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SWELLING KINETIC OF HYDROGELS FROM METHYL CELLULOSE AND POLY(ACRYLAMIDE)

CINÉTICA DE HINCHAMIENTO DE HIDROGELES A PARTIR DE METIL CELULOSA Y POLI(ACRILAMIDA)

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Abstract

The poly (acrylamide) (PAAm) and methyl cellulose (MC) hydrogels were prepared with a crosslinker using N, N'-methylene bisacrylamide (NNMBA) and glutaraldehyde (GA). In order to do this, it was necessary to modify the percentages of catalyst (potassium persulfate, KPS) and crosslinker (NNMBA) for poly (acrylamide). To evaluate their maximum degree of swelling and to determine the swelling kinetics, the quantity of fluids absorbed by films was measured at different temperatures (20, 30, and 40°C) and pH's (acidic, basic, and neutral). According to the results obtained from the experiment, the most suitable temperature and pH were 30°C and neutral, conditions under which the highest swelling values were obtained. In the kinetic study, during the first hours, a first order kinetic (Fick Model) was observed. The results were non–Fickian, revealing that the chain's diffusion and relaxation processes occur at the same time during the absorption of the solution. For longer periods of time, with the exception of a 40 °C temperature (where the first order kinetic was identified), a second order kinetic was observed (Schott Model), indicating that there is no polymeric chain relaxation, but rather, contraction and collapse of the material. The relaxations of the polymer chain were observed after swelling via SEM pictures.

Keywords: swelling kinetic, hydrogels, methyl cellulose, poly (acrylamide).

Resumen

Los hidrogeles de poli(acrilamida) (PAAm) y metil celulosa (MC) fueron preparados utilizando N, N-Metilenbisacrilamida (NNMBA) y glutaraldehído (GA). Para esto, fue necesario para modificar los porcentajes de catalizador (persulfato de potasio, KPS) y entrecruzante (NNMBA) para la poliacrilamida. Para evaluar el grado máximo de hinchamiento y determinar la cinética de hinchamiento, la cantidad de fluidos absorbidos por las películas fue medido a diferentes temperaturas (20, 30, y 40°C) y el pH (ácido, básico y neutro). De acuerdo a los resultados obtenidos de la experimentación, la temperatura y pH fue de 30ºC y pH neutro, condiciones en las cuales el grado de hinchamiento fue el máximo. En los estudios cinéticos, durante las primeras horas se observa un modelo cinético de primer orden (Modelo de Fick). Los resultados fueron del tipo no-Fickiano revelando que el proceso presenta difusión y relajación de las cadenas al mismo tiempo que ocurre la absorción de la solución. Para periodos largos de tiempo, con excepción de 40ºC (cinética de primer orden), el orden de la cinética fue de segundo orden (modelo de Schott), indicando que el polímero no sufre una relajación en la cadena, por el contrario presenta una contracción y colapso del material. La relajación de la cadena polimérica fue observado después del hinchamiento por SEM.

Palabras clave: cinética de hinchamiento, hidrogeles, metilcelulosa, poli(acrilamida).

1. Introduction

Hydrogels are interesting materials that, due to their low toxicity and high biocompatibility properties, have become the center of attention for a large amount of research, mainly agricultural, biomedical, and pharmacobiological. The hydrogels are capable of collecting large quantities of water, maintaining their tridimensional structure, in quantities that depend on the hydrophilicity of the component polymers. This process is reversible, and dependent on the environmental conditions. The quantity of water that a macromolecular compound is capable of absorbing depends on the polarity of the

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chains, and the polymer's disposition in the space. These physicochemical properties of the hydrogels depend on knowing a series of parameters: chemical composition, degree of crosslinking, presence of functional groups, and variety of solvents that are used. The volume phase transition of a thermosensitive gel was first published by Hirokawa and Tanaka (1984) for N-isopropylacrylamide (NIPAAm) gels in water upon increasing the temperature to above 33°C. This thermal dependency is due to the *hydrophobic interaction* between the polymer network and the water. At high temperatures, the network deflates and becomes more ordered, but the excluded water molecules become less ordered. The gel's collapse increases the entire system's entropy. Some hydrogels experience transition phases upon varying the dissolvent's composition. An example of this type of behavior is observed in the swelling of NIPAAm and acrylamide (Aam) gels in dimethyl sulfoxide (DMSO) mixtures and water (Hirokawa *et al.*, 1984).

