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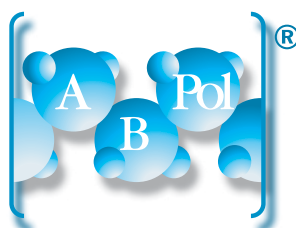# 17º Congresso Brasileiro de Polímeros

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PVOH HYDROGELS CROSSLINKED BY ORGANIC ACIDS. PART I: SWELLING-KINETICS STUDY

Dione P. de Castro*, Vanessa Z. Kieffer and Ruth Marlene C. Santana

Department of Materials Engineering, Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil
*dione.castro@ufrgs.br

Abstract - In the present research, poly (vinyl alcohol) (PVOH) hydrogels have been synthesized using organic acids (citric, malic and tartaric) as a crosslinker agent. The hydrogels were characterized by water uptake analysis and kinetics-chemical parameters. The effect of organic acids and time of synthesis on the equilibrium swelling has been investigated. With organic acids (malic and tartaric) contents, the swelling capacity increases, due to a degree of swelling promoted, while the citric acid used causes a disintegration of the hydrogel after the swelling times are extended. Fick's law was applied to the swelling ratio of hydrogels to explain the mass transfer mechanism and specify kinetic-swelling parameters. The swelling parameters such as equilibrium swelling capacity, and swelling rate constant, have been evaluated. The results obtained show that the incorporation of citric acid, due to its chemical functionalization, did not obtain dimensional stability, contributing to the disintegration of the hydrogels after a while. The incorporation of malic and tartaric acids shows good kinetics for both, especially for malic acid with a rate n and k elevated in comparison with the tartaric acid, bringing sustainable options for the development of PVOH hydrogels with a release control system.

Keywords: *PVOH hydrogels, organic acids, kinetic-swelling study.*

Introduction

Hydrogels are efficient to absorb large amounts of water and organic solutions, thus, the absorption of large amounts of aqueous solution brings a potential for applications in different fields [1]. PVOH is a water-soluble polymer containing a large number of hydroxyl groups because it has many advantages such as low cost and high chemical stability for hydrogel synthesis [1]. Chemical crosslinking forms chemical bonds between the polymeric chains of PVOH. Various carboxylic acids such as dicarboxylic, polycarboxylic and their derivatives are used as good crosslinking agents due to their reactive sites that form a stable and high-density crosslinked network in PVOH through esterification reactions and different forms of intermolecular/intramolecular bonds [2,3].

One of the most important characteristics of hydrogels is their capacity for absorption and retention of liquids, which can be high performance or not depending on the parameters used [3,4]. One of these parameters considered is the water absorption kinetics that can be estimated and calculated by the linear derivation of Fick's law [1,4]. This work aims to investigate the swelling and the individual performance data of the hydrogel samples with different organic acids when submitted to the swelling-kinetics test to evaluate the uptake systems.

Experimental

Materials

Poly(vinyl alcohol) (PVOH) (87% hydrolyzed) and citric acid (AC) were supplied from Neon®; Malic acid (AM) was obtained from Êxodo Científica®; tartaric acid (AT) was obtained from Synth® and hydrochloric acid catalyst (HCl) (37% w/w) was obtained from Química Moderna®. All chemicals were used as received without further purification.

Preparation and characterization of Organic acids/PVOH hydrogels

Initially, a solution of distilled water (~494 mL) and PVOH (~26g) was solubilized at 85°C for 40 min to make a casting solution. For the synthesis of hydrogels, the PVOH solution was mixed with ~114g of distilled water and 1% (w/w) of specific organic acids used in the total volume final solution and HCl was used (1M, 4mL) as a catalyst [5-7]. The mixture was stirred continuously for 20 min, 1 h, 2 h and 3 h, following a previous method [8]. Subsequently, hydrogel aliquots were weighed and placed in Petri dishes and dried in an oven at 65°C for 24 h and stored in a desiccator for 6 days for the final curing process following an adapted methodology [9]. The nomenclature of the PVOH hydrogels, as prepared, is presented in Table 1.

