Effect of temperature and pH on swelling behaviour of carboxymethyl cellulose-acrylic acid hydrogel

Antonio Cruz, R.*[1], Rivera Armenta, J. L.[1], Rivas Orta, V.[1], Mendoza Martínez, A. M.[1], Chávez Cinco, M. Y.[1], Ramírez Mesa, R.[2], Cruz Gómez, M. J.[3]
[1] División de Estudios de Posgrado e Investigación del Instituto Tecnológico de Ciudad Madero, Juventino Rosas y Jesús Urueta S/N, Col. Los Mangos, Ciudad Madero, Tamaulipas, 89440
[2] Instituto Tecnológico de Minatitlán, Dpto. Posgrado
[3] Universidad del País Vasco, Bilbao, España
e-mail: rantonio70@yahoo.com

1. Abstract

The swelling behavior of carboxymethyl cellulose–poly (acrylic acid) hydrogels at different pH and temperatures was studied. The absorption increased for the first 24 hours until degree swelling maximum (192 hours). Three carboxymethyl cellulose–poly (acrylic acid) ratios were studied and when increasing carboxymethyl cellulose amount swelling decrease, because poly (acrylic acid) is a hydrophilic polymer. Three different levels of crosslinking agent were studied. Highest swelling capacity was found at pH 2 and 30ºC. All samples were characterized by means of infrared spectroscopy (FTIR). Characteristic absorbance peaks for both materials were found, showing the presence of carboxymethyl cellulose and poly (acrylic acid) on hydrogel.

2. Introduction

Super absorbent polymers have become an important component of many products due to their use in biomedical and pharmacobiologic fields such as personal hygiene items. Hydrogels are an example of such polymers since they are crosslinked materials capable of trapping a very large amount of water without being dissolved. [1]

Poly (acrylic acid) (PAA) is a polyelectrolyte polymer able to form ions when subjected to an aqueous environment causing considerable volume swelling due to Hydrogen Bridge or covalent bond formation. This property is an important advantage for hydrogels made from poly (acrylic acid) and must be considered. PAA is not toxic and is very sensitive to temperature and pH changes.

On the other hand, cellulose derivates have high rigidity; some can swell and be soluble in water or solvents depending on the extent of their degree of substitution. They can provide biodegradable character to any material when they are mixed with other materials since they are polysaccharide derivates. They can also enhance physical hydrogel properties.

Therefore, a study of chemically crosslinked acrylic acid with carboxymethyl cellulose (CMC) was carried out in order to see the impact of cellulose derivative on hydrogel properties and determine a probable application of the material as controlled drug release system. PAA/CMC hydrogels was prepared by chemical crosslinking with glutaraldehyde (GA) and N,N´-methylene bisacrylamide (N´N-MBA) using potassium persulfate (KPS) as initiator and hydrochloric acid (HCl) as catalyst, in aqueous solution. All samples were characterized by FTIR spectroscopy and swelling behavior at different temperatures and different pH values were measured.

3. Experimental Conditions

3.1 Synthesis of PAA/CMC hydrogels

As suitable examples of hydrogels, we have chosen the hydrogels of PAA/CMC with composition ratios of 75/25, 50/50, 25/75. Hydrogels composed of PAA and CMC were prepared by free radical polymerization. For the CMC the GA (2.5 X 10^{-3} M) and HCl (1.0 x 10^{-2} M) were used as crosslinker and catalysts respectively. The AA was crosslinked by using N,N´-MBA and KPS as initiator. Percentage of KPS and MBA were changed and tested between three values: 1%, 3% and 5%wt for KPS and 1%, 3% and 5%wt for MBA. Polymerization process was carried out under inert atmosphere (N_2) to avoid oxidation. The solution was heated to 80ºC with constant stirring for 30 minutes. GA (1 wt%) and MBA (3 wt%) were used as cross-linker for each hydrogels. KPS as initiator (1 wt% of total AA monomer) and HCl as catalyst were also added to the mixture and placed at 80ºC temperature bath for 3h following the procedure given elsewhere [2-4] with minor changes. The mixture was then poured into a small Petri dish to obtain a film by slow drying at 60ºC for one week. Films were stored in an open dish overnight at 50ºC to allow solvent evaporation which led to their flexibility. Xerogels films were washed with water several times in order to eliminate the water soluble impurities and un-reacted monomer.

