Swelling Properties of CMC-g-Poly (AAm-co-AMPS) Superabsorbent Hydrogel

Ali Pourjavadi, Hossein Ghasemzadeh, Fatemeh Mojahedi

Polymer Research Laboratory, Department of Chemistry, Sharif University of Technology, Tehran 11365-9516, Iran

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ABSTRACT: A series of biopolymer-based superabsorbent hydrogels based on carboxymethyl cellulose has been prepared by free-radical graft copolymerization of acrylamide and 2-acrylamido-2-methylpropan sulfonic acid (AMPS) in aqueous solution using methylenebisacrylamide as a crosslinking agent and ammonium persulfate as an initiator. The effect of variables on the swelling capacity such as: acrylamide/AMPS weight ratio, reaction temperature, and concentration of the initiator and crosslinker were systematically optimized. The results indicated that with increasing the amount of AMPS, the swelling capacity is increased. FT-IR spectroscopy and scanning electron microscope analysis were used to confirm the hydrogel structure. Swelling measurements of the synthesized hydrogels in different salt solutions indicated considerable swelling capacity. The absorbency under load of the superabsorbent hydrogels was determined by using an absorbency under load tester at various applied pressures. A preliminary swelling and deswelling behaviors of the hydrogels were also studied. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3442–3449, 2009

Key words: Superabsorbent; carboxymethyl cellulose; hydrogel; acrylamide; 2-acrylamido-2-methylpropan sulfonic acid

INTRODUCTION

Superabsorbent hydrogels can absorb a large amount of liquid in such a way that the absorbed liquid is hardly removable even under some pressure.^{1,2} These materials have been reported to be very useful in many applications such as agriculture and horticul-ture,^{3,4} tissue engineering,^{5,6} biosensors and bioseparation,^{7,8} health care,⁹ and drug delivery systems.^{10–12} Hydrogels responding to external stimuli are often referred to as "intelligent" or "smart" hydrogels. These responsive hydrogels have become an important area of research and development in the field of medicine, pharmacy, and biotechnology.^{13–15} These materials can be actuated by a variety of stim-uli such as pH,¹⁶⁻¹⁸ temperature,¹⁹⁻²¹ salinity,^{22,23} electrical field,^{24,25} magnetic field,^{26,27} and antigens.^{28,29} Because of their unique properties, *i.e.*, biocompatibility, biodegradability, renewability, and nontoxicity, polysaccharides are the main parts of the natural-based superabsorbent hydrogels. Carboxymethyl cellulose (CMC) is an ionic ether of the cellulose with too many major commercial applications. It is a highly water-soluble anionic polysaccharide that is widely used in pharmaceuticals, cosmetics, and food industry.^{30–32} In this article, synthesis and characterization of a smart superabsorbent hydrogel from CMC-*g*-poly (AAm-*co*-AMPS) was reported. The effect of the reaction variables on the swelling properties as well as the salt and temperature sensitivity of the hydrogels were investigated in details.

EXPERIMENTAL

Materials

CMC sample (degree of substitution = 0.52) was purchased from Merck Co. Acrylamide (AAm, Fluka), 2-acrylamido-2-methylpropan sulfonic acid (AMPS, Merck), and ammonium persulfate (APS, Merck) were used without purification. Methylenebisacrylamide (MBA, Fluka) was used as received. All other chemicals were of analytical grade.

Hydrogel synthesis

CMC solution was prepared in a 1-L reactor equipped with mechanical stirrer and gas inlet. The reactor was placed in a water bath preset at 70°C. CMC (1.0 g) was dissolved in 35.0 mL degassed distillated water. After complete dissolution of CMC, various weight ratios of AMPS/AAm monomers were added to the CMC solutions and stirred (200 rpm) for 15 min. Then, MBA crosslinker (0.03– 0.21 g dissolved in 5 mL water) was added to the reaction mixture. APS initiator (0.03–0.3 g dissolved in 5 mL water) was then added to the CMC solution

Correspondence to: A. Pourjavadi (purjavad@sharif.edu).