Table 1 - Nomenclature of the PVOH hydrogels and your reaction times used

Organic acid	PVOH Hydrogels crosslinking time			
	20 min	1 h	2 h	3 h
Citric acid	PVOH-AC (-AC)	PVOH-AC1 (-AC1)	PVOH-AC2 (-AC2)	PVOH-AC3 (-AC3)
Malic acid	PVOH-AM (-AM)	PVOH-AM1 (-AM1)	PVOH-AM2 (-AM2)	PVOH-AM3 (-AM3)
Tartaric acid	PVOH-AT (-AT)	PVOH-AT1 (-AT1)	PVOH-AT2 (-AT2)	PVOH-AT3 (-AT3)

The kinetic profiles of swelling of the hydrogels by sample size studied were modelled using Fick's law, in which the rate of the degree of relaxation of the hydrogel chain is directly linked to the degree of chemical crosslinking promoted by organic acids. These mechanisms of water absorption in the three-dimensional structure of a hydrogel have been described by diffusion and macromolecular relaxation or only by macromolecular relaxation in the literature [1]. In Eq. 1 the parameters of swelling kinetics including the diffusion exponent (n) and diffusion constant (k) were calculated [1,4].

$$\frac{M_t}{M_{eq}} = kt^n$$

(1)

Where: t is time; k is the diffusion constant of the studied hydrogel and the swelling medium; n is the solvent diffusion exponent; M_t and M_{eq} are the hydrogel mass at a defined swelling time and the equilibrium state, respectively.

Results and Discussion

Fig. 1 to 3 show the swelling-kinetics plots for the PVOH hydrogels with AC, AM and AT and their reaction time variations. The graphs were plotted to have the reaction kinetics defined by a linear

trend line, where the values of *n* and *k* were assigned for the intumescence kinetics and the solvent diffusion coefficient respectively. The error of the applied model was assigned to R^2.
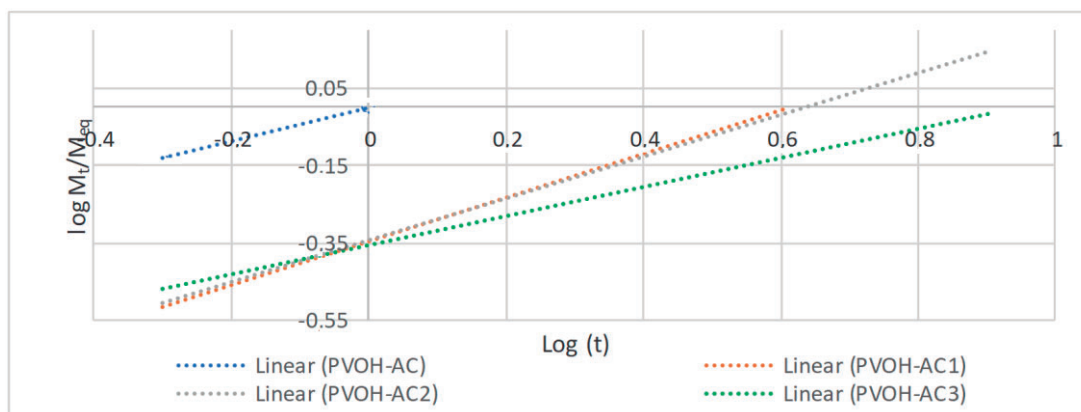