3.2 Swelling behavior

Hydrogels swelling was done at three different temperatures; 30, 40 and 50°C, and at three different pH values (2, 7 and 13). Completely dried hydrogels samples were cut into pieces and weighed until obtained 400 mg. Afterwards, each sample was placed in a glass vial with a lid; the sample was left to swell in a solution at the desired pH (2, 7 and 13) and constant temperature (30, 40 and 50º C). The water absorbed in the hydrogels films after swelling was calculated from the relation:

$$\% \text{ Swelling } (W_C) = [(W_S - W_D) / W_D)] \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where W_C is the hold water in percentage absorbed by the hydrogel film after 288 hours swelling, and W_S and W_D are hydrogel film weights after and before swelling, respectively.

4. Discussions and Results.

The infrared spectra of samples of PAA/CMC are shown in the figure 1. Spectrum of the films with 75PAA/25CMC and 25PAA/75CMC proportion shows the characteristic stretching absorptions of PAA and CMC. Figure 1(a) at 3234 cm^{-1} shows a wide pronounced corresponding to OH bending from COOH group that posse PAA. At 3590 cm^{-1} a weak band appears due to υOH group free from CMC. The presence symmetric stretching of the carbonyl group (C=O) is shown at 1716 cm^{-1} and the C-O-H bending corresponding to pendant group (COOH) of PAA is shown at 1414 cm^{-1}. By the way, at 1044 cm^{-1} a band appears due to υCOC of CMC, we can see a peak little around 1416 cm^{-1} corresponding to movement δCOONa and at 1600 cm^{-1} exist a peak due to υCOONa from CMC, too is observed around 2900 cm^{-1} a peak little corresponding to υCH. Figure 1 (b) present the same bands, but exist an increment and decrement in some bands due to PAA and CMC concentration.

Figure 2 showed the effect of pH on the %swelling of the PAA/CMC hydrogels tested at 30ºC and different pH values with 1% KPS and 3%MBA. In this test, the quantity of water absorbed by the PAA/CMC films with 25/75 composition ratio was found to be the highest with respect to the other compositions, indicating that CMC predominates in the matrix exhibiting superabsorbent characteristics. The films respond much better when were placed in acid solutions due to the presence of Na cations in CMC, which allowed ionic bonds with anions present in acid solutions. It is worth mentioning that the hydrogels which have maximum absorption have 3% MBA. If crosslinking density is higher and the free spaces inside the three-dimensional hydrogel are lower, the Cl ions (Cl^-) are bigger than these spaces.

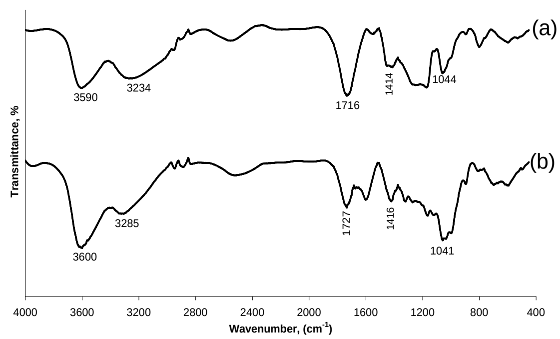

Figure 1. FTIR Spectra of PAA/CMC hydrogel using 1%wt KPS and 3%wt MBA for two rates: (a) 75PAA/25CMC and (b) 25PAA/75CMC

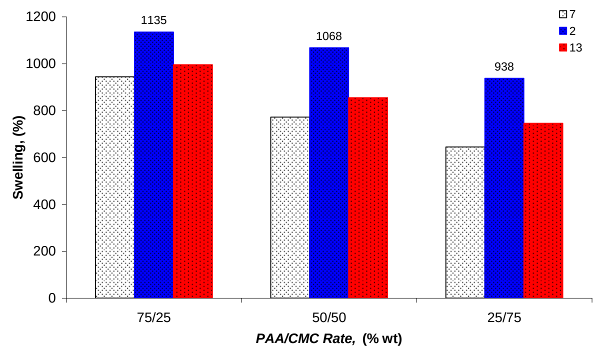

Figure 3. Swelling behavior of PAA/CMC hydrogel at 30ºC using 1%wt KPS and 3%wt MBA to pH different

5. Conclusion

PAA and CMC were crosslinked to different concentrations of MBA and KPS in order to observe changes in their properties. The characterization by means FTIR indicates the presence of the poly (acrylic acid) crosslinking with carboxymethyl cellulose. PAA/CMC hydrogels showed that the best temperature for water absorption was 30° C and CMC showed more compatibility with acid ions (Cl^-) in acid solution due to Na^+ cations which are present in this derivate, so that, the better pH was 2.

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