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and the reaction mixture was continuously stirred (300 rpm) for 1 h under atmospheric condition. Then, ethanol (300 mL) was added to the gel product while stirring. After complete dewatering for 48 h, the hardened superabsorbent particles were filtered, washed with fresh ethanol (3 \times 200 mL) and dried in an oven at 50°C for 12 h.

Measurement of water absorbency

The accurately weighed CMC-*g*-poly (AAm-*co*-AMPS) superabsorbent hydrogel (0.2–0.5 g) with average particle sizes between 40 and 60 mesh (250–350 μ m) was immersed in glass cups full of distilled water at 25°C. Then, the unabsorbed water was screened with 160 mesh nylon bag and the bag was weighed to determine the weight of the swollen gel. The water absorbency (*Q*) was calculated using the following equation:

$$Q = (W_s - W_d)/W_d \tag{1}$$

where, W_s and W_d are the mass of swollen gel and dry gel, respectively. The water absorbency of the hydrogels in aqueous solutions of the salts (0.15*M* of NaCl, CaCl₂, and AlCl₃) was determined in a similar manner.

Deswelling water ratio of the hydrogels was evaluated from the following equation:

Deswelling water ratio(%) =
$$Wt/Wt_0 \times 100$$
 (2)

where Wt_0 and Wt are the initial weight of the fully swollen sample and the weight of sample at the deswelling time *t*, respectively.

Gel and sol content determination

The weighed crude product particles were dispersed in distilled water to swell completely. The hydrogel was washed with distilled water frequently and then filtered, dewatered in excess ethanol for 48 h, and dried at 50° C for 12 h. The soluble content (sol) was calculated as the weight loss of the initial crude product.

Measurement of absorbency under load

A macroporous sintered glass filter plate (porosity 0, d = 80 mm, h = 7 mm) was placed in a Petri dish (d = 118 mm, h = 12 mm), and a weighed dried hydrogel sample (0.9 ± 0.01 g) was uniformly placed on the surface of a polyester gauze located on a sintered glass. A cylindrical solid load (Teflon, d = 60 mm, variable height) is put on the dry hydrogel particles while it can be freely slipped in a glass cylinder (d = 60 mm, h = 50 mm). Desired load (applied pressure 0.3 psi) was placed on the hydrogel sample (Fig. 12). Then, 0.9% saline solution was added so that the liquid level was equal to the height of the sintered glass filter. Whole of the set was covered to prevent surface evaporation and probable change in the saline concentration. After 180 min, the swollen particles were weighed again, and absorbency under load (AUL) was calculated using eq. (1).

Morphologies of the hydrogels

Scanning electron microscopy (SEM) of the dry samples of the superabsorbent hydrogels was performed to visualize the hydrogel pores. The microstructure of the hydrogel was imaged using an SEM (Philips, XL30) operated at 25 kV.

FT-IR analysis

FT-IR spectra of samples in the form of KBr pellets were recorded using an ABB Bomem MB-100 FT-IR spectrophotometer.

RESULTS AND DISCUSSIONS

Synthesis and spectral characterization

Graft copolymerization of AAm and AMPS onto CMC were carried out in the presence of MBA as a crosslinking agent, and APS as an initiator. The persulfate decompose on heating and produces sulfate anion radicals that abstract hydrogen atoms from the hydroxyl groups of CMC backbones. This redox system results in active centers capable of radically initiating the polymerization of AAm and AMPS, leading to a graft copolymer. Since a crosslinking agent (MBA) is present in this system, the copolymer comprises a crosslinked structure. Infrared spectroscopy was carried out to confirm the chemical structure of the superabsorbent hydrogel. FT-IR spectra of CMC and CMC-g-poly (AAm-co-AMPS) superabsorbent are shown in Figure 1. Figure 1(a) shows the characteristic absorption bands of CMC at around 1611 cm⁻¹ attributed to carboxylate



Figure 1 FT-IR spectra of (a) CMC, (b) CMC-g-poly (AMPS-*co*-AAm) hydrogel.

