

Study of the Kinetics Swelling of Poly(Acrylamide-Co-Acrylonitrile) Hydrogel for Removal of Water Content from Biodiesel

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Hydrogels are polymeric materials that have absorption and retention capacities of high quantity of water in their tridimensional structure. This characteristic enables the hydrogel to remove soluble and insoluble water from liquid fuels. In this context, this work aims to study the swelling kinetics of the hydrogel of acrylamide copolymerized with acrylonitrile and use it to remove water in biodiesel. The kinetic parameters and hydrophilic properties were obtained from the study of swelling of the hydrogel in free water at 25 and 40 °C. The removal of soluble water (%) in biodiesel by the hydrogel was performed in 72 h in batch experiments at 25 and 40 °C, which corresponds to the equilibrium time. The hydrogel synthesized with acrylonitrile and acrylamide obtained a swelling ratio (weight of the swollen sample to that of the dry sample) of $W_{eq} = 8.46$ (g water/g hydrogel) and, $W_{eq} = 7.25$ (g water/g hydrogel) for 25 and 40 °C, respectively. The removal of soluble water from saturated biodiesel using poly(acrylamide-co-acrylonitrile) hydrogel was approximately 62 and 74% for 25 and 40 °C, respectively. The experiments performed showed the ability of the hydrogel synthesized to reduce water content from biodiesel.

1. Introduction

The high water present can harm the quality of the fuels, due mainly to microorganism growth. In this case, some of the consequences of microbiological development are sludge generation, increased turbidity, and corrosion of tanks and mechanical components of motor vehicles. The incorporation of water into fuels can occur not only during the production processes, but also in the storage, and transportation of fuels. ANP (National Agency of Petroleum, Natural Gas and Biofuels) establishes that the maximum water content allowed in biodiesel is 350 ppm (Resolution 45 of 2014). In contrast, according EN 14214 (2012), the maximum water content for biodiesel is 500 ppm. Conventional methods to remove water from fuels involve the usage of coalescent filters, treatments with salt, vacuum drying, or, in the case of biodiesel, vacuum flash or even heating. Therefore, it is proposed in this work the use of hydrogels as an alternative water removal tool to replace expensive heating and vacuum methods because of their high hydrophilic and swelling characteristics (Fregolente et al., 2015; Paula et al., 2019).

Hydrogels are polymers with a cross-linked network of one or more monomers. The characteristics of these gels are resulting from their different composition and functional groups in their three-dimensional network. Moreover, these characteristics are influenced by the reticulation process and the concentration of monomers, crosslinking agents, and initiator (Ahmed 2015). Polyacrylamide hydrogels present a broad range of applications in academia and industry because of their high swelling behavior and hydrophilicity.

Some works reported in the open literature show the application of hydrogel for oil/water separation process. Ao et al. (2018) used wire meshes coated with cellulose hydrogel to remove water from oil. In their work, they immersed wire meshes in a solution of 25 % in mass of cellulose for 2 h, and then the wire meshes were immersed in ethanol with citric acid at room temperature during 1h for gelation. Then the coated meshes were

heated at 100 °C for 2 h in order to enhance the crosslinks. The resulting meshes presented an efficiency higher than 98.9 % in removing water from oil.

Fregolente et al. (2018) synthesized poly(acrylamide-co- sodium acrylate) hydrogels to study their swelling behavior and hydrophilic properties. The polyacrylamide polymer presented very hydrophilic groups from sodium acrylate monomers that enhanced their swelling capacity in nearly 5 times. They removed about 870 ppm of water content from biodiesel with initial water content of 2200 ppm.

In this paper, synthesis of poly(acrylamide-co-acrylonitrile) hydrogel, as well as, swelling behavior, swelling kinetic parameters, and study of the removal of water in biodiesel are presented.

2. Experimental

2.1 Materials

Acrylamide (AAm – 99.9 %) from Amresco, acrylonitrile (AC – 99%) from Dynamic, 1,2-Bis(dimethylamino)ethane (TEMED – 99.0 %) was purchased from Sigma Aldrich, N,N'-methylenebis(acrylamide) (MBAAm – 99.0 %) from USB, sodium persulfate (initiator – 97.0 %) from Fisher, demulsifier from Croda, commercial biodiesel, and ultra-pure gas nitrogen from White Martins (99.996%).

