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HYDROGELS BASED ON 2-HYDROXYETHYL METHACRYLATE: SYNTHESIS, CHARACTERIZATION AND HYDRATION CAPACITY

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ABSTRACT

In the present work, three hydrogels of poly(2-hydroxyethyl methacrylate-co-itaconic acid), p(HEMA-co-IA), poly(2-hydroxyethyl methacrylate-co-acrylic acid), p(HEMA-co-AA) and poly(2-hydroxyethyl methacrylate-co-(1-vinyl-2-pyrrolidone)), p(HEMA-co-NVP) were prepared by free radical polymerization in aqueous solution (1:1 monomer mole ratio) using ammonium persulfate as initiator and N,N´-methylenebisacrylamide as crosslinking agent at two different amount (0.3 and 0.9 mol%). The obtained hydrogels were characterized by Fourier transform infrared spectroscopy (FT-IR), which allowed to verify the structural composition. Thermal analysis of the hydrogels was carried out by thermogravimetric analysis (TGA). In addition, hydration capacity (U%) was studied at different experimental conditions such as: time, pH, concentrations of interfering salts (KCl, NaCl and LiCl). The results showed a good polymerization yield (95%). FTIR characterization shows the absorption bands of the functional groups of copolymers. TGA exhibited the characteristic thermal stability of this type of hydrogels. The presence of comonomer AI, AA or NVP in copolymer determine the thermal behavior. Hydration experiments revealed a higher U% in copolymer containing more carboxylic acid groups. The maximum U% values in water were 400% and 250% for p(HEMA-co-AI) and p(HEMA-co-AA), respectively. For P(HEMA-co-NVP) a maximum of U% value was only 74% in water. The effect of interferent salts affects the hydration capacity decreasing U% when the concentration of salts increase.

Keywords: Copolymerization; crosslinking; hydrogels; salts; water uptake.

INTRODUCTION

Polymeric hydrogels have received great attention, due to the different applications such as in water purification, controlled drug release, food industry, and so on [1-4]. These materials are composed by three-dimensional cross-linked polymer networks, produced from the simple reaction of one or more monomers [5,6]. These materials can be from natural or synthetic origin and they show swelling or hydration capacity and retain a significant part of water or other fluid solvent in its structures, which generally do not dissolve [7]. This hydration capacity is due to the hydrophilic functional groups (-OH, -COOH, -CONH2, -CONR, -SO3H) linked to the main polymer chain, and its resistance to dissolution arises from cross-links of chains among networks [8]. Polymeric hydrogels can be modified chemically improving physicochemical and thermomechanical properties as well as the stability of the material. In dry state they are a resilient solid known as xerogel, but when they make contact with an aqueous medium they swell until reaching a physicochemical equilibrium, becoming elastic or soft solids known as hydrogels [9-11].

One of the most used monomers for the synthesis of hydrogel materials is 2-hydroxyethylmethacrylate (HEMA). Hydrogels generated from HEMA are capable to adsorb from 10% to 600% of water in relation to the dry weight (xerogel). This occurs due to the interaction between hydrophilic group (OH^-) of HEMA and the water molecules, which generates hydrogen bonds that allow its absorption and produce swelling [12,13]. On the other hand, in literature it has been described that crosslinked polymers that are composed of acrylic acid (AA) monomers [14,15], N- vinylpyrrolidone (NVP) [16,17], and itaconic acid (IA) [18,19], also possess a high hydration capacity due to the functional groups that have in its molecular structure, generating proper hydrophilicity. Among the structural features of these materials predominate its superficial properties, permselectivity and permeability, which gives hydrogels its unique and interesting properties [20,21].

In this study the synthesis of three copolymer hydrogels (p(HEMA-co-IA), p(HEMA-co-AA), and p(HEMA-co-NVP)) was proposed evaluating the effect of the cross-linking agent and varying its concentration in 0.3 and 0.9 mol%. After synthesis, the reaction yield was evaluated gravimetrically for each copolymer. Subsequently, the three copolymers were characterized by FTIR and TGA. Finally, hydration capacity (U%) was studied at different experimental conditions such as: time, pH, concentrations of interfering salts (KCl, NaCl and LiCl).