Ohmine and Tanaka (1982) and Brandon-Peppas (1990) observed the abrupt collapse of ionic networks in response to sudden changes in the swelling environment's ionic force. It wasn't until 1990 that Grimshaw *et al.* developed a quantitative model to treat the swelling kinetics of gels sensitive to pH. Frusawa and Hayakawaalsky (1998) devised the first work on the dynamic swelling of pH sensitive networks, establishing that the collapse and expansion of poly-gels (methacrylic acid) (PMA) occur reversibly, adjusting the environment's pH. Khare and Peppas (1995) studied the swelling kinetics of PMAAc and PAA, and observed that for these gels, they depend upon the pH and the ionic force.

Escobar *et al.* (2001) carried out an in vitro study and preliminary evaluation of poly (acrylamide-co-methacrylic acid) hydrogel biocompatibility. They determined that as the acrylamide percentage diminishes, the swelling diminishes, due to the strong hydrophilic character supplied by the acrylamide units in the copolymer chains. In addition, as the pH increases from 4.0 to 7.4, swelling is favored. The nature of water diffusion of said hydrogels has an anomalous character; that is to say that the diffusion processes and relaxation of chain tensions take place in the same time order, such that the greater the deviation with respect to the Fickian behavior, the more related the predomination of one process over the other is. For longer times, the swelling process is not governed by the diffusion, but rather by the relaxation, of the polymeric chains.

The hydrogel studied is made of polyacrylamide (PAAm) and methyl cellulose (MC). The polyacrylamide hydrogels are transparent, with poor mechanical properties and are capable of retaining a great quantity of water depending on the percentage of crosslinking agent. An important advantage is that they are chemically inert and relatively stable under the physiological conditions of pH and temperature. Those that were synthesized from methyl cellulose upon increasing the catalyst (HCl) and crosslinking agent (glutaraldehyde) increase the degree of crosslinking and present a lower swelling degree. One of the factors that contributes to environmental contamination is the use of large quantities of non-degradable synthetic polymers. The polymer conserves its hydrophilic nature provided by the polyacrylamide, and the cellulose derivative (methyl cellulose) gives the hydrogel a certain degradation. The purpose of the project is to determine the effect of temperature and pH on the MC/PAAm hydrogel's swelling kinetic, to substantiate the presence of the components, and to determine the thermal properties after swelling.

2. Experimental part.

2.1. Materials

Acrylamide (Aam, Aldrich 97%), methyl cellulose (MC, Aldrich, M_w=40000. substitution grade of 1.6-1.9, methoxy), glutaraldehyde (GA, Merck- Schuchardt at 25% weight in water), and crosslinking agent: N, N'-methylene-bis-acrylamide (NNMBA, Aldrich 99% purity), potassium persulfate (Fischer- Chemical), HCl (Productos Químicos de Monterrey), and double/distilled water.

2.2. Preparation of hydrogel

A polymeric solution at 5% weight in AAm and MC was prepared at the temperature of 80 °C undergoing 30 minutes of constant stirring. The AAm and MC weight ratios were varied (Table 1). Subsequently, the GA at 2.5×10^{-6} mol/mL and the HCl 2.25 x 10^{-1} mol/L were added. Both concentrations were taken from Park *et al.*, (2001); the crosslinker NNMBA and the $K_2S_2O_8$ at their respective weight percentage ratios were taken at the same conditions during a reaction time of 2 hours. The reaction time having elapsed, the mixture was placed in a petri dish to carry out the gelling at 40 ºC and obtain the film. In Table 1, the ratios for preparing films with a weight of 2 g are shown; said ratios of MC/PAAm and variations of initiator/crosslinker were selected for their swelling degree at room temperature, which was superior to 660%. Preliminary experiments demonstrated that the homogeneity depends on the percentage of polyacrylamide and cellulose derivates. When the PAAm percentages were greater than 20 wt%, the gel presented a non-homogeneous surface and the degree of swelling was under 500%.

Table 1. Ratios used to prepare films with 2 g.