2.2 Poly(acrylamide-co-acrylonitrile) hydrogel synthesis

Poly(acrylamide-co-acrylonitrile) or (poly(AAm-co-AC) hydrogel was obtained by free radical polymerization. Approximately 3 g of AAm, 2.5 g of AC, 0.079 g of MBAAm, 1 mL of TEMED, 0.02 g of initiator, and 46 mL of water were mixed until complete solubilization. Also, nitrogen gas was bubbled into the reaction medium until completion of the reaction. After approximately 24 hours (relative to completion of the reaction), excess monomers were removed with distilled water, and the sample was dehydrated at 60 °C until constant mass.

2.3 Swelling degree measurements

In this method, a sample of the dry hydrogel is weighted (m_0) and 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 and 40 °C and in pH 7. Eq(1) reports the swelling ratio, where m_t is the hydrogel mass in time, t .

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

The equilibrium water (W_{eq}) was defined as the ratio between the absorbed water and the mass of hydrogel at equilibrium swelling, as shown in Eq(2).

$$W_{eq} = \frac{m_{eq} - m_0}{m_0} \quad (2)$$

2.4 Kinetic Parameters

The evaluation of kinetic parameters related to swelling kinetics were obtained through the Korsmeyer – Peppas equation (Eq(3)). These parameters are essential to understand the swelling process that involves the water diffusion to the hydrogel polymer network. The kinetic parameters were adjusted to the experimental data of swelling ratio as a function of time in linear form using least-squares method.

$$W = \frac{m_{max} - m_0}{m_0} = kt^n \quad (3)$$

In Eq(3), k is a kinetic constant that incorporates structural and geometric characteristics of the mechanism, and n is the diffusional exponent that indicates the transport mechanism. Three different mechanisms may occur according to the value of n . If $n \leq 0.5$, the swelling mechanism is governed by fickian diffusion. If $0.5 < n < 1$, the mechanism is characterized by non-Fickian or anomalous diffusion. For $n = 1$ (Case II transport), the water transport rate is constant over time. Finally, if $n > 1$, the system kinetic is called super transport case II (Fregolente et al., 2018).

2.5 Batch tests for removal of water in biodiesel on the equilibrium

In order to evaluate the capacity of the poly(AAm-co-AC) hydrogel in removing water from biodiesel, batch tests were performed in triplicate, adding 0.4 g of hydrogel in 100 mL of saturated biodiesel. The experiments were performed in 72 hours at 25 and 40 °C with a speed of 200 rpm (IKA, model KS 4000 ic control). The time mentioned correspond in the equilibrium time conform described by Santos et al. (2019). Biodiesel water content was determined by automatic coulometric titration (Metrohm, model 860 KF Thermoprep), according to ENISO 12937. The removal of water in biodiesel was determined by Eq(4).

$$\% \text{ Removal of Water} = \left(\frac{C_0 - C_e}{C_0} \right) \cdot 100 \quad (4)$$

C_0 and C_e are the initial and final concentration of water in biodiesel (ppm), respectively.

2.6 Determination of free, emulsified and soluble water

Initially, the free water content of saturated biodiesel was determined according to ASTM D1796. Then, to quantify the emulsified water content (according to ASTM D1796), the demulsifier was added in the biodiesel, and the mixture was stirred with a centrifuge (Eppendorf, model 5810R) at 800 rpm for 10 minutes. The remaining water concentration in the biofuel corresponded to the soluble water content.

3. Results

Figure 1 shows the swelling curve of the poly(AAm-co-AC) hydrogel as a function of time at 25 and 40 °C. The chart indicates that the equilibrium time occurred in approximately 10 hours at 40 °C and 8 hours a 25 °C of experimental testing. Moreover, the tests indicated an equilibrium swelling of 8.46 (g water/g dry hydrogel) and 7.25 (g water/g dry hydrogel) at 40 and 25 °C, respectively. Increases in swelling time did not lead to a further increment in swelling capacity, observing a practically constant value of W . This can be because after reaching equilibrium swelling, the three-dimensional porous networks of the poly(AAm-co-AC) hydrogel becomes completely saturated, without sites available to place water molecules (MITTAL et al., 2014). Consequently, no increase in swelling capacity was observed after 10 and 8 hours for 40 and 25 °C, respectively.