EXPERIMENTAL

Regents and materials

In this research, the following vinyl monomers were used: 2-hydroxyethyl methacrylate (HEMA), itaconic acid (IA), acrylic acid (AA) and 1-vinyl-2-pyrrolidone (NVP). Ammonium persulfate (APS) was used as initiator and N,N´-methylenebisacrylamide (MBA) as cross-linking agent. All reagents were obtained commercially from Sigma-Aldrich and no additional purification process was carried out before synthesis of copolymers.

Synthesis of copolymers

HEMA-based copolymers were prepared in a 1:1 co-monomer mole ratio in the feed, keeping a total monomer concentration of 40 mM. The free radical copolymerization method was performed using 0.5 mol% APS as initiator and different amounts of crosslinker MBA (0.3 and 0.9 mol% respect to monomer) in 4 mL of solvent (bi-destilled water). The solution reaction was purged with N_2 (g) to get inert atmosphere for polymerization and then the reactive solution was put into a thermoregulated bath at 70°C, until copolymerization reaction time of 1 h. The schematic representation of the synthesis of HEMA based hydrogels is presented in Figure 1.

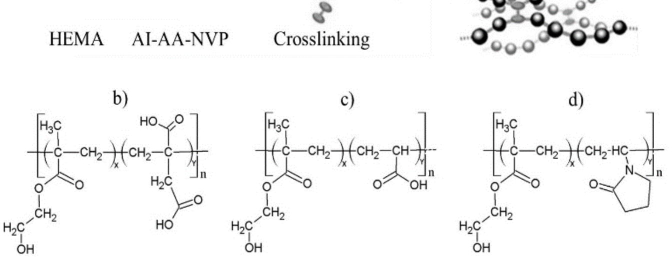

Figure 1. a) Schematic representation of the synthesis of HEMA based hydrogels and its molecular structures. Copolymers of: (b) HEMA-itaconic acid (AI). (c) HEMA-acrylic acid (AA). (d) HEMA-1-vynil-2-pyrrolidone (NVP).

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After polymerization reaction, hydrogels were washed in water in order to remove rest of monomers. Then hydrogels were filtered and freeze-dried during seven days. After that, the polymerization yield, characterization and hydration capacity were determined.

Characterization of copolymers by FTIR

Dried copolymers were grinded to a suitable size for the FTIR analysis. The spectra were obtained using spectrometer "Spectrum Two" with diamond ATR accessory (PerkinElmer, USA), in the range of 4000 cm^{-1} and 400 cm^{-1} with a resolution of 1 cm^{-1}. The sample was placed directly over the diamond and a pressure of 30% was applied. Graphs of spectra were prepared using Origin8 software (OriginLab Corp., USA).

Characterization of copolymers by thermal analysis

Thermogravimetric analysis (TGA) of the copolymers was carried out using equipment TGA 'Star System 1' (Mettler Toledo, USA). 3 mg of dry sample and a heating flux of 10°C/min from 25°C to 500°Cat inert atmosphere (gaseous N_2).

Hydration capacity of copolymers

In order to determine the hydration capacity (U%) of copolymers, 0.1 g of each xerogel was submerged in 100 mL of de-ionized water. Afterwards, the weight of the hydrated copolymer was determined every 30 minutes, removing the excess of water with sorbent paper. This is repeated until the weight of the copolymer maintains constant. This experiment was done in triplicate.

Additionally, U% was analysed in function of pH and ionic strength of solution for each copolymer. In order to study the effect of pH, 0.1 g of each xerogel was submerged in 100 mL of water at pH 3, 6 and 9. In order to adjust the pH of solution, 0.1 mol/L HCl (Merck) or 0.1 mol/L NaOH (merck) were used.

To study the effect of ionic strength, 0.1 g of each xerogel was submerged in 100 mL of ionic solution at certain concentration (0.2, 0.4, 0.6, 0.8 and 1.0 mg/L) of KCl, NaCl and LiCl.

Hydration capacity was determined according to the amount of water absorbed by the hydrogel in equilibrium (Equation 1).

$$\boldsymbol{U\% = \frac{m_h - m_x}{m_x} \times 100} \qquad (\mathbf{1})$$

Where U% is the hydration capacity or swelling, $\boldsymbol{m_h}$ is the hydrogel mass (g), mx is the xerogel mass. Figure 2 shows the schematic representation of the hydration capacity of the hydrogels.