Sample	% of MC	% of AAm	% Initiator	% Crosslinker
MC/PAAm 1	80	20	0.5 wt%	1.0 wt%
MC/PAAm2	90	10	1.0 wt%	0.5 wt%
MC/PAAm3	80	20	1.0 wt%	1.0 wt%

2.3. Swelling kinetic

For the swelling characterization, three types of solution were used: acidic (pH of 4), basic (pH of 10), and neutral (pH of 7, distilled water). The swelling tests were carried out at temperatures of 20, 30, and 40 ºC, using a heating bath with controlled temperature. First, 1.3 cm^2 pieces were cut from each film (using a Vernier) and were weighed. This weight is considered the initial weight or W_D. Each piece of a hydrogel was inserted into a vial inside the heating bath at each temperature, adding 0.01 g of solution (acidic, basic, neutral). The sample was weighed every 30 minutes for the first hour; afterward, every hour for the first 12 hours; and subsequently, every 24 hours until the sample stopped absorbing, the point at which there is desorption, or the swelling equilibrium is reached. The quantity of water retained inside the hydrogel in the equilibrium can be expressed mathematically in various forms (Katime *et al.*, 2004), as is mentioned next—hydration percentage or weight swelling index:

$$W_C\left(\%\right) = \frac{W_S - W_D}{W_D} \times 100 \qquad (1)$$

where: W_C (%) is the hydration percentage, W_S is the film's weight after swelling, and W_D is the weight of the dry film.

The swelling degree was calculated using the following equation, where D_h is the swelling degree:

$$D_h = \frac{\text{wet weight}}{\text{dry weight}} \qquad (2)$$

The adequate temperature over the maximum swelling degree is established by the gravimetric method in agreement with the maximum water retention and the determination of the water absorbed by the hydrogel. This was carried out using Equation 1; for all practical intents and purposes, *swelling degree* was used as a technical term for W_c.

In order to determine the nature of the water's diffusion toward the inside of the gel, the following equation was used:

$$\ln\left(W_t / W_{max}\right) = \ln k + n \ln t \qquad (3)$$

In this equation, W_t and W_{max} represent the quantities of water absorbed by the gel in the time t, and in the equilibrium; k is a constant characteristic of the system, and n is the diffusional exponent that takes the water's mode of transport into account. A value of $n = 0.50$ indicates a Fickian diffusion mechanism, while if it reaches $0.50 < n < 1$, it indicates that the diffusion is of a non-Fickian or anomalous type. In the special case in which n = 1, the transport mechanism is known by the name of Type II and is particularly interesting due to the fact that the solute's migration occurs at constant speeds and is purely controlled by the relaxation of the chains.

This equation is applied to the initial swelling states (when the density of the device does not vary)

observing linearity when the ln (W_t / W_{max}) is related in function of the ln t up to fractional swelling values less than 0.60 (Woerly *et al.*, 1996).

For the second kinetic order, the reciprocal of the swelling average (t / W_t) is related to the treatment time according to the following linear equation (Schott, 1992):

$$\frac{t}{W_t} = A + Bt \qquad (4)$$

In this equation, A and B are two coefficients with physical meaning which are interpreted in the following manner: for long treatment times, Bt » A and the pending B will be the reciprocal of the swelling in the equilibrium (B = $1/W_{max}$). On the contrary, at very short treatment times A » Bt can reject Bt, and in this case A is equal to the inverse of the initial swelling speed

$$\lim_{t \to 0}\left(\frac{dW}{dt}\right) = \frac{1}{A} \qquad (5)$$

Therefore, the ordinate at the origin (A) represents the inverse of the initial swelling.

2.4. Differential Scanning Calorimetry

For equipment, A TA Instruments model 2010 was used to research the behavior of hydrogels in a dry state after swelling. The sample quantity was approximately 10 mg. Two scans were carried out: the first scan at 10 °C/min, the second scan at 5°C/min, in the range of 0 ºC up to 120 ºC with a nitrogen flow of 20 ml/min.

2.5. Scanning Electromicroscopy

The surface morphologies of the hydrogels were examined in a dry state after swelling using the EOL JSM 5900 scanning electron microcopies with an operating voltage of 5 Kv.

3. Results and Discussion.

In this case, swelling tests were carried out on the three ratios at different pH's (acidic, basic, and neutral) and at temperatures of 20, 30, and 40 °C.