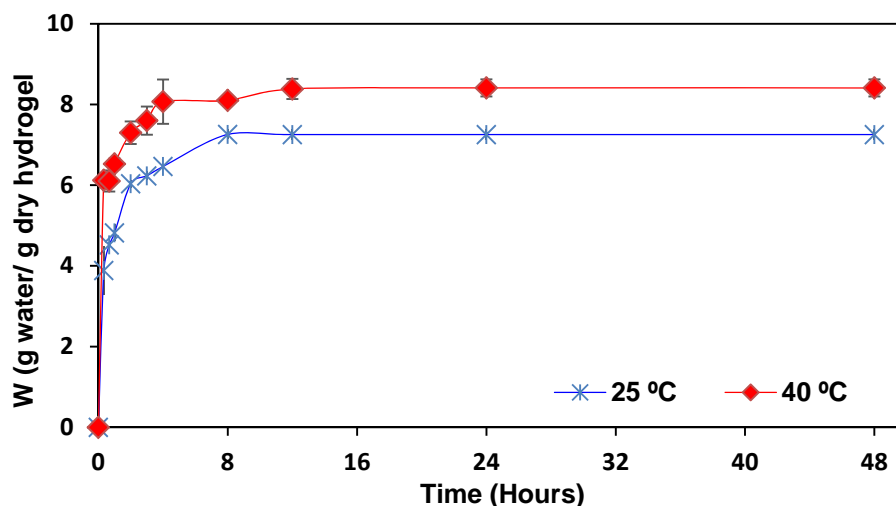


Figure 1: Swelling ratio for poly(AAm-co-AC) hydrogel sample as a function of time at 25 and 40 °C

It is evident that in the highest temperature (40 °C) the value of swelling was higher. It because the increase in temperature increased the elasticity of the cross-linked hydrogel polymer network and the hydrogen bonds of the water molecules with hydrophilic groups of the hydrogel, resulting in higher W_{eq} (Zhang et al., 2001).

Rajeev et al. (2014) found inferior values for gum ghatti and poly(acrylamide-co-acrylonitrile) hydrogel, about 6.20(g water/g dry hydrogel) in 16 hours at 40 °C. Moreover, they found $W_{eq} = 9.21$ (g water/g dry hydrogel) in 16 hours at 60 °C. That research does not report swelling data at 25 °C. Kajjari et al. (2011) obtained a W_{eq}

2.13 (g water/g dry hydrogel) in 24 hours at 37 °C for hydrogel microspheres of chitosan and poly(acrylamide)-grafted-guar gum. These researches point out that the kinetic constant was inferior in both cases in detriment of the greater equilibrium time. Furthermore, in comparison with poly(AAm-co-AC) hydrogel synthesized in this work, they present a lesser degree of hydrophilicity, given the equilibrium values swelling. Some error bars do not exhibit in Figure 1, because the errors were very small.

Figure 2 exhibits the linearized experimental data obtained through the Korsmeyer – Peppas equation at 25 and 40 °C.

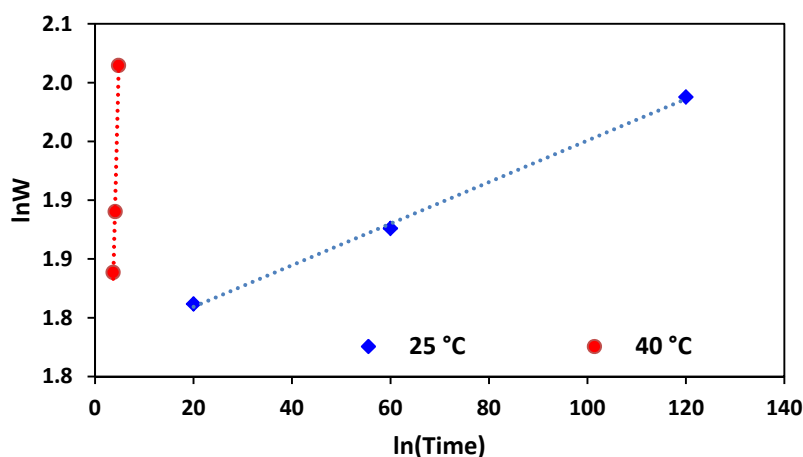


Figure 2: Kinetic parameters adjust

Table 1 presents the kinetic parameter values of the swelling of the poly(AAm-co-AC) hydrogel. The values obtained for diffusional exponent (Table 1) indicated a fickian diffusion of water for poly(AAm-co-AC) hydrogel in both temperatures. The kinetic constant (k) was higher at 25 °C, which explains the fastest equilibrium time. Fregolente et al. (2018) identified greater value for n with super transport case II diffusion process and the k value was smaller.