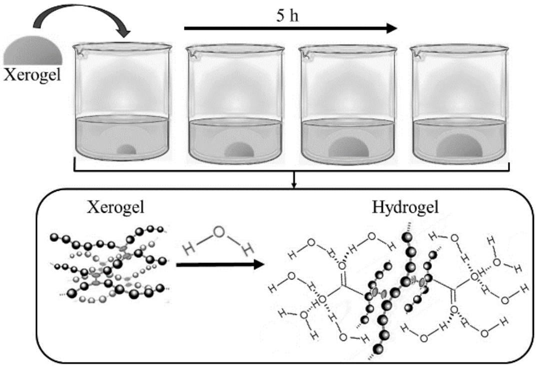

Figure 2. Schematic representation of the hydration capacity of hydrogels constituted by COOH

RESULTS AND DISCUSSION

Synthesis of P(HEMA-co-AI), P(HEMA-co-AA) and P(HEMA-co-NVP)

Three copolymers were obtained by free radical polymerization reaction using HEMA monomer in combination with AI, AA and NVP using 1:1 mole composition (0.02 mol:0.02 mol). Reaction yields over 83% were obtained for the three synthesized copolymers using 1h of reaction time. The series of copolymers prepared with 0.3 mol% of MBA needed a longer polymerization time to obtain the copolymers in comparison with the series prepared with 0.9 mol% of MBA (see Table 1). By adding a higher concentration of crosslinking agent in the feed, a major number of reactive centers are generated and more interactions with monomers, and therefore shorter polymerization reaction time compared to the systems that contain a lower concentration of crosslinking agent [22].

Table 1. Experimental conditions of polymerization and yield (%) of reactions.

Polymer	[MBA] (mol%)	Yield (%)
P(HEMA-co-AI)	0.3	95.8
	0.9	96.9
P(HEMA-co-AA)	0.3	96.7
	0.9	98.8
P(HEMA-co-NVP)	0.3	97.7
	0.9	95.5

Characterization of P(HEMA-co-AI), P(HEMA-co-AA) and P(HEMA-co-NVP) by FTIR-ATR

The FTIR spectra show characteristic absorption bands of the functional groups for each copolymer (see Figure 3). The main absorption bands are described for each copolymer as follows.

P(HEMA-co-AI): It is observed at 3017 cm^{-1} (O-H stretching of the acid group), 2730 cm^{-1} (C-H, $-CH_3$ and $-CH_2-$ stretching, aliphatic), 1693 cm^{-1} (C=O stretching, ester and carboxylic acid) and 1438 cm^{-1} – 1217 cm^{-1} (C-O-C bending and C-C stretching).

P(HEMA-co-AA): It is observed at 3274 cm^{-1} (O-H stretching of the acid group), 2947 cm^{-1} (C-H, $-CH_3$ and $-CH_2-$ stretching, aliphatic), 1705 cm^{-1} (C=O stretching, ester and carboxylic acid) and 1429 cm^{-1} – 1151 cm^{-1} (C-O-C bending and C-C stretching).

P(HEMA-co-NVP): It is observed at 3385 cm^{-1} (O-H stretching, alcohol), 2942 cm^{-1} (C-H, $-CH_3$ and $-CH_2-$ stretching, aliphatic), 1724 cm^{-1} -1668 cm^{-1} (C=O stretching, ester carbonyl and asymmetric cyclic anhydride amide) and 1426 cm^{-1} -1152 cm^{-1} (C-O-C bending and C-N stretching).

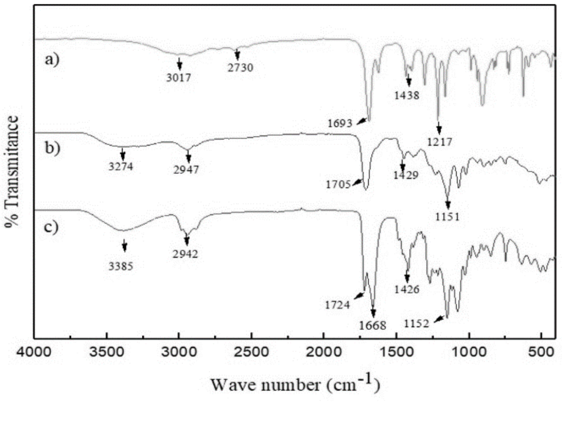

Figure 3. Infrared spectra of (a) P(HEMA-co-AI), (b) P(HEMA-co-AA) and (c) P(HEMA-co-NVP)