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stretching and bending modes. The broad band at 3200–3500 cm⁻¹ was due to stretching mode of the hydroxyl groups of the polysaccharide. The CMC-*g*-poly (AAm-*co*-AMPS) comprises a CMC backbone that carries carboxamide functional groups that are evidenced by a new characteristic absorption band at 1660 cm⁻¹ [Fig. 1(b)]. A new characteristic absorption band in the spectrum of the hydrogel at 1685 cm⁻¹ may be attributed to the C=O stretching mode of amide groups and verifying the grafting of AAm and AMPS onto CMC. The stretching band of -NH overlapped with the -OH stretching band of the CMC portion of the copolymer.

Effect of crosslinker concentration on the swelling

Crosslinker have to be present in a hydrogel to prevent dissolution of the hydrophilic polymer chains in an aqueous medium. Efficiency of crosslinker incorporation controls the overall crosslink density in the final hydrogel. The effect of the extent of crosslinking on the water absorbency and the gel content values of CMC-g-poly (AAm-co-AMPS) hydrogels are shown in Figure 2. In this reaction series, the AAm/AMPS weight ratio in monomer feed was chosen to be 1. The results indicate a well-known behavior of swelling-[MBA] power law relationship so that the higher the crosslinking concentration, the lower the water absorbency capacity. Higher crosslinker concentration produce more crosslinked points in polymeric chains and increases the extent of crosslinking of the polymer network, which results in less swelling. Similar observations have been reported in the literature.^{33,34} Maximum swelling capacity of the hydrogel was achieved at 0.008 mol/L of MBA concentration. According to the data in Figure 2, a sample of 0.01M of MBA provides the best values of swelling and gel



Figure 2 Effect of the crosslinker concentration on water absorbency and gel content of the superabsorbent hydrogel (reaction conditions: AMPS/AAm weight ratio = 1.0, APS = 0.008 mol/L, 70° C, 60 min).

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content. At lesser than the latter amount, the gel content is diminished appreciably because of the formation of very loosely crosslinked networks, resulting in highly swollen hydrogels with very low gel strength.

Figure 3 shows SEM photographs of the superabsorbent hydrogel obtained under different conditions. Figure 3(a,b) shows the influence of the crosslinking agent on the porosity. The porosity of the hydrogel particles in optimized Sample 3a (with MBA = 0.008 mol/L) is greater than that in Sample 3b (with MBA = 0.020 mol/L). These observed morphologies are confirmed by the fact that the equilibrium water absorbency in Sample 3a (1332 g/g) was higher than in Sample 3b (544 g/g).

Effect of the reaction temperature on the swelling

To study the influence of temperature on the water absorbency of the CMC-g-poly (AAm-co-AMPS) hydrogels, the grafting of monomers onto CMC were carried out at different temperatures, ranging from 65 to 90°C. As shown in Figure 4, water absorbency of the hydrogels is increased by increasing the temperature up to 70°C and then it is decreased. At 70°C, maximum water absorbency (1386 g/g) was obtained. Increase in the water absorbency and the gel content could be attributed to the following factors: increased number of free radicals formed on the CMC backbone, enhanced diffusion of monomers and initiator onto backbone structure, and increased mobility of the monomers molecules and their higher collision probability with the macroradicals. However, decreasing in water absorbency beyond 70°C can be attributed to the higher chain-radical termination at higher temperatures. The slight loss of gel content at higher temperature may be attributed to the rapid gelation of the system that prevents the monomers and polysaccharide to fully participate in the crosslinking polymerization.

Effect of APS initiator concentration on the swelling capacity

The effect of the initiator concentration on the water absorbency and the gel content of the hydrogel were studied by varying the concentration of APS from 0.003 to 0.026 mol/L. As shown in Figure 5, the water absorbency and the gel content are increased initially with increasing the initiator concentration up to 0.005 and 0.019 mol/L, respectively, but they are decreased later. Maximum swelling (1375 g/g) was obtained at 0.005 mol/L of initiator concentration. Increase in the water absorbency and the gel content with increasing APS concentration may be attributed to an increase in the concentration of free radicals produced by decomposition of APS. The subsequent decrease in the water absorbency and the gel content may be attributed to:



Figure 3 SEM photographs of the superabsorbent hydrogel with different crosslinker concentrations (a, MBA = 0.008 mol/L; b, MBA = 0.020 mol/L) and with different AMPS/AAm weight ratio (c, AMPS/AAm weight ratio = 1/4; d, AMPS/AAm weight ratio = 2/1).

