 3%, b) 1%

4. CONCLUSIONS

Poly(Aam-co-Aac) hydrogels were synthesized in water solution via free-radical polymerization using the two type of initiators. Type of initiator, monomers ratio and amount of crosslinking agent were varied in order to investigate the influence of gel composition on swelling and thermal properties of obtained hydrogels.

In alkaline medium, the swelling ratio increases with increasing the amount of acrylic acid in hydrogel composition achieving the maximum value of 2965% for APS initiated 70:30 hydrogel and even 5179% for KPS initiated hydrogel with the same composition. The same pattern is noticed for swelling behaviour of hydrogels in physiological conditions, at pH 7.4. This pH value is between pK_a and pK_b value of poly(Aam-co-Aac) hydrogels, what implies ionization of both functional groups. Obtained results have showed that Aac has a greater impact on swelling capacity than Aam in those conditions.

In acidic medium swelling ratio decreases with increasing the amount of acrylic acid in copolymer. The highest value of maximum swelling ratio of 939% is observed for APS initiated poly(Aam) hydrogel at pH 4.5. The same value for the KPS initiated hydrogel with the same composition is almost two times lower (523%). At lower pH (2.2), almost all amine groups are in protonated form as opposite to carboxylic groups, those are non-dissociated and in such state do not contribute to water absorption. The highest value of maximum swelling ratio is observed for poly(Aam) hydrogel in series with KPS. The value of maximum swelling ratio increases with increasing of AAm amount and concentration of amine groups. The same orderliness is not noticed for APS initiated hydrogels with 3% MBAM. In that series, 50:50 hydrogels has the highest value of maximum swelling ratio (770%), because of achieved balance between flexibility of polymer chains and Aam amount.

Investigated poly(Aam-co-Aac) hydrogels have similar T_g values in the range between 63.90 and 65.50 °C. Poly(Aam) hydrogel has a greater T_g value (81.45 °C) than copolymer hydrogels. The reason is stronger intermolecular attraction due to the increased presence of amide groups. The initiator type does not affect significantly the T_g value. Hydrogels with the same composition (70:30 Aac/Aam, 1% MBAM) synthesized using the APS and KPS as initiators have very close T_g values (65.27 and 65.45 °C, respectively). The amount of crosslinking agent, on the other hand, has a great impact on hydrogel T_g value. Increasing of crosslinking agent amount reduces segmental mobility of polymer chains, that contributes the increase of T_g value. Therefore, KPS initiated hydrogel 30:70 with 1% of MBAM has T_g value at 63.97 °C and the hydrogel with the same monomers ratio, but 3% MBAM has significantly higher T_g value, at 79.55 °C.

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IZVOD

UTICAJ PARAMETARA SINTEZE NA BUBRENJE pH OSETLJIVIH AKRILATNIH HIDROGELOVA

U ovom radu su sintetisani hidrogelovi na osnovu poli(akrilamid-ko-akrilne kiseline) primenom dva tipa inicijatora – kalijum persulfata (KPS) i amonijum persulfata (APS) i akceleratora N,N,N',N'-tetrametil etilen diamina (TEMED). Umrežavanje je vršeno posredstvom N,N'-metilen bisakrilamida (MBAM) koji je korišćen u udelima 1 i 3% u odnosu na ukupnu masu monomera. Pripremljeni su hidrogelovi sa sledećim masenim odnosima monomera akrilne kiseline i akrilamida: 70:30, 50:50, 30:70 i 0:100%. Svojstva bubrenja sintetisanih gelova ispitana su u kiseloj (pH=4.5) i alkalnoj sredini (pH=10) na konstantnoj temperaturi od 37 °C. Niži udeo umreživača dao je hidrogelove sa većom sposobnošću bubrenja. Struktura hidrogelova potvrđena je FT-IR metodom. Toplotna svojstva su ispitana diferencijalnom skenirajućom kalorimetrijom (DSC). Dobijeni rezultati pokazali su postojanje izražene korelacije između sastava hidrogela i njegovih toplotnih svojstava i svojstava bubrenja.

Ključne reči: *hidrogel, stepen bubrenja, akrilna kiselina, akrilamid, odnos monomera.*

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