In Fig. 1, the pH effect is observed; the MC/PAAm 3 (80/20, 1.0 wt% initiator and 1.0 wt% crosslinker) demonstrates acceptance toward the neutral pH, and strong interactions with water (hydrogen bond, OH groups of the solution with the material) occur. On the MC/PAAm 1 film (80/20, 0.5 wt% of initiator and 1.0 wt% of crosslinker) the pH effect is not marked, but presents an inclination toward the neutral environment, and the water forms hydrogen bonds with the polymer's polar groups; this is logical due to the fact that MC/PAAm 1 and MC/PAAm 3 have the same MC and PAAm ratio. MC/PAAm 2 (90/10, 1.0 wt% of initiator and 0.5 wt% of crosslinker) behaves in a different manner toward the environments at different temperatures: at

20 °C it has an affinity toward the basic pH; at 30 °C, toward the basic and acidic; and at 40 °C, toward the neutral. Under the study conditions, the groups present in this hydrogel have a different disposition from the material's structure, chain relaxation, and interactions, due to monomers. Hydrogels with groups OH, COC, C=O, NH present an impediment or freedom to interact in accordance with the combination of the variables (temperature and pH).
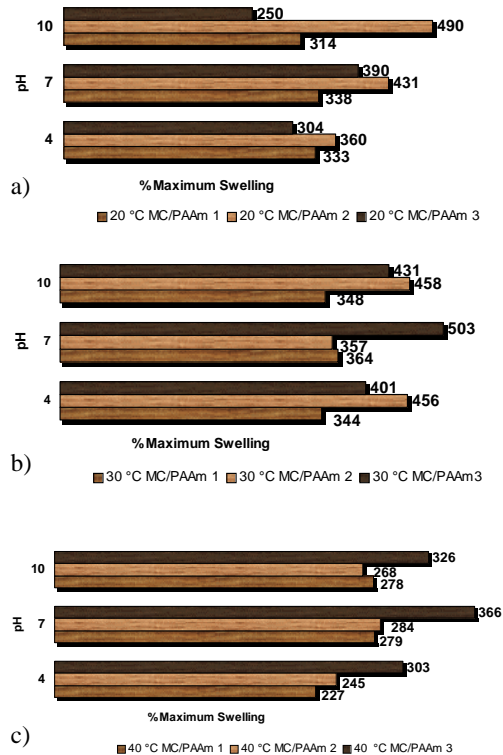

a)

Fig. 1. Effect of the pH on the swelling of the samples MC/PAAm 1, MC/PAAm 2, and MC/PAAm 3 at the temperatures of a) 20ºC, b) 30ºC, and c) 40°C in the equilibrium.

The kinetic study allows the hydrogel's swelling order to be determined: first order (Fick Model), second order (Schott Model), or if it adjusts to both at a particular time. This study also helps the preliminary tests in drug delivery and in understanding or determining the environment's diffusion toward the inside of the hydrogel. The Fick study was applied for the first swelling times, due to the fact that for longer times there is a deviation in this behavior; in this case, swelling fraction values (W_t/W_{max}) less than or equal to 0.60 were established in accordance with bibliographic data (Woerly *et al.*, 1996). The Schott Model was used for longer times than the one mentioned when the density of the sample has increased.

As can be observed in the Fick Model (first order) of Table 2, for the study of swelling at 20 °C in the three environments, the n values are anomalous (0.5<n<1.0).

Likewise, Table 2 summarizes the results with the Schott Model (second order) for determining the swelling degree of the hydrogels studied at different pH's. All cases have excellent correlation coefficients, and Fig. 2 shows their straight lines, thus demonstrating that this system's swelling behavior follows a second-order diffusion kinetic, and the swelling process for long times is not governed by the diffusion, but by the relaxation of the polymeric chains.
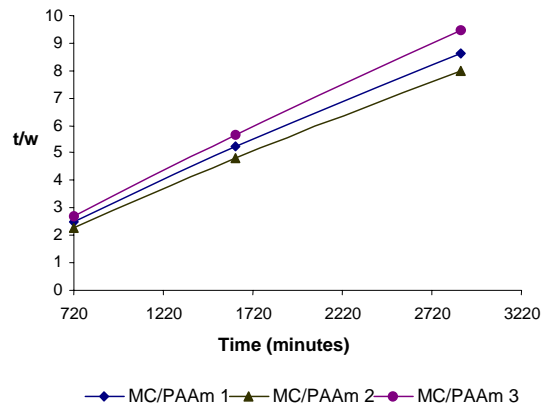

Fig. 2 Graphic of the Schott Model for the three hydrogels studied in an acidic environment at 20 °C.

In agreement with the values determined in Table 3 for the first order model (Fick Model) at 30 °C, the n parameter yields anomalous results (0.5<n<1.0) for all three hydrogels. The Schott Model at 30 ºC has acceptable correlation coefficients in the evaluation of the swelling degree in different environments.

