SWELLING EVALUATION ON NANOGELS OF HYDROXYPROPYLCELLULOSE / POLYACRYLAMIDE

García J. C. [1], Castro C. F. [1], Pérez Tijerina E.[2], Rivera Armenta J. L. [1], Morales Ana B. [1]

[1]*División de Estudios de Posgrado e Investigación del Instituto Tecnológico de Cd. Madero. Av. 1o. de Mayo esq. Sor Juana Inés de la Cruz s/n Col. Los Mangos C.P.89440, Cd. Madero Tamaulipas, México.*

[2]*Facultad de Ciencias Físico-Matemáticas de la Universidad Autónoma de Nuevo León. Ciudad Universitaria San Nicolás de los Garza, C.P 66450, Nuevo León. Tel: (83) 76-95-46 Fax: (83) 52-38-50*

E-mail: jc_garciacruz@hotmail.com, abmoralesc@prodigy.net.mx

1. Abstract

In this work was reported the swelling behavior of hydroxypropylcellulose (HPC)/polyacrylamide (PAAm) gels synthesized with 25% wt of HPC and 75% wt of PAAm. The swelling behavior was evaluated at 3 different pH's (4, 7 and 10) and at 3 different temperatures (30, 40 and 50°C). The swelling kinetics of the gels followed Fick's model for short times and a temperature of 30°C, and they followed Schott's model for long times and temperature between 30 and 50°C. The gels were dried after swelling and analyzed with Atomic Force Microscopy (AFM), some lamellae were formed on the hydrogel surface.

2. Introduction

The hydrogels are interesting materials because of their properties of low toxicity and high bio-compatibility, they have become the center a lot of research, mainly biomedical, farmacobiology and agricultural. The hydrogels are polymer materials that have the ability of absorbing water and swelling in the process. These properties depend on a number of parameters such as chemical composition, cross-linking degree, functional groups, and the solvent that was used for synthesis. A description of a gel is a cross-linked polymeric material in form of three-dimensional network of a natural or synthetic material that swells with water, softening the material and making it elastic while keeping its form without dissolving in the solvent [1, 2, 3].

3. Experimental section

3.1 Preparation of hydrogel from HPC / PAAm and swelling test.

In a glass reactor with an atmosphere of nitrogen, 36 ml of distilled and deionized water (DI) are added, then 27.8 gr/L of HPC (Aldrich, M_n=10000, MS=3.6) are dissolved in the water and the solution is stirred for 15 hours. Then 83.3 g/L of acrylamide (Aldrich, 97%)

are added and the initiators ammonium persulfate (APS, Sigma-Adrich, 98%) and tetramethylethylenediamine (TEMED, Sigma-Aldrich, 99%) are injected in the reactor along with the crosslinkers, vynil sulfone (DVS, Aldrich, 97%) and methylene bisacrylamide (MBAm, Aldrich, 99%), after this the pH is raised with 1 mL of NaOH (Aldrich, 97%+) and the solution is let to react for 3 hours with constant stirring under at atmosphere of nitrogen at 40°C [4]. After finishing the reaction the solution is poured from the reactor and dried at 40°C under vacuum. Once the hydrogel is dried it is rinsed several times with DI water in order to remove the NaOH and non reacted monomer and it is dried again under vacuum. The swelling behaviour was evaluated at 3different pH's and different temperatures [5]. The dry gel was measured and weighed and let to absorb water; during the first hour the weight was recorded every 10 min and then it was recorded every hour for an interval of 24 hours. The weight was measured until the equilibrium was reached.The swelling percentage was calculated by using the following equation with the gravimetric method:

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

Where:
W_C (%) is the percentage of hydration.
W_S is the weight of the film after the swelling.
W_D is the weight of dry film.

The microscopy characterization was done with the atomic force microscope (AFM) brand VEECO di CPII and software SPMLAb Vr. 5.01, in the contact mode.

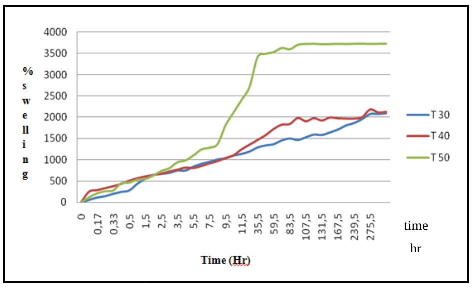
Table 1. – Samples tested.

Sample	Composition, %wt HPC/PAAm	gDVS/gHPC	pH at reaction
BG121	25/75	0.36	7
BG122	25/75	0.36	12
BG111	25/75	0.18	7
BG212	25/75	0.18	12

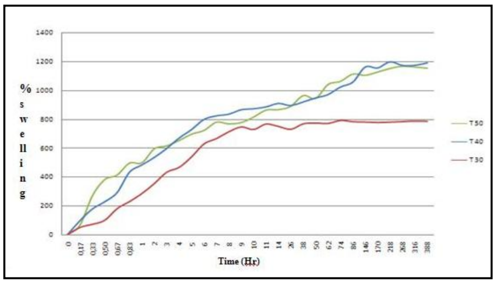
4. Results and discussion

Figure 1(a) shows the swelling behaviour of sample BG111, it was put in a basic solution at 3 different temperatures (30, 40 and 50ºC), if temperature is raised the swelling percentage of water is increased, it had at maximum of 3800% at 50ºC. In the figure 1(b) the swelling behavior of sample BG212 is shown, it was put in a acid solution at 30, 40 and 50°C, it is clear that the increment of temperature increases the swelling percentage in the sample; the maximum was 1200% at 40 and 50ºC. Into table 2 and 3 showed the value of n and k for the

Fick and Schott models on the gels swollen with basic and acid solutions at the 3 different temperatures respectively. In the table 2 show the values of the Fick model which throws the results anomalous (0.5< n < 1.0) for some gels as BG121, BG111 at temperature of 30 and 40ºC , having it a less value of 0.5 with the sample BG122 at 30ºC and higher than 1.0 for the sample BG111 at 50 º C.



