

Swelling Degree and Diffusion Parameters of Poly(Sodium Acrylate-Co-Acrylamide) Hydrogel for Removal of Water Content From Biodiesel

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Hydrogels particles swell in the presence of an adequate solvent and soak the solvent into the cross-linked matrix of the particle, therefore they have great potential to remove soluble and insoluble water from liquid fuels, such as biodiesel, diesel and blends. In this paper, kinetic parameters and hydrophilic properties of polyacrylamide and poly(sodium acrylate-co-acrylamide) (AAM-co-SA) hydrogels were investigated to provide data for future equipment designs and devices that use these materials in removing water from Biodiesel. New hydrogels synthesized with sodium acrylate and acrylamide obtained a swelling ratio (weight of the swollen sample to that of the dry sample) of $W_{\infty}=108.8$ g water/g hydrogel, much higher than hydrogels developed in previous research ($W_{\infty}=14.36$ g/g) to remove water from biodiesel. Preliminary tests with the new hydrogel developed showed its ability to reduce water content from biodiesel.

1. Introduction

Hydrogels are crosslinked polymeric materials in a three-dimensional network that absorb and retain significant amount of water. That feature of hydrogels increases their initial volume several times without losing their original form (Hussain, et al., 2013; Schacht, 2004). Hydrogels have been investigated by many researchers for applications in biotechnological, medical, pharmaceutical and environmental fields (Costa and Mansur, 2008; Ashmed, 2015; Peppas et al., 2006; González-Delgado et al., 2016; Meri et al., 2017). Due to water uptake property, there is particular interest of using hydrogels in water separation processes, more specifically in the water removal from fuels such as diesel and biodiesel (Fregolente et al., 2015). High content of water in fuels promotes damage on fuel-injection equipment, sludge formation due microbial growth and contributes to corrosion in storage tanks (Sørensen et al., 2011). For biodiesel, these problems are intensified as it has strong hygroscopic nature and, therefore, can absorb naturally water from ambient leading to an increase of soluble water content during production and storage. This hydrophilic property is associated with the presence of esters (Zuleta, et al., 2012; Fregolente et al., 2012).

In this work, it was synthesized polyacrylamide and poly(sodium acrylate-co-acrylamide) (AAM-co-SA) hydrogels and the parameters of the swelling kinetics were obtained to provide data for future equipment designs that use these materials in removing water from Biodiesel. It was also carried out a study comparing the swelling capacity of a recently synthesized hydrogel sample based on polyacrylamide networks and an old sample (5 years) with the same composition, as it is essential that the polymeric material preserves its capacity of removing water along the time. Finally, experimental data were obtained to evaluate the capacity of the developed hydrogel to reduce water content from biodiesel.

2. Experimental

2.1 Materials

The reagents used in this work are: Acrylamide (AAm; Aldrich, Japan), Sodium Acrylate (SA, Aldrich, Japan), Sodium Persulfate (SP; Fischer Scientific, USA), *N,N*-Methylenebisacrylamide (MBAAm; USB Corporation, Germany), *N,N,N,N* Tetramethylethylenediamine (TEMED; Fluka, Buchs, Switzerland), distilled water and nitrogen gas (Whitemartins, Brazil). Biodiesel was obtained from the local market. Karl Fischer analyses were performed using a Titrando 841 Karl Fischer titrator from Metrohm, Switzerland. Samples were weighted using an analytical balance model ML 204 from Mettler Toledo, Brazil.

2.2 Preparation of hydrogels networks

Hydrogels were prepared by free radical polymerization of AAm and co-polymerization of the monomers AAm and SA. MBAAm was used as the cross-linker in the presence of SP as an initiator. The total volume was fixed in 50 mL. A certain mass of AAm and SA, together with MBAAm, SP (1.5×10^{-3} mol/L) and 1 mL of TEMED (0.57 mol/L), were added and stirred for 10 minutes at room temperature. Initial composition (% wt) of the reaction mixtures for the preparation of hydrogels is reported in Table 1. Polyacrylamide Hydrogel is referred as (AAm - co - 0) and the co-polymer hydrogel of AAm and SA is referred as (AAm -co - SA). The cross-linker mass fraction (MBAAm) was kept in 0.0325, as a function of the double bonds concentration of the monomers involved in the polymerization reaction.