(a) an increase in the importance of the terminating step reaction which in turn increases the crosslink density³⁵; (b) free-radical degradation of the CMC substrate. On other word, free-radical degradation of

CMC can take place at high APS levels. A similar observation has been reported in connection with the degradation of carrageenan³⁶ and chitosan^{37,38} with potassium persulfate.



Figure 4 Effect of the reaction temperature on water absorbency and gel content of the superabsorbent hydrogel (reaction conditions: MBA = 0.008 mol/L, AMPS/AAm weight ratio = 1.0, APS = 0.008 mol/L, 60 min).



Figure 5 Effect of initiator concentration on water absorbency and gel content of the superabsorbent hydrogel (reaction conditions: MBA = 0.008 mol/L, AMPS/AAm weight ratio = $1.0, 75^{\circ}$ C, 60 min).

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Figure 6 Effect of AMPS/AAm weight ratio on water absorbency and gel content of the superabsorbent hydrogel (reaction conditions: MBA = 0.008 mol/L, APS = 0.008 mol/L, 75°C, 60 min).

Effect of monomer ratio on the swelling capacity

The swelling capacity of the hydrogels prepared with various ratios of the monomers is shown in Figure 6. The presence of the ionic groups in polymer chains results in increasing of swelling because the ionic groups are more strongly solvated than nonionic groups in the aqueous medium. The highest swelling capacity was obtained at 2/1 weight ratio of AMPS/ AAm. The increase in the water absorbency of the CMC-g-poly (AMPS-co-AAm) hydrogels with increasing the AMPS weight ratio can be attributed to the charge repulsion of sulfonate groups in the grafted AMPS. The subsequent decrease in water absorbency of the hydrogel after initial increase can be attributed to the low reactivity of the AMPS monomer. In fact, the monomer grafting onto CMC is decreased with increasing the AMPS/AAm weight ratio; therefore, the swelling capacity is decreased. For the gel content variation shown in Figure 6, it can be proposed that, comparing with AAm, AAm-AMPS tends to react with the crosslinker less readily. Consequently, the gel content is dramatically reduced at high AMPS/AAm weight ratio.

Figure 3(c-d) shows the SEM photographs of the superabsorbent hydrogels obtained with various ratios of the monomers. These images clearly show a porous structure in the hydrogels. As shown in these figures, the hydrogels with 2/1 weight ratio of AMPS/AAm is more porous than that in the hydrogels with 1/4 weight ratio of AMPS/AAm. These observed morphologies are confirmed by the higher equilibrium water absorption in Sample 3c (1375 g/g) than that in Sample 3d (700 g/g).

Effect of pH on swelling

The swelling behavior of the superabsorbent hydrogel was studied at various pH values between 1.0 and

13.0 at room temperature (Fig. 7). To prepare the pH media, standard HCl (pH 1.0) and NaOH (pH 13.0) solutions were diluted with distilled water to reach the desired acidic and basic pHs, respectively. The swelling of the superabsorbent hydrogels increased with increasing the pH from 1 to 7, but it is decreased in the pH range between 7 and 13. This can be attributed to the change in the ionic strength of the medium and the effect of the counter ions that shielded the charge of the $-COO^-$ and $-SO_3^-$ cations so prevent efficient repulsion.³⁹ The maximum water absorbency of the hydrogel was achieved at pH 7. At this point, nearly all of the -COOH and -SO₃H groups are converted to -COO⁻ and -SO₃⁻ resulting in high anionanion repulsion and high swelling capacity. The osmotic pressure difference between the internal and external solutions of the network is balanced by the swelling of the gel. At higher pH, the Na⁺ cations from NaOH shielded the -COO⁻ and -SO₃⁻ groups and prevented the perfect anion–anion repulsion.