Thermogravimetric analysis of P(HEMA-co-AI), P(HEMA-co-AA) and P(HEMA-co-NVP)

Thermograms of the three copolymers are observed in Figure 4. In general, the presence of comonomer AI, AA or NVP in copolymer determine the thermal behavior. P(HEMA-co-AI) showed two thermal decomposition curves, the first is in a range between 165° and 256°C, with a decomposition of 25% and a second curve concentrated in a range of temperature between 330° and 450°, with a decomposition of 70% respect to the total mass. The complete decomposition of all the copolymer samples was observed around 450 °C. For P(HEMA-co-AA) a thermal decomposition curve is appreciated in a range of temperature between 334°C and 450°C, where the polymer material was decomposed completely. It showed a high decomposition temperature, typical of this kind of polymers.

In the case of P(HEMA-co-NVP) two thermal decomposition curves are exhibited, the first in a range of 128°C and 272°C with a decomposition percentage of 25% and the second curve located in a temperature range between 331°C and 450°C, with a decomposition percentage of 70%.

All the HEMA based hydrogel systems showed a thermal stability similar to the P(HEMA) homopolymer reported in the literature [23]. The stability conferred for these hydrogels is a product of the reticulated structural network, constituted by the formation of covalent bonds between vinyl monomers (HEMA, AA, NVP, and AI) and the MBA crosslinker.

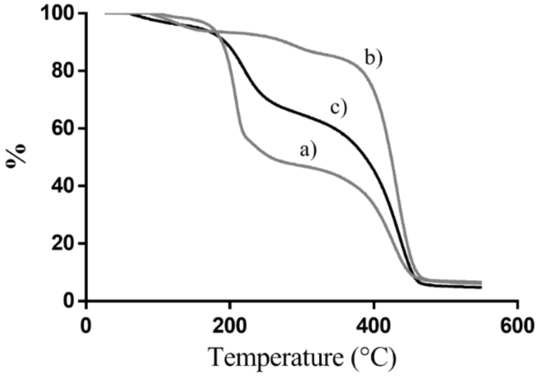

Figure 4. TGA thermograms: (a) P (HEMA-co-AI), (b) P (HEMA-co-AA) and (c) P (HEMA-co-NVP)

Hydration capacity of P(HEMA-co-AI), P(HEMA-co-AA) and P(HEMA-co-NVP)

The obtained copolymer gels are transparent, with a soft consistency and slightly elastic. On the contrary, in its dehydration state (xerogel) they show stiffness, hardness and turn into white color as it can be seen in Figure 5.

The hydration capacity in distilled water for the three HEMA-based copolymers with 0.3 and 0.9 mol% of MBA is also shown in the Figure 5. In general, the hydration in water increased in function of time until reach the equilibrium, in a total period of 5 h. Basically, the water interacts with the hydrophilic groups of the copolymers (-COOH, OH- and -CONH) mainly by hydrogen bonds, thus allowing its diffusion between the polymeric chains of the material.

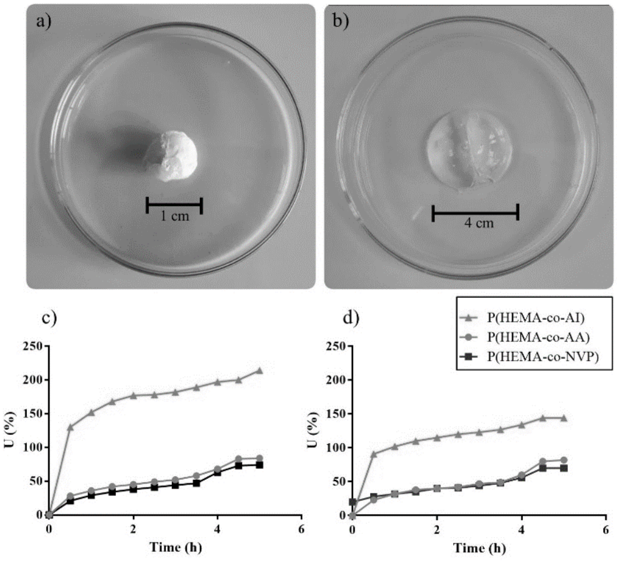

Figure 5. Copolymer of p(HEMA-co-AA) with 0.3 mol% MBA in two states: a) xerogel, b) hydrogel hydrated in water after 5 h. c) hydration capacity (U%) depending on the time of 0.1 g of hydrogel for systems with 0.3 mol% MBA, d) hydration capacity (U%) depending on the time of 0.1 g of hydrogel for systems with 0.9 mol% MBA.