In Fig. 3, the Schott Model is presented in a neutral environment at 30 °C. It is observed that in all three cases (MC/PAAm 1, MC/PAAm 2, MC/PAAm 3) straight lines occur; therefore, the system mentioned continues the second order kinetic for longer times, which is to say, relaxation of the polymeric chains exists.
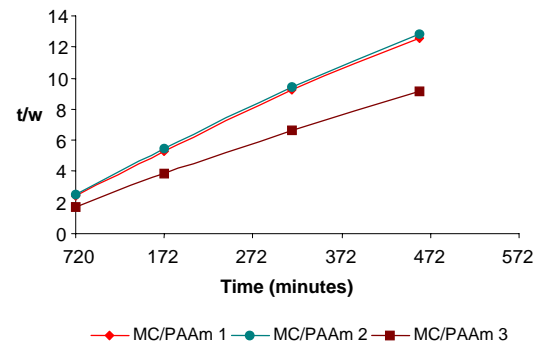

Fig. 3. Graphic of the Schott Model for the three hydrogels studied in a neutral environment at 30 °C.

Table 2. *n* and *k* values at 20 °C for both the Fick and Schott Models.

Sample	Fick Model			Schott Model		
	n	*k*	*r*	*n*	*k*	*r*
MC/PAAm 1 pH=4	0.8614	0.0028	0.9859	0.0028	0.5212	0.9995
MC/PAAm 2 pH=4	0.8937	0.0024	0.9909	0.0026	0.4402	0.9996
MC/PAAm 3 pH=4	0.8630	0.0030	0.9884	0.0031	0.5345	0.9997
MC/PAAm 1 pH=10	0.8007	0.0042	0.9914	0.0030	0.5483	0.9999
MC/PAAm 2 pH=10	0.8618	0.0028	0.9856	0.0019	0.3846	0.9995
MC/PAAm 3 pH=10	0.8571	0.0030	0.9881	0.0038	0.7400	0.9996
MC/PAAm 1 pH=7	0.7728	0.0050	0.9903	0.0028	0.4364	0.9997
MC/PAAm 2 pH=7	0.8322	0.0035	0.9920	0.0022	0.4028	0.9995
MC/PAAm 3 pH=7	0.8647	0.0028	0.9872	0.0024	0.3868	0.9997

Table 3. *n* and *k* values at 30 °C for both the Fick and Schott Models

Sample	Fick Model			Schott Model		
	n	*k*	*r*	*n*	*k*	*r*
MC/PAAm 1 pH=4	0.7986	0.0040	0.9978	0.0028	0.8210	0.9982
MC/PAAm 2 pH=4	0.7636	0.0047	0.9968	0.0021	0.6134	0.9989
MC/PAAm 3 pH=4	0.7662	0.0047	0.9981	0.0024	0.6760	0.9988
MC/PAAm 1 pH=10	0.7542	0.0050	0.9968	0.0027	0.8248	0.9986
MC/PAAm 2 pH=10	0.7651	0.0049	0.9980	0.0021	0.5423	0.9990
MC/PAAm 3 pH=10	0.7545	0.0051	0.9971	0.0022	0.6589	0.9981
MC/PAAm 1 pH=7	0.6930	0.0075	0.9966	0.0026	0.6633	0.9989
MC/PAAm 2 pH=7	0.7615	0.0047	0.9974	0.0027	0.7268	0.9989
MC/PAAm 3 pH=7	0.7355	0.0059	0.9982	0.0019	0.4959	0.9991

Table 4. *n* and *k* values at 40 °C

Sample	Fick Model			Schott Model		
	n	*k*	*r*	*n*	*K*	*r*
MC/PAAm 1 pH=4	0.7101	0.0094	0.9912	-	-	-
MC/PAAm 2 pH=4	0.7846	0.0063	0.9978	-	-	-
MC/PAAm 3 pH=4	0.9295	0.0038	0.9962	-	-	-
MC/PAAm 1 pH=10	0.7451	0.0085	0.9954	-	-	-
MC/PAAm 2 pH=10	0.6863	0.0119	0.9968	-	-	-
MC/PAAm 3 pH=10	0.7546	0.0080	0.9902	-	-	-
MC/PAAm 1 pH=7	0.7082	0.0097	0.9895	-	-	-
MC/PAAm 2 pH=7	0.7038	0.0097	0.9895	-	-	-
MC/PAAm 3 pH=7	0.7578	0.0075	0.9977	-	-	-

On the contrary, Table 4 summarizes the values solely for the Fick Model, which is very reasonable since said model is for short study times, while the Schott Model is for longer times, and in the evaluation of the swelling degree at 40 °C, the average absorption of the hydrogels was established up to 600 minutes. At this point, desorption was presented; this explains why the model is not adjusted for swelling at this temperature. The first order results are anomalous (0.5<*n*<1.0).

