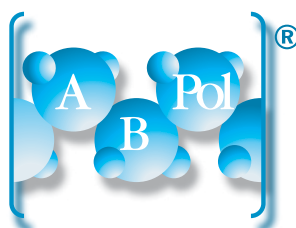


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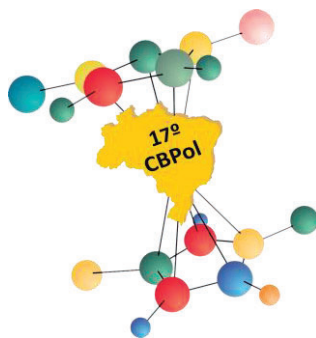
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## PVOH HYDROGELS CROSSLINKED BY ORGANIC ACIDS. PART II: KINETICS OF CONTROLLED DYE RELEASE

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**Abstract** - In the present study, poly (vinyl alcohol) (PVOH) hydrogels have been synthesized using organic acids - OA (malic and tartaric) as a crosslinker agent. The hydrogels were characterized by Flory-Rehner theory to crosslink degree and migration dye time parameters. Methylred was used as a model dye for the diffusion experiments, and the diffusion of dyes into hydrogel was monitored over time, using a UV-VIS analysis. The effects of OA type and time of synthesis on the equilibrium swelling have been investigated. With OA content and time of the synthesis, the swelling capacity decreases, due to the crosslink PVOH matrix, while the tartaric acid had good migration dye times compared with the malic acid, with more PVOH chain chemical flexibility. Flory-Rehner was applied to the crosslinking ratio of hydrogels to explain the mass transfer mechanism and specify swelling kinetic-chemical parameters with the water uptake. The swelling parameters such as equilibrium swelling capacity, and swelling rate constant, have been evaluated. The results obtained show that the incorporation of malic and tartaric acids is a good option for the development of PVOH hydrogels and the dye released controlled showed different results in both samples, with a highlight on malic acid for more control dye release. Was observed also that both acids have chemical and dimensional stability for use in hydrogels crosslink.

**Keywords:** *PVOH hydrogels, organic acids, Flory-Rehner theory, dye release.*

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### Introduction

Hydrogels are widely studied in the synthesis of novel scaffolds and controlled release systems [1-3]. Due to their water absorption and retention properties, however, hydrogels can suffer a phenomenon called migration, which is the displacement of the polymer to regions of higher solute concentration, swelling it [3,4]. Flory-Rehner theory is a mathematical model [1,5-7] used to describe the behavior of polymers in solutions, considering the interaction between the polymer and the solvent, and the interaction/migration of these dyes to the medium [4]. However, this migration may affect the efficiency of its application, and an unwanted release of dyes or degradation of the hydrogel may occur.

Thus, several studies have been conducted to investigate the migration of dyes/pigments in PVOH hydrogels [1,4,8,9]. Another study, published in 2020 [8], investigated the incorporation of tomato-derived pigments into PVOH and polyol hydrogels. The results showed that the natural pigments extracted did not influence the biofilms' malleability but confirmed their aesthetic impact in coloring the biofilm matrices regardless of the presence of polyols, and lower transparency

values compared with control biofilms (without vegetal pigments). However, the study of migration in PVOH hydrogels and the Flory-Rehner theory are important concepts for understanding the behavior in aqueous solutions [1,4,6,7,9]. The study of migration and diffusion of dyes in hydrogels has shown that migration can be controlled by several factors including dye concentration, immersion time, pH of the medium, and incorporation of other materials [8,9].

This work aims to investigate the chemical crosslinking of hydrogels by dye migration kinetic and its importance for the development of new materials incorporated as essential oils and control release systems.

## Experimental

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 [10-13]. The mixture was stirred continuously for 20 min, 1 h, 2 h, and 3 h, following a previous method [2].

The methods used in the preparation of PVOH hydrogels are described in detail in the manuscript *Part I: Swelling-kinetics study*, and the nomenclature of the PVOH hydrogels is shown 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
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)

### 1 - Flory-Rehner theory

Theoretical evaluation of the yield of the reactions under the different cross-linking agent's mechanisms and catalyst/time studied were modeled using Flory-Rehner theory [2,7,14], in which the rate of the degree of swelling of the hydrogel chain is directly linked to the degree of chemical crosslinking ( $G_X$ ) promoted by organic acids. Flory-Rehner's theory is described in detail with the swelling volume ratio ( $v_{2m}$ ) from Eq. 1.