The observed U% values of the hydrogels prepared with same amount of crosslinker depends on the hydrophilicity and amount of the functional groups present in the structure. P(HEMA-co-AI) and P(HEMA-co-AA) hydrogels contain same functional groups of –COOH, however AI has two and AA only one –COOH per repeat unit in the polymer. For this reason P(HEMA-co-AI) can swell more than P(HEMA-co-AA) in the same conditions. In the case of P(HEMA-co-NVP), NVP unit has tertiary amides which also could interact with water reaching lower hydration capacity compared with P(HEMA-co-AI), but similar compared to P(HEMA-co-AA).

On the other hand, the amount of crosslinker used in the preparation of the hydrogels can affect the hydratation capacity. The results showed that P(HEMA-co-AI), P(HEMA-co-AA) and P(HEMA-co-NVP) prepared with 0.3 mol% of MBA, the hydration values (U%) at the equilibrium are 214%, 84% and 74% respectively. For P(HEMA-co-AI), P(HEMA-co-AA) and P(HEMA-co-NVP) prepared with 0.9 mol% of MBA, the hydration values (U%) at the equilibrium are 144%, 82% and 70% respectively. Increasing the crosslinker amount in the synthesis produce a denser network polymer, reducing the free volume available for interaction with water molecules and therefore decreasing the hydration capacity for hydrogels with 0.9 mol% of MBA.

Effect of pH on hydration capacity

The maximum hydration capacity of hydrogels in function of pH is shown in Figure 6. At pH 9, a considerable increase in the hydration of hydrogels constituted by carboxylic acids was exhibited, reaching U% values of 400% and 250% for P(HEMA-co-AI) and P(HEMA-co-AA) respectively, which were prepared with 0.3 mol% MBA. In the case of hydrogels prepared with 0.9 mol% MBA, similar behavior is observed reaching a maximum hydration capacity of 306% for P(HEMA-co-AI) and 200% for P(HEMA-co-AA). This swelling results are in concordance with previous experiments related to influence of amount of MBA on the hydration capacity.

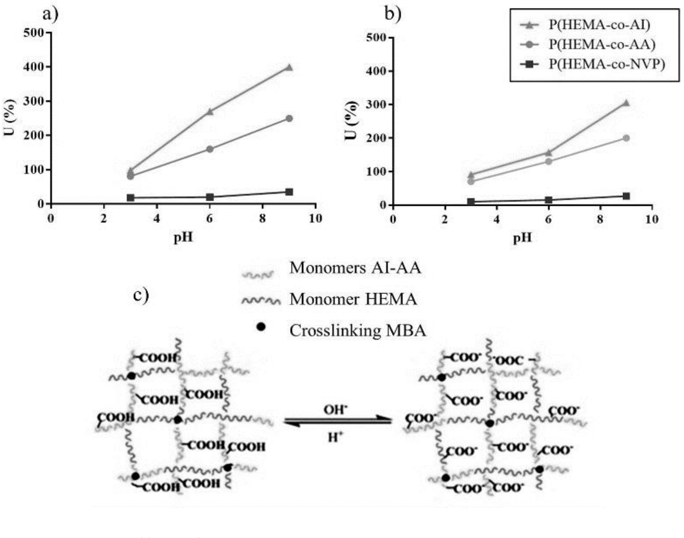

Figure 6. Effect of pH on hydration capacity: (a) hydrogels prepared with 0.3 mol% of MBA, (b) Hydrogels prepared with 0.9 mol% of MBA. (c) Schematic representation of the protonation-deprotonation of the -COOH groups in function of pH.

The dissociation constant of the monomers is reported in literature: pKa of (AI) = 3.85) [24] and pKa of (AA) = 4.3) [25]. Therefore, the observed behavior of increased hydration capacity to 400–306% for P(HEMA-co-AI) and 250-200% P(HEMA-co-AA), both prepared with 0.3 and 0.9 mol% of MBA, is the consequence of the ionizable groups of monomers AA and AI in the copolymer hydrogel. Increasing the ionization of the -COOH to -COO- groups from acid to basic pH. It leads to the separation of the polymer chains both by electrostatic repulsions between the negative charges, as well as by the breaking of the bridges of intramolecular hydrogen allowing thus an increase in the hydration of the material. For P(HEMA-co-NVP) (with both 0.3 and 0.9 mol% MBA), the hydration capacity exhibited was minimal with 35% and 27%, due to the presence of amides in their structure which are dissociated at a higher pH [25].