Swelling behavior in salt solutions

In salt solutions, the osmotic pressure difference between the gel and aqueous phases decreases. Therefore, the amounts of absorbency will decrease significantly. This undesired swelling loss is often attributed to the "charge screening effect" of the additional cations that cause a none perfect anion–anion electrostatic repulsion.⁴⁰ With multivalent cations, "ionic crosslinking" at the surface of particles causes an appreciably decrease in swelling capacity. To study the effect of cation radius on the swelling behaviors, the equilibrium swelling absorbency was measured in a series of 0.15*M* chloride salt solutions of Li⁺, Na⁺, K⁺, Cs⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, and Al³⁺(Fig. 8). It seems that intermolecular interaction between the carboxylate



Figure 7 pH-dependent swelling of the superabsorbent hydrogel (reaction conditions: AMPS/AAm weight ratio = 2.0, MBA = 0.008 mol/L, APS = 0.008 mol/L, 75° C, 60 min).



Figure 8 Swelling capacity variation of the superabsorbent hydrogel in saline solutions (0.15*M*), (reaction conditions: MBA = 0.008 mol/L, AMPS/AAm weight ratio = 2.0, APS = 0.008 mol/L, 75° C, 60 min).

group of CMC with large cations, such as K⁺ and Cs⁺ is grater than the small cation such as Li⁺ and Na⁺. Thus, CMC has the higher affinity for crosslinking with K⁺ and Cs⁺ among monovalent cations of the studied salt solutions. As a result, swelling of the synthesized hydrogels in KCl and CsCl solutions is lower than in LiCl and NaCl. Similar behavior was reported for carrageenan by Tako et al.⁴¹ In addition, as shown in Figure 8, multivalent cations decrease the swelling capacity considerably. The decrease was attributed to the complexing ability of the carboxylate groups that induced interchain complex formation. Consequently, the network crosslink density is enhanced.⁴² With increasing the charge of these cations, the degree of crosslinking is increased. As a result, swelling capacity is decreased considerably (NaCl > CaCl₂ > AlCl₃).

Effect of temperature on swelling

In an aqueous system, the temperature sensitivity of a hydrogel is closely related to the temperature dependence of the polymer-water and polymer-polymer interactions. In other word, the temperature sensitivity of polymeric gels is associated with the temperature dependence of hydrogen bonding and hydrophobic interactions.43 At lower temperatures, water molecules in the vicinity of hydrophobic polymer chains are highly hydrogen bonded. Because these hydrogen-bonding interactions decrease the free energy of mixing considerably, the polymer swell in water at low temperatures. At higher temperatures, the hydrogen bonds weaken, so the contact between water and hydrophobic surfaces, i.e., the hydrophobic interaction increases.⁴⁴ As a result, on heating a polymer gel, a transition from swollen to shrinking state occurs.

The swelling behavior of CMC-g-poly (AAm-co-AMPS) superabsorbent hydrogels was studied at different temperatures. Figure 9 shows the influence of the temperature on the swelling behavior of CMC-gpoly (AAm-co-AMPS) hydrogels at various AMPS content. It can be seen that the gels are swollen at low temperatures, whereas they are shrunken at high temperatures. Thus, the swelling ratios of the hydrogels decreased with increasing the temperature of medium. Higher equilibrium swelling ratios is obtained at constant temperature by increasing the AMPS content of the gel structure. This behavior can be attributed to the presence of AMPS as a strong electrolyte ionic comonomer and a temperaturesensitive monomer in the polymer network. The sulfonate groups in AMPS have an important role in the formation of hydrogen bonding. Figure 9 also shows that with increasing the AMPS content in the hydrogel the temperature sensitivity is increased.

Swelling and deswelling kinetics

A preliminary study was conducted on swelling kinetics of the superabsorbent hydrogels. Figure 10 represents the dynamic swelling behavior of the CMC-*g*-poly (AMPS-*co*-AAm) superabsorbent hydrogels with various AMPS/AAm weight ratios. Initially, the rate of water uptake sharply increases and then it begins to level off. The equilibrium swelling was achieved after 30 min. A power law behavior is obvious from Figure 10. The data may be well fitted with the following Voigt-based equation⁴⁵:

$$S_t = S_e (1 - e^{-t/\tau})$$
 (3)

where S_t (g/g) is swelling at time t, S_e is equilibrium swelling (power parameter, g/g), t is time (min) for swelling S_t , and τ (min) stand for the "rate parameter."