A) BG111



B) BG212

Figure 1.- Effect of temperature on the sample a) BG111 swollen in a basic solution and b) BG212 swollen in a acid solution.

Table 3 shows the values of n results for temperature of 30ºC and a temperature of 40 and 50 º C the value of n is less than 0.5 for these temperatures the first order model doesn´t work. Everyone has a good correlation coefficient in the evaluation of the swelling degree. We have that Schott model have an acceptable value in the correlation coefficient, taking the system remains second-order kinetics for times higher, and the swelling process is not governed by diffusion, if not by the relaxation of the polymer chains.

Table 2 Values of n and k at different temperatures (swelling with basic solution)

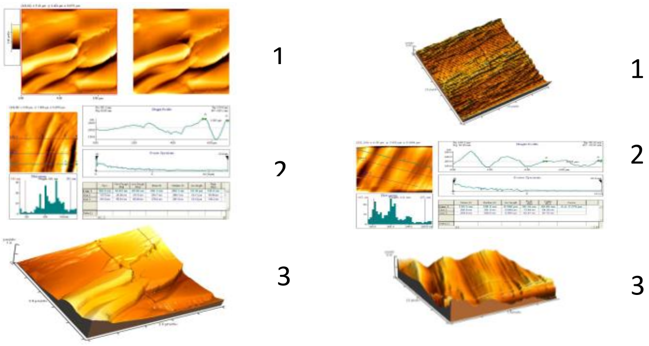
Temperature °C	Sample	Fick Model			Schott Model		
		n	k	Correlated coefficient	n	K	Correlated coefficient
30°	BG121	0.831	2.243	0.971	0.507	1.176	0.991
	BG122	0.445	1.221	0.912	1.036	6.901	0.987
	BG111	0.896	2.563	0.977	0.338	3.117	0.978
40°	BG121	0.754	2.027	0.903	1.602	2.643	0.942
	BG122	0.672	2.008	0.957	0.988	2.684	0.975
	BG111	0.695	2.14	0.884	0.719	0.321	0.945
50°	BG111	1.165	3.401	0.888	0.11	0.595	0.777

Table 3 Values of n and k at different temperatures (swelling with acid solution)

Temperature °C	Sample	Fick Model			Schott Model		
		n	k	Correlated coefficient	n	K	Correlated coefficient
30°	BG121	0.804	2.651	0.886	0.898	0.025	0.861
	BG122	0.648	1.827	0.915	2.256	0.991	0.923
	BG111	0.872	2.595	0.958	1.092	0.294	0.912
40°	BG122	0.487	1.718	.983	1.387	12.84	0.971
50°	BG122	0.363	1.24	0.942	1.433	0.977	0.974

4.1 AFM Characterization

Samples of hydrogels previously swollen temperature of 30 degrees C and pH = 10. Figure 3a shows the gel BG212 swollen in a basic solution of pH 10 at temperature of 30 degrees C. The average pore diameter is 1.0 µm with size lamellae between 48 to 111 nm is not homogeneous, its depth between 9.24 nm. Figures 3b shows the topography of the gel BG111 after swelling that typically has more uniform training of lamellae on range from 2.7 to 1.9 µm spacing.



a) BG212 b) BG11

Figure 3. Images of atomic force microscopy of the sample BG212 and BG111 previously swollen to temperature of 30° C and pH = 10: a) Topography in two dimensions, b) measurements of the surface and c) three-dimensional topography.

5. Conclusions

The swelling degree of the hydrogel hydroxypropylcellulose / poly (acrylamide) is favored toward a basic medium during the swelling; the samples has better results in a basic solution and temperatures over 30 °C, increasing the swelling percentage. After the swelling of the hydrogel HPC / PAAm suffer change its surface structure showing the appearance of lamellae of different sizes.

6. Acknowledgments

At the National Science and Technology (CONACYT) for the scholarship with the registration number 210322.Proyecto supported by the DGEST 829.08-P.

7. References

[1]. Pedley, G., Skelly, P. J., Tighe, B. J.; Br. Polym. J., R: 99 (1980).

[2]. Ratner, B. D., Hoffman, A. S.; Hydrogels for Medical and Related Applications, Ed. J. D. Andrade, ACS Symposium Series 31, American Chemical Society, Washington, pp. 1 (1976).

[3]. Wichterle, O.; Encyclop. Polym. Sci. and Technol., 1ª edición, 15 (1971) 273.

[4]. Carlos Fernando Castro Guerrero, José Luis Rivera Armenta, Alberto Álvarez Castillo, Ana M. Mendoza Mtz, Ana B. Morales Cepeda. Gels from Acrylic Acid and Hydroxypropyl Cellulose Using Crosslinkers and a Catalyst via Free Radical Polymerization, by publishing in e-polymers 2008.

[5]. Neyda Martínez Vázquez, Rocío Antonio Cruz, Ana Maria Mendoza, Ana B. Morales Cepeda Swelling Kinetic of Hydrogels from Methyl Cellulose and Poly Acrylamyde, , Diciembre 2007,Revista Mexicana de Ingeniería Química, ISSN 1665-2738 (2007)