Figure 1 – Swelling-kinetics for PVOH-AC hydrogels

The PVOH-AC sample had a shorter reaction time compared to the others due to its reaction kinetics (*n* = 0.4399). The samples of hydrogels with -AC1 (*n* = 0.5637) and -AC2 (*n* = 0.5396) had similar reaction kinetics and percentages of swelling, besides having suffered mass disintegration in the same time scale. The sample -AC3 obtained more stable kinetics and consequently presented dimensional stability in the swelling test, due to the crosslink PVOH partial after the time synthesis applied (3 h), but with gradual mass loss. This behaviour is a result of a decrease in the final dimensional strength of the hydrogel and its disintegration due to high interaction with water hydrolysis, depending on the elaborate reaction kinetics and the time for hydrogel crosslinking [4,8]. It can be seen that the swelling ratio of a hydrogel is affected by both the concentration of citric acid and the final pH medium (3.5) of the solution in the swelling medium, through the conversion of carboxylic molecules (-COOH) into protonated acids that can result in a reduction of swelling [1,10].

In Fig. 2 it is observed that the hydrogel samples with -AM had similar reaction kinetics which resulted in dimensional and chemical stability, however with lower values of intumescence (*n* = 0.1344 to *n* = 0.1465). This behaviour is presented previously in the swelling test. It is also described in the literature that the pH of the solution also influences the intumescence of the samples and consequently in its swelling kinetics [1]. This interaction of the organic acids [3] of the protonated hydrogels in the aqueous conditions of acidic pH, resulted in the reduction of the swelling rate [1].
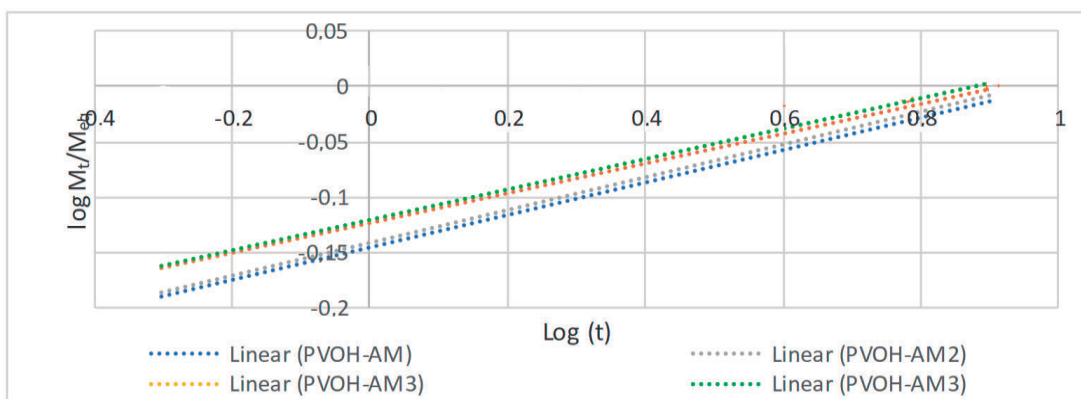

Figure 2 – Swelling-kinetics for PVOH-AM hydrogels

The samples of hydrogels with -AT (Fig. 3) had the second highest values of the kinetics of swelling (n = 0.2198 - 0.3170) and the sample -AT3 (n = 0.3170) that obtained this highest percentage due to the end of the reaction kinetics of the sample, shown by the swelling test and its dimensional stability by 8 h of the test. The behaviour of its swelling kinetics occurred due to the intumescence being dependent on the pH (3.5) obtained experimentally from the crosslinked hydrogels via chemical catalysis (HCl) and the presence of unreacted free -COOH group of the tartaric acid. This behaviour was also studied and observed by Kanmaz et al. [1].
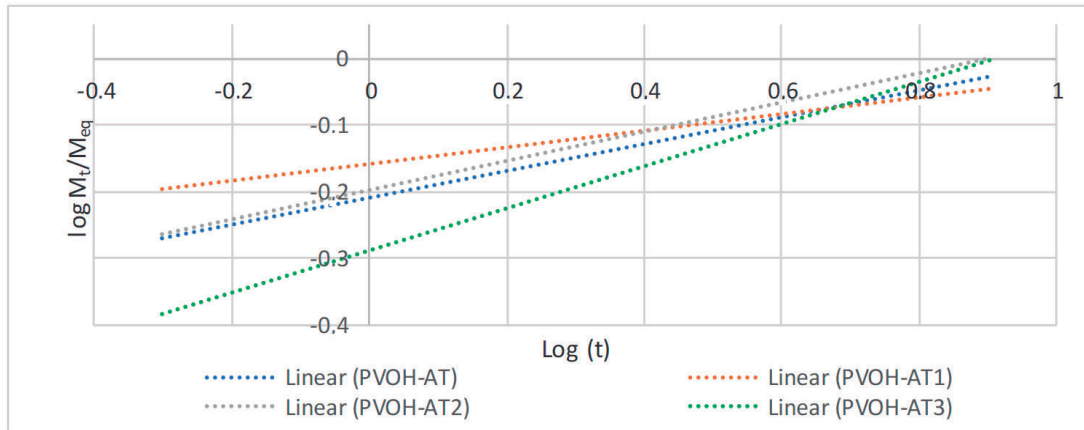