Table 1: Initial composition (% wt) of the reaction mixtures for the preparation of hydrogels.

Sample	AAm	SA	MBAAm
(AAm-co-SA)	4	4	3.25
(AAm - co-0)	4	0	3.25

The solution was placed in a glass tube, degassed and sealed for approximately 4 - 5 min until the formation of hydrogel. Hydrogels were obtained in cylindrical shapes and then were sliced into pieces taking a disk-shape. Each sample was washed in distilled water for approximately 48 hours to remove unreacted monomer and then dried to constant weight at 50°C in a vacuum oven.

2.3 Swelling degree measurements

Swelling experiment by gravimetric approach is a simple and low-cost method to characterize polymer networks. In this method, a sample of dry hydrogel is weighted (m_0) then immersed in the solvent (water). The swelling ratio (W) was calculated by measuring the mass gain of the sample at different times. Runs in triplicate were carried out at 25°C. The swelling ratio is reported in Equation 1, where m_t is the hydrogel mass in time t .

$$W = \frac{m_t - m_0}{m_0} \quad (1)$$

2.4 Kinetics Parameters

Parameters associated with swelling kinetics are of great importance for understanding the process of diffusion swelling solution into the interior of the hydrogel. In this work, as reported by Jabbari and Nozari, 2000, the swelling mechanism was determined using Equation 2, where n is the swelling exponent and k the swelling constant. The kinetic parameters were adjusted to the experimental data of swelling ratio as a function of time in linear form ($\ln W \times \ln t$), using least squares method.

$$W = \frac{m_t - m_0}{m_0} = kt^n \quad (2)$$

Ritger and Peppas (1987) shown that constant k is related to the macromolecular network system, whereas the diffusional exponent, n , is indicative of the transport mechanism. According to Jabbari and Nozari (2000), for disk-shape, the value of n is 0.5 if the swelling mechanism is governed by Fickian diffusion of water. If n is between 0.5 and 1.0, the mechanism is characterized by non-Fickian or anomalous diffusion. When n is 1, the water transport rate is constant with the time (Case II transport). Finally, n is greater than 1 for supercase-II diffusion.

2.5 Swelling stability study

The swelling ratio is an important parameter for quality control of hydrogels. For this reason, a comparative study of swelling ratio of two polyacrylamide hydrogel samples was conducted using a recently synthesized hydrogel sample named (AAm-co-0) and an old sample so called (AAm-co-0) *after 5 years*. The hydrogel sample (AAm-co-0) *after 5 years* was used over 5 years in experiments of water removal from liquid fuels (diesel and biodiesel).

2.6 Water removal from biodiesel

In order to evaluate the ability of the (AAm-co-SA) hydrogel to remove water from biodiesel, experimental runs were performed in duplicate (vial 1 and vial 2), adding 10 g of (AAm-co-SA) hydrogel in a previously prepared mixture of 80 g of biodiesel and 0.08 g of water. The water content in biodiesel was monitored along the time and the ambient temperature and air relative humidity was kept constant at 20°C and 60% respectively. To verify if the reduction of water content in biodiesel was due to the hydrogel action and not due to mass transfer of water from biodiesel to air, a mixture of biodiesel and water without hydrogel was also monitored (blank sample). All Karl Fischer analyses were done in triplicate and the values are reported as the average.