Figure 9 Effect of temperature on swelling behavior of the superabsorbent hydrogel (reaction conditions: MBA = 0.008 mol/L, APS = 0.008 mol/L, $75^{\circ}C$, 60 min).

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Figure 10 Effect of AMPS/AAm weight ratio on swelling kinetics of the superabsorbent hydrogel (reaction conditions: MBA = 0.008 mol/L, APS = 0.008 mol/L, 75° C, 60 min).

The rate parameters are found to be 6.8, 6.1, and 5.2 min for the superabsorbent hydrogels with AMPS/ AAm weight ratio of 0.2, 1.0, and 2.0, respectively.

To quantify the degree of deswelling, the deswelling water ratios of the hydrogels were measured using eq. (2). Figure 11 shows the ratio of the remaining water as a function dependent on the temperature. As shown in this figure, the deswelling water ratio of the hydrogels indicate a weight reduction of about 20% at room temperature and about 50% at 50°C from its original weight after 15 h. As a result, the hydrogel have a good potential to hold water at room temperature.

Absorbency under load

Although the values of load-free absorbance (free swelling) are usually given in the original literature,



Figure 11 Deswelling water ratio of the hydrogels at 25 and 50° C (reaction conditions: MBA = 0.008 mol/L, AMPS/ AAm weight ratio = 2.0, APS = 0.008 mol/L, 75°C, 60 min).



Figure 12 AUL values for the superabsorbent hydrogels with various AMPS/AAm weight ratio in saline solution (0.9% NaCl) at the applied pressure 0.3 psi (reaction conditions: MBA = 0.008 mol/L, APS = 0.008 mol/L, 75%C, 60 min).

the more real values, i.e., AUL, are often reported in the technical data sheets and patent articles.⁴⁶ Since AUL values are logically changed with mechanical strength of the swollen gel proportionally, AUL can be considered as a measure of the gel strength of the superabsorbent hydrogels. So, many efforts have been made to achieve superabsorbents having higher AUL or higher strength of the swollen gel.47,48 To determine the swollen gel strength, we used the superabsorbent hydrogels that were synthesized under the optimum reaction conditions (MBA = 0.008 mol/L, APS = 0.008 mol/L, 75°C) with various AMPS/AAm weight ratio in saline solution (0.9% NaCl). As shown in Figure 12, the minimum time needed for the highest AUL in the case of each load is estimated to be 180 min. After this time, the AUL values were almost unchanged. In addition, the curves exhibit that AUL decreases with increasing the amount of AAm. At the applied pressure (0.3 psi) maximum swelling was found to be 22, 17, and 13(g/g) for the superabsorbent hydrogels with AMPS/AAm weight ratio of 2.0, 1.0, and 0.2, respectively. These experimental results show that there is a similar behavior in the values of load-free absorbance (free swelling) and the AUL. Similar observations were reported in our previous works.^{49,50}

CONCLUSION

The CMC-*g*-poly (AAm-*co*-AMPS) superabsorbent hydrogel was synthesized by graft copolymerization of AAm and AMPS onto CMC backbones under normal conditions of atmosphere. The effect of reaction parameters, such as concentration of crosslinker (MBA), initiator (APS), AMPS/AAm weight ratio, and reaction temperature on the swelling behavior of the superabsorbent hydrogel was investigated. The maximum water absorbency (about 1400 g/g) was achieved under the optimum reaction conditions that found to be: AMPS/AAm weight ratio = 2.0, MBA = 0.008 mol/L, APS = 0.008 mol/L, and reaction temperature 75°C. Regarding swelling ratios, at various temperatures it is shown that swelling decreases with increasing the temperature. In addition, with increasing the AMPS content in the hydrogel the temperature sensitivity is increased. Swelling measurements of the synthesized hydrogels in different salt solutions indicated appreciable swelling capacity, especially in sodium chloride solution. The deswelling behavior of the hydrogels was also investigated and the result indicate that the hydrogel have a good potential to hold water especially at room temperature. The morphological changes in the superabsorbent structure with different concentrations of crosslinkers and with different AMPS/ AAm weight ratio are in good agreement with the swelling behavior of the hydrogels. These hydrogels may find applications in biomedical field due to the super swelling in water as well as the temperatureresponsive character.

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