Fig. 4 illustrates the ln (W_t /W_{max}) against ln (*t*) of the Fick Model for the hydrogel ratios at one single temperature and environment (40 °C, basic).

In all cases in which the Fick Model has anomalous values, the diffusion and relaxation processes of chain tensions take place in the same time order, such that the predomination of one process over the other is related to how much greater the deviation is with respect to the Fickian behavior (Brandon - Peppas, 1990).
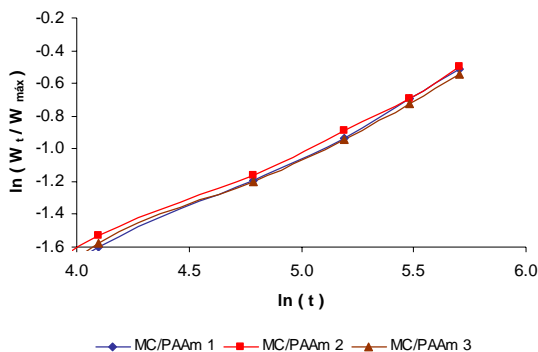
Fig. 4. Graphic of the Fick Model for the three hydrogels studied in a basic environment at 40 °C.

3.1. DSC analysis

In Fig. 5, the thermogram of the 80/20 MC/PAAm ratio with 0.5/1.0 initiator/crosslinker (MC/PAAm 1) after swelling in a neutral environment at 30 °C is observed. It presents a T_g at 39.06 °C, which is a small T_g due to the fact that upon being subjected to swelling, its chains are relaxed and this causes it to diminish.
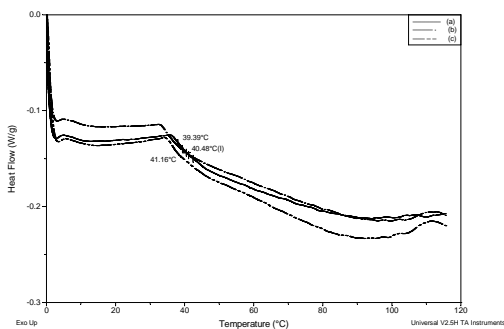

Fig. 5. DSC curves of MC/PAAm hydrogels after the swelling: a) 80/20 MC/PAAm with 0.5/1.0 initiator/crosslinker (MC/PAAm 1) after the swelling in a neutral environment at 30 °C, b) 90/10 MC/PAAm with 1.0/0.5 initiator/crosslinker (MC/PAAm 2) after the swelling in a basic solution at 30 °C, and 80/20 MC/PAAm with 1.0/1.0 initiator/crosslinker (MC/PAAm 3) after the swelling in a neutral solution at 30 °C.

According to Ortiz *et al*. (2006) and Murali (2006 a,b), the film obtained a T_g of 79 °C before swelling. In the 90/10 MC/PAAm ratio with 1.0/0.5 initiator/crosslinker (MC/PAAm 2) after swelling in

a basic environment at 30 °C, a T_g at 40.87 °C is observed for the film (Fig. 5). Fig. 5 presents the thermogram of the 80/20 MC/PAAm ratio with 1.0/1.0 initiator/crosslinker (MC/PAAm 3) after swelling in a neutral environment at 30 °C; a T_g of 40.70 °C is observed. The film presented a T_g of 89 °C before swelling (Ortiz *et al*., 2006).

As observed in Table 5, the vitreous transition temperature (T_g) in general is very similar on the MC/PAAm films that presented greater swelling, which indicates that the conditions to which they were exposed (solution environment and swelling temperature, study period) produced the same effect (chain relaxation) on all the films. It also happens that the vitreous transition temperature diminishes by approximately 50%, corroborating that which was observed in the kinetic study: a relaxation in the polymeric chains.

3.2. Surface morphologies

In Fig. 6(a), small AAm incrustations are shown without reacting between 8-10 µm due to the low concentration of KPS. Having less swelling, this is corroborated by Fig. 6(c), where, upon increasing the initiator from 0.5 to 1.0% with a constant cross-linking concentration, the hydrogel presents a more homogenous surface without AAm incrustation (Fig. 6c). Furthermore, in Fig. 6(b) it is observed that incrustations are not present at a neutral pH and a temperature of 30ºC, due to the effects of the temperature and pH, and because hydrogels tend to suffer changes in their morphology as a result of these variables, they present a homogenous surface free of monomers and without reacting.