3. Results

Figure 1a shows the experimental data of swelling ratio (W) as function of the time for the synthesized hydrogels. As can be seen in Figure 1a, the presence of units of Sodium Acrylate (SA) monomer in the (AAm-co-SA) hydrogel led to an expressive increase in the swelling ratio when it is compared with Polyacrylamide hydrogel (AAm-co-0) without SA. As shown in Table 2, the result of maximum swelling ratio W_{∞} increased from 22.8 to 108.5. It may be due the significant higher hydrophilicity of SA compared with AAm. In Figure 1b, it can be observed the good adjust of the model to the experimental data. R^2 are reported in Table 2.

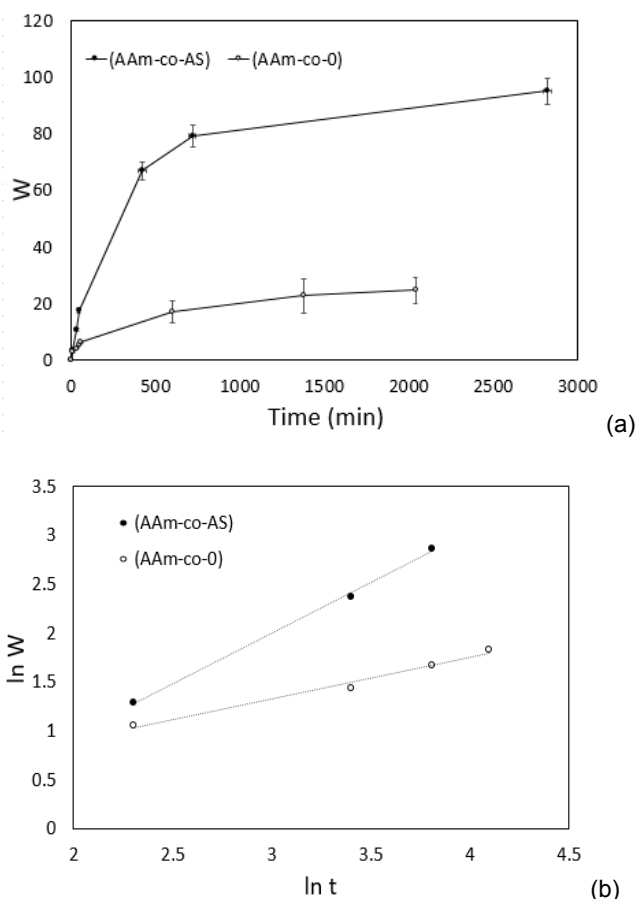


Figure 1 – a) Swelling ratio for (AAm-co-SA) and (AAm-co-0) hydrogels samples as a function of time. b) Kinetic parameters adjust.

Table 2 also shows values obtained for kinetic constants n and k for hydrogel through the linearization of the experimental data of swelling in the first run times. Results of W are presented with the standard deviation. The swelling process presented by (AAm-co-SA) hydrogel was faster ($k = 0.33$) than the presented by the (AAm-co-0) hydrogel ($k = 0.27$). For the experimental conditions studied, there is a different mechanism of mass transport for the two type of hydrogels prepared. Results of swelling exponent (Table 2) indicated an anomalous transport of water for (AAm-co-0) hydrogel and it seems (AAm-co-SA) hydrogel presented a case II transport. According to Karadag and Saraydin (2002), the greater the (AAm-co-SA) copolymers content, the greater the n values.

Table 2 – Swelling ratio and kinetic parameters values for (AAm-co-SA) and AAm-co-0) hydrogel samples.

Sample	W_{∞} (g water/g hydrogel)	n	k^{\dagger}	R^2
(AAm-co-SA)	108.5 ± 4.34	1.04	0.33	0.99
(AAm-co-0)	22.8 ± 6.0	0.57	0.27	0.98

[†]Adjusted using time in minutes.

Results of the swelling stability study are shown in Figure 2a, together with results of the adjust of the model to the experimental data (Figure 2b). It can be observed a good adjust of the model to the experimental data, giving $R^2 = 0.98$ (Table 3). It can be observed that there was a significant reduction in the W_{∞} of the (AAm-co-0) after 5 years sample, what may be related to a change in the characteristics of the macromolecular network due to the use of hydrogel over the years. According to Table 3, the water transport mechanism seems to approximate to a Fickian diffusion, as n value decreased from 0.57 to 0.51. However, more detailed data is needed to confirm this tendency.