Table 1: Kinetic parameter values for poly(AAm-co-AC) hydrogel samples

Temperature (°C)	k	n	R^2
25	3.4415	0.1560	0.9990
40	3.4356	0.1623	0.9930

Table 2 shows the concentrations of free, soluble, and emulsified water in saturated biodiesel. According to this table, only soluble water was removed by hydrogel during the mass transfer process by adsorption

Table 2: Water content for free, emulsified and soluble fuel water

Kind of water	Water content (ppm)
Free	0
Emulsion	0
Soluble (25 °C)	1303.10 ± 12.05
Soluble (40 °C)	1219.22 ± 7.56

Figure 3 shows that at 40 °C occurred more significant removal of water from biofuel. This may be because high temperature permitted an increased elasticity of the cross-linked hydrogel polymer network and the hydrogen bonds of the water molecules with hydrophilic groups of the hydrogel and reduction of the viscosity. These three factors may allow the water incorporation in the three-dimensional hydrogel network. Furthermore, the decrease in the viscosity increases fluid wettability on the polymer surface, facilitating the mass transfer (Zhang et al., 2001). After 72 hours of batch tests, the water content in biodiesel was 502.37 and 320.35 ppm at 25 and 40 °C, respectively. Only at 40 °C, the water content was below the maximum

allowed by ANP (Resolution 45 of 2014) and EN 14214. Santos et al. (2019) achieved similar values for removal of water in biodiesel, using poly(acrylamide-co-sodium acrylate) and poly(acrylamide-co-acid acrylic) hydrogels at 25 and 40 °C. In that research, the authors obtained about 57 and 59 % of removal of water at 25 °C using poly(AAm-co-AAc) and poly(AAm-co-SA) respectively. This percentage increased to 80 % at 40 °C in both polymers and the water content was below the maximum allowed by ANP (Resolution 45 of 2014) and EN 14214 (2012).

The study of swelling and the removal of water in biodiesel were more efficient at 40 °C, for reasons already mentioned in this paper

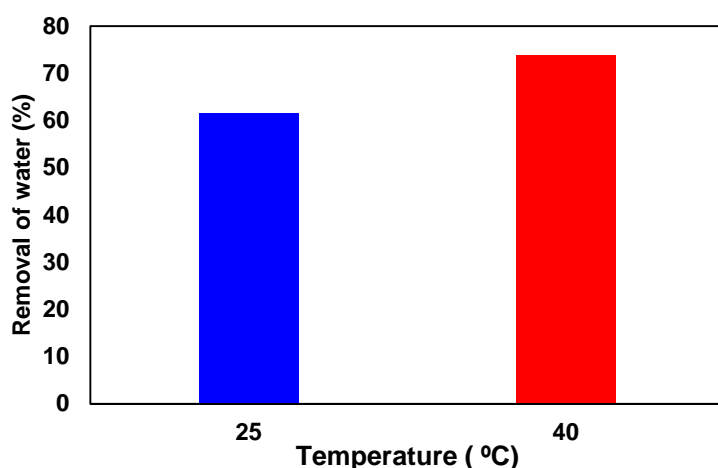


Figure 3: Removal of water in biodiesel as a function of the temperature

4. Conclusion

Swelling tests pointed out the high hydrophilic of the poly(AAm-co-AC) hydrogel. Upon reaching the equilibrium time identified a mass increase of more than 40 times the initial hydrogel mass has been identified at 40 °C. Moreover, in both temperatures, the transport mechanism was considered fickian with similar kinetic constants.

In addition, the batch experiments indicated efficient performance this copolymer in the removal of water in biodiesel, where it was detected about 74% removal, like the values, pointed in literature for other copolymer networks.

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