Fig. 7(a) shows a homogenous surface, while Fig. 7(b) presents a porous structure capable of retaining and transferring liquids after swelling, which is to be expected since the porosity of the material yields a better swelling degree. With regards to Fig. 7(c), it presents a lesser swelling degree under the same conditions but with a different concentration of initiator. Therefore, the hydrogel shows a more homogenous structure and an increase in the swelling percentage upon increasing the concentration of initiator (KPS). This is corroborated by Fig. 1, since Fig. 7(b) showed 503% swelling, while Fig. 7(c) decreased its swelling degree to 364%.

Table 5. MC/PAAm hydrogel vitreous transition temperatures.

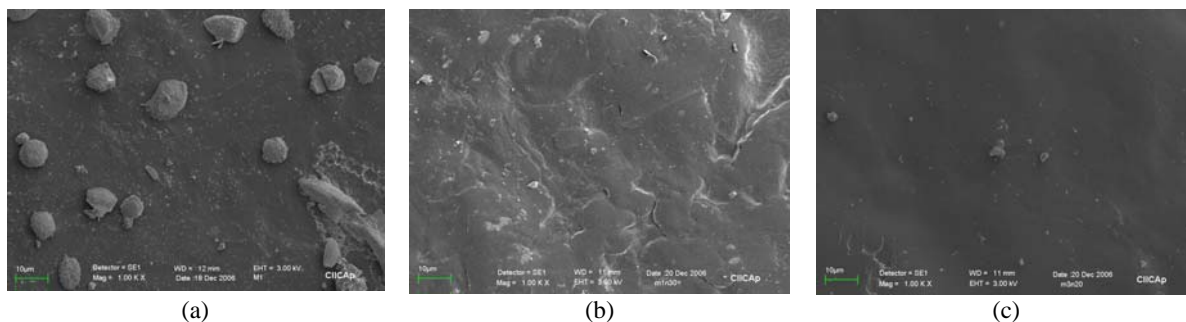| Sample	Test conditions of the swelling test	T_g (°C), before swelling	T_g (°C), after swelling
MC/PAAm 1	Neutral medium to 30 °C	79	39.39
MC/PAAm 2	Basic Medium to 30 °C	86	40.48
MC/PAAm 3	Neutral Medium to 20 °C	89	39.85
MC/PAAm 3	Neutral Medium to 30 °C	89	41.16
MC/PAAm 3	Neutral Medium to 40 °C	89	41.19

Fig. 6. SEM pictures of methylcellulose & poly (acrylamide) hydrogels with a rate of 80/20. (a) 0.5% initiator and 1.0% crosslinker (b) the same, but with swelling at 30ºC and pH=7, and (c) the same, but with an increase of initiator from 0.5 to 1.0%.
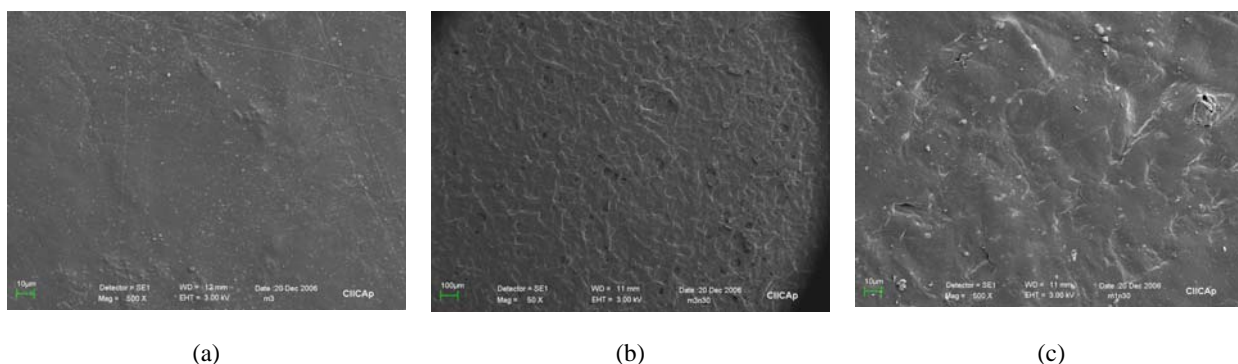