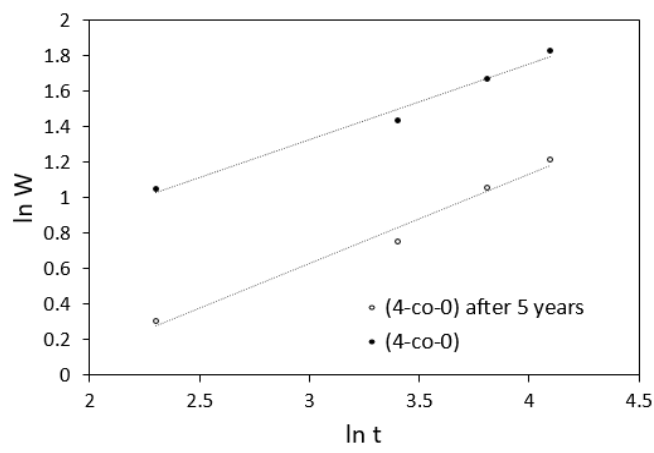
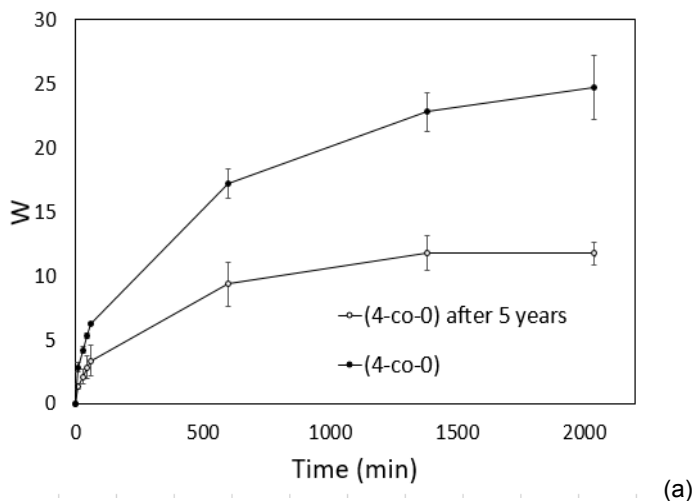


Figure 2 – Comparison between swelling ratio for (AAm-co-0) hydrogels of different ages. (AAm-co-0) after 5 years was synthesized 5 years ago; (AAm-co-0) was recently prepared. a) Swelling ratio data b) Kinetic parameters adjust.

Table 3 - Swelling ratio and kinetic parameters values for polyacrylamide hydrogel samples.

Sample	W_{∞} (g water/g hydrogel)	n	k^1	R^2
(AAM-co-0)	24.7 ± 2.5	0.57	0.27	0.98
(AAM-co-0) after 5 years	11.7 ± 0.87	0.51	0.41	0.98

¹Adjusted using time in minutes.

The higher W results obtained for the (AAM-co-SA) hydrogel compared with (AAM-co-0) suggest that (AAM-co-SA) hydrogel can have better performance to remove water from liquid fuels when compared with (AAM-co-0) hydrogel. Fregolente et al. (2015) carried out experiments applying (AAM-co-0) hydrogel for removal of water content of biodiesel using (AAM-co-0) at temperature of 20 °C and air relative humidity of 65%. In this work, the water content was reduced from 2100 ppm (w/w) to 1000 ppm. In the present work, the same biodiesel sample used by Fregolente et al. (2015) was submitted of a water removal process with (AAM-co-SA) hydrogel. Results are shown in Figure 3, where it is possible to verify an expressive water removal from biodiesel. Starting from a sample with water content slightly higher than 2200 ppm, the average final water content for the two vials was 1121 ppm. It is important to consider that the blank sample presented a decrease of 215 ppm in the water content along the experiment, which may be related to the loss of water to the air. This amount should be discounted in the water content reduction observed in the vials with hydrogel.