Effect of interfering salts on hydration capacity

The effect of the concentration of different salts on the hydration capacity is shown in Figure 7. Solvatation of the salts can affect the interactions between the copolymer and water and therefore the hydration of the copolymer hydrogel decreases. In addition, the decreasing of the hydration could be explained by the nature of the cation (Li^+, Na^+ and K^+) that can interact with the functional groups of polymer inducing a saturation in the internal network and increasing the repulsion forces between the aqueous solution and the hydrogel [26].

The obtained value of %U showed that the hydration of all the copolymers, prepared with 0.3 mol% of MBA, decreased dramatically by the presence of the minimum salt concentration (0.2 mol/L). In addition, the hydration of the copolymers decrease gradually as the salt concentration increase, compared to salt-free hydration as shown in Figure 5 c) and d). For copolymers prepared with 0.9 mol% of MBA, the same hydration behavior was observed in presence of different salts concentrations.

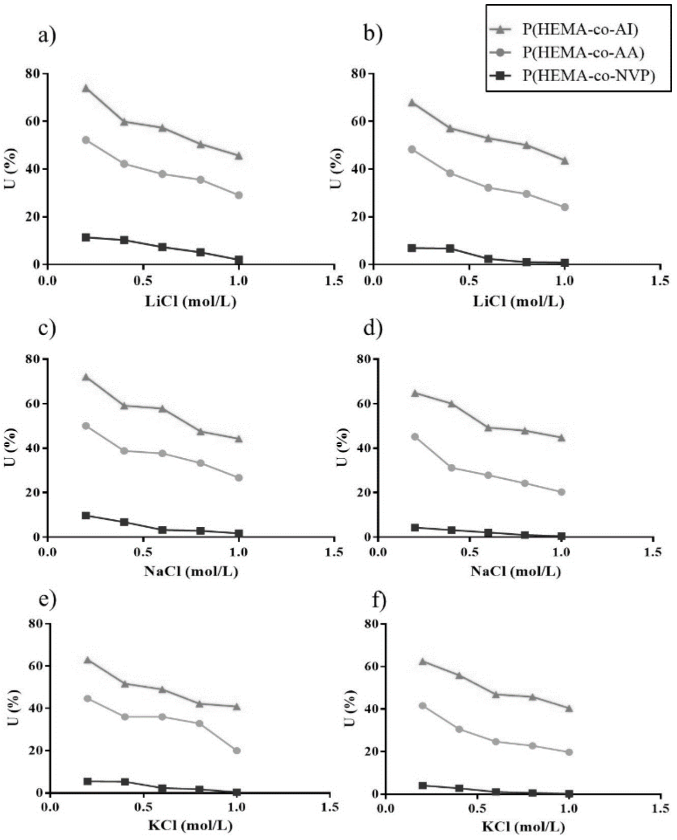

Figure 7. Effect of the concentration of different interfering salts (LiCl, NaCl and KCl) on the hydration capacity of the hydrogels with 0.3 mol% MBA (a, c, e) and 0.9 mol% MBA (b, d, f).

CONCLUSIONS

The synthesis via free radical polymerization is a simple, short and effective way for the preparation of functional hydrogels. Through FTIR characterization, it was possible to confirm the structural composition of these materials, constituted mainly by groups such as -OH, -COOH and CONR. TGA analysis showed the higher thermal stability of the copolymers.

Concerning to hydration capacity, the increase in the crosslinking agent (MBA) in the polymer synthesis produce a more rigid polymer with lower hydration capacity. In addition, it was confirmed that the copolymers with carboxylic acids reach a higher U% values than copolymers with amide functional groups.

The amount of carboxylic acid by repeating unit in the polymer was also important for hydration, reaching a maximum U% values of 400% for P(HEMA-co-AI) and 250% for (HEMA-co-AA) at pH 9.

The hydration of the studied copolymers is highly affected by the pH of the aqueous solution, being the carboxylic acid copolymer less hydrated in an acid medium and more hydrated in basic media. On the other hand, the increase in the concentration of salts in the solution increase the ionic strength, producing less water absorption.

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