$$v_{2m} = \frac{V_p}{V_g} = \frac{V_g - V_w}{V_g} = 1 - \frac{m_w \rho_g}{\rho_w m_g} \quad (1)$$

Where  $V_p$  is the volume of the dry polymer (hydrogel);  $V_g$  (gel) is the volume in the equilibrium state,  $V_w$  is a volume of water inside the hydrogel;  $\rho_g$  is the density of the swollen hydrogel at equilibrium,  $\rho_w$  is the density of the water,  $m_g$  is the mass of the swollen polymer at equilibrium and  $m_w$  is the mass of water present in the swollen polymer. After the  $v_{2m}$  value, the  $G_X$  is calculated using Eq. 2.

$$G_X = \frac{V_1 [(v_{2m})^{\frac{1}{3}} - (\frac{2}{f} v_{2m})]}{- [\ln(1 - v_{2m}) + v_{2m} + x_1 (v_{2m})^2]} \quad (2)$$

Where  $x_1$  is the Flory-Huggins solvent-polymer interaction parameter (0.49) [2],  $V_1$  is the molar volume of water as solvent (18 cm<sup>3</sup> mol<sup>-1</sup>) [7] and  $f$  is the functionality of available hydroxyl groups

[7] of the organic acids for crosslink formation, In this case: AM = 3 and AT = 4. The relationship between  $GX$  and  $\nu$  is assigned by the following Equation:

$$GX = \frac{\rho_p}{\nu} \quad (3)$$

Where  $GX$  is a polymer molecular weight between crosslinked bonds (g/mol);  $\rho_p$  is the polymer density (g/cm<sup>3</sup>);  $\nu$  is the hydrogel crosslinking density (mol/cm<sup>3</sup>).

## 2 - Migration dye in hydrogels

Hydrogels were prepared and incorporated with an aqueous solution containing the dye methyl red (Neon®) at a concentration of 0.05  $\mu$ M, following an adapted methodology [9]. The solution was added at the end of each synthesis reaction (5 min remaining) to the hydrogels to avoid early degradation and change of physical-chemical behavior. Hydrogels were placed in Erlenmeyer's containing 100 mL of distilled water and submitted to different controlled release times (1, 2, 3, 5, 8, 10, and 24 h) with constant stirring of 96.5 rpm and temperature of 27.5°C using a Shaker® incubator. Aliquots of liquid containing the dye released from the hydrogels were separated and the evolution time of the dye concentration released was monitored using UV-VIS spectrophotometry, with the wavelength of maximum absorbance obtained ( $\lambda_{max}$  513 nm) for accurate and reliable results, thus obtaining the final calibration equation ( $y = 0.0003e^{1.7733x} / R^2 = 0.9924$ ) for the dye methyl red. After the analysis, the samples were dried in an oven at 65°C for 24h to evaluate the dye migration.

## Results and Discussion

Fig. 1-a and 1-b show the migration-kinetics range for the PVOH hydrogels with AM, AT, and their reaction time variations.