Analysing the results, despite the high capacity of water removal from biodiesel presented by (AAM-co-SA) hydrogel, for this formulation, it was not verified significant difference between the results obtained using (AAM-co-0). The observed quantity of removed water in the equilibrium condition was similar to that obtained by Fregolente et al. (2015). Different hydrogel formulations should also be evaluated, but it seems that the hydrophilicity effect of the hydrogel was not so evident for low water content in biodiesel. To better evaluate the potential of (AAM-co-SA) to remove water from biodiesel, different initial water content should be tested, including experiments with free water, so that experimental conditions would be more similar to the established conditions in the swelling tests. Conducting future studies with significant free water content, the swelling kinetic parameters obtained here for (AAM-co-SA) and (AAM-co-0) hydrogels could be also evaluated. Another factor that may have influenced the comparative analysis with the results obtained by Fregolente, 2015 is the biodiesel age. With more than 3 years, the ethyl esters present in the biodiesel sample may have degraded altering its hydrophilicity.

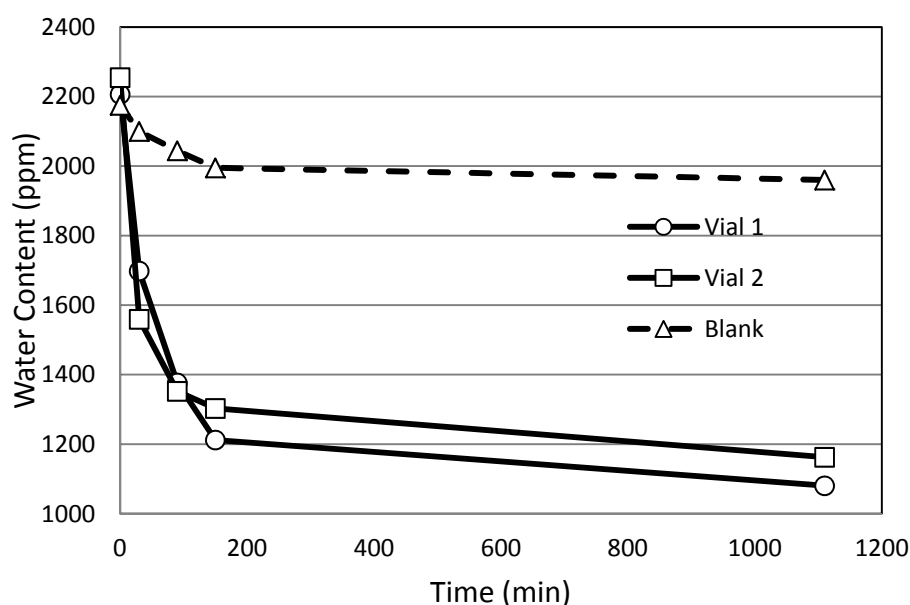


Figure 3 – Water removal from biodiesel using (AAM-co-SA)-(4-co-4) hydrogel.

4. Conclusions

Clearly it is observed that the inclusion of highly hydrophilic groups derived from sodium acrylate monomers were responsible for increase in almost 5 times the swelling capacity of the polyacrylamide hydrogel. The swelling ratio reached by AAM-co-SA hydrogel was 108.5 g water/g hydrogel.

Different mechanisms of mass transport were observed for the two types of hydrogels prepared. Results of swelling exponent (n) indicated anomalous transport for (AAm-co-0) hydrogel and case II transport for (AAm-co-SA) hydrogel.

(AAm-co-SA) hydrogel presented high capacity of removing water from biodiesel. In the experimental condition studied, it was possible to remove almost 870 ppm of water from a biodiesel sample with initial water content of 2200 ppm. For (AAm-co-0) hydrogel, it was observed a loss in the swelling capacity, probably due to changes in the macromolecular network due to the use of hydrogel over 5 years.

Acknowledgments

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