Figure 3 – Swelling-kinetics for PVOH-AT hydrogels

Table 1 shows the values of the swelling-kinetic constants of n and k for the hydrogels, obtained from the graphs of $\log \left(\frac{M_t}{M_{eq}} \right)$ vs log (t) and were calculated from the slope and intercept of the lines of the previous graphs, with a value of n as 0.5 being a description of Fickian mass transfer, and between 0.5 and 0.89 showing a non-Fickian transport mechanism [1,4]. The evaluation of data for the calculation of swelling kinetics was assigned in the time interval from 0.5 to 8 h of the test.

Table 1 - Values of n and k to swelling-kinetic

Hydrogel	n	k	Model error (%)
PVOH-AC	0.4399	1	1
PVOH-AC1	0.5637	0.4501	0.3184
PVOH-AC2	0.5396	0.4525	0.5893
PVOH-AC3	0.3768	0.4402	0.1861
PVOH-AM	0.1465	0.7160	0.1463
PVOH-AM1	0.1344	0.7537	0.0985
PVOH-AM2	0.1485	0.7219	0.1186
PVOH-AM3	0.1364	0.7575	0.1001
PVOH-AT	0.2004	0.6194	0.0733
PVOH-AT1	0.1248	0.6934	0.0340
PVOH-AT2	0.2198	0.6329	0.1572
PVOH-AT3	0.3170	0.5146	0.1360

The values of n were below 0.5 for all hydrogels which are attributed to higher kinetics of solvent swelling for the hydrogels studied, and the samples of PVOH-AC (n = 0.4399);

PVOH-AM2 (n = 0.1485) and PVOH-AT3 (n = 0.3170) obtained the highest values in their respective groups. This is attributed to the higher reaction kinetics for swelling of these samples and partially converges with the swelling data shown in other studies submitted by this group [11]. Kanmaz et al. [1] describe that hydrogels may have sufficient chemical mobility to allow solvent diffusion and this model can be expressed as Fickian mass transfer. The PVOH-AC hydrogel sample, by having the highest swelling kinetics, showed the highest percentage, while the other samples consisting of -AM2 and -AT3 due to chemical crosslinking and had dimensional stability and did not reach higher diffusion plateaus than -AC.

Conclusions

This investigated the synergistic effect of organic acids (OA) and time of synthesis on PVOH to obtain a good swelling hydrogel. The embedding of OA into PVOH the crosslink groups were addicted and the swelling capacity of the hydrogel was increased effectively. It was also found that the use of the malic and tartaric acids exhibited the best results for uptake properties with interconnected narrow bonds, which made it more attractive for water diffusion calculated by Fick's law. Insertion of citric acid into the network, loading ratios caused a peak in swelling values up to nearly 0.5396 and n = 0.5637, respectively. Malic and tartaric acids embedded hydrogels showed a good response to uptake/swelling properties. Finally, it is concluded that OA incorporated in hydrogels can be tuned to serve as water uptake/swelling for essential oils released systems.

Acknowledgements

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