Fig. 7. SEM pictures of methylcellulose & poly (acrylamide) hydrogels with a rate of 80/20. (a) 1.0% initiator and 1.0% crosslinker, (b) the same, but with swelling at 30ºC and pH=7, and (c) the same, but with a decrease in initiator from 1.0 to 0.5%.
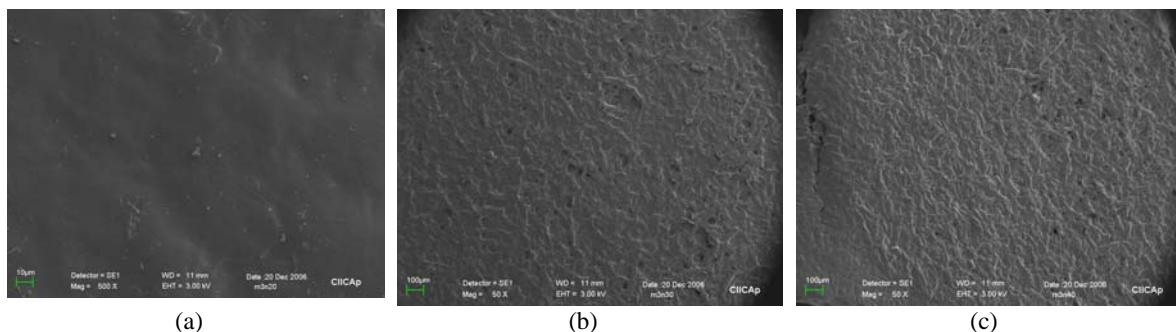

Fig. 8. SEM pictures of methylcellulose & poly (acrylamide) hydrogels with a rate of 80/20, pH=7, and 1.0% initiator and 1.0% crosslinker at (a) 20ºC, (b) 30ºC, and (c) 40ºC.

These results are very similar to those presented by Chen and Park (2000) where they indicate that a material's porous structure remains intact after drying in ethanol, contrary to when it is dried without adding the ethanol.

In Fig. 8, the same material is observed with equal ratios and concentrations of initiator and cross-linker, varying the swelling evaluation since it is at different temperatures: (a) 20º, (b) 30º, and (c) 40ºC. Here, it is observed that the structure in Fig. 8a did not show a change in its surface after swelling, while Fig. 8b presented a porous structure after swelling and its surface changed significantly upon increasing it by 10º, in addition to obtaining the maximum swelling degree at this temperature. On the other hand, Fig. 8c showed a very similar surface to that of 7b, with the difference being that at this temperature, a crack of approximately 600 µm with an opening of 10 µm was shown due to an increase in temperature causing a decrease in the swelling degree. For this reason, the conclusion was drawn that the adequate temperature for this material presenting a porous structure is 30ºC due to the presence of available pore volume (less crosslink junctions), which in turn accommodates larger amounts of water molecules within the hydrogel networks.

Conclusions

Chemically crosslinked MC/PAAm hydrogels were prepared in the presence of a crosslinker. Swelling results indicate that this system's swelling behavior follows a second-order diffusion kinetic, and the swelling process for longer times is not governed by the diffusion, but by the relaxation of the polymeric chains. The relaxation of the polymeric chains can be observed as the vitreous transition temperature diminishes. The surface morphology demonstrated fewer crosslink junctions at 30ºC.

It is clear that the dependence of the swelling kinetics on the cellulosic derivatives is present in the hydrogels studied. The rate of swelling is assumed to be directly proportional to the following two quantities: first, to the relative or fractional amount of swelling capacity still available at time *t,* and second, to the internal specific boundary area (S_{int}) enclosing those sites of the polymer network that have not yet interacted with water at time *t* but will be hydrated and swell in due course. The polyacrylamide and cellulose networks are held together by hydrogen bonds and other secondary valence forces between adjacent polymer chains. Hydrogen bonds between adjacent polyacrylamide chains are formed by their amide groups while those between adjacent cellulose chains are formed by their hydroxyl and acetal groups. Water swells the polymer networks because it penetrates between the chains and breaks interchain secondary valence bonds by forming hydrogen bonds with hydroxyl and acetal groups of cellulose, and with amide groups of gelatin. Rupture of interchain secondary valence bonds permits the polymer networks to expand to accommodate the influx of water through relaxation of the stresses produced by osmotic pressure. The process is entropy driven (Schoot, 1992).

Acknowledgment

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