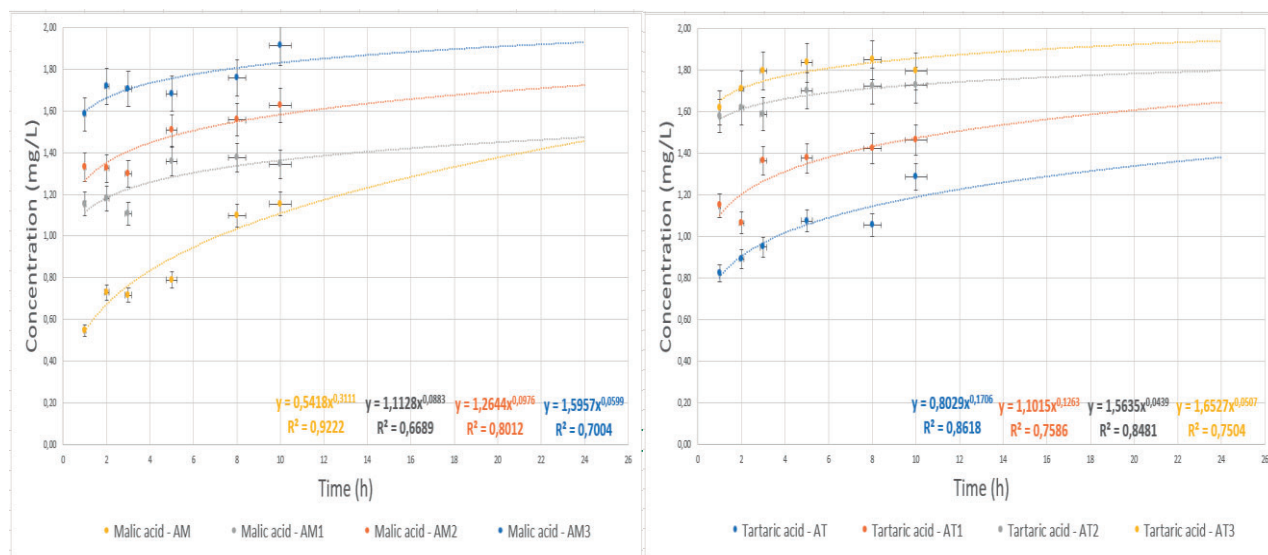


Figure 1 – Migration-kinetics for hydrogels PVOH-based: Malic acid (left) and Tartaric acid (right)

The results show that the migration of dye used, increased with the synthesis time, being that with lower times obtained a greater chemical crosslinking for the hydrogels constituted of malic acid and consequently lower release. The release process occurred exponentially and was based on the factors approximately calculated and described in the figures above. The samples -AM and -AT obtained better release results (20 min/1 h reaction) when compared with the other times employed,

the sample -AM having a slower release when compared with tartaric acid, due to the chemical interaction promoted by specific functionalization from hydroxyls (-OH) [2,15]. For the AM and AT samples the concentration (mg/L) at 3 h had approximate values due to a faster dye release because of a lower degree of crosslinking promoted at the end of the 3 h reaction.

In a more recent study, the researchers investigated the migration of dyes in hydrogels using models and migration theories [4,9,10]. The results indicated that dye migration was influenced by concentration, temperature, dye molecular size, and polymer matrix support. In addition, it was observed that dye migration increased with increasing temperature.

Fig. 2 and 3 show the migration stages and crosslinking density ( $G_X$ ) applied for the PVOH hydrogels with AM and AT and their reaction time variations in crosslinked molar mass function in the reaction synthesis time for comparison.

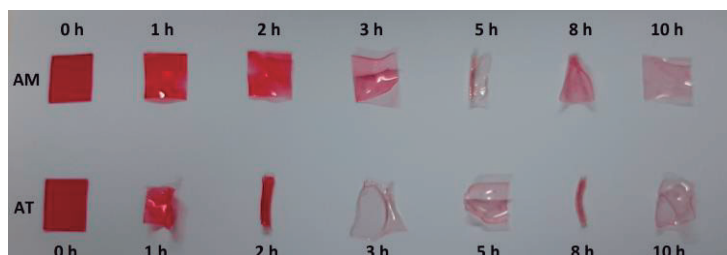


Figure 2 – Migration stages for PVOH-AM and PVOH-AT hydrogels in function on the time

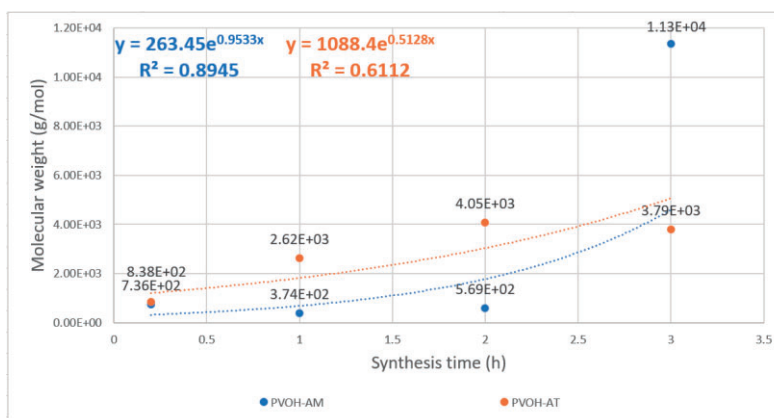


Figure 3 – Crosslinking density for PVOH-AM and PVOH-AT hydrogels

The average  $G_X$  obtained from the hydrogels was analyzed using the Flory-Rehner theory [5]. For analysis, the values were assigned to the respective swelling rate determined at 1 h for the -AM hydrogels and 2 h for the -AT. Also, the Flory-Rehner was applied to each time selected (20 min, 1, 2, and 3 h) to show the changes for each synthesis studied and show the influence of the synthesis time on the mass weight obtained.

The results obtained for the hydrogels of -AM and -AT, show that the reactions with a shorter time, generated more chemically esterified hydrogels with average  $G_X$  of  $7.36 \times 10^2$ ;  $3.74 \times 10^2$ ;  $5.69 \times 10^2$  and  $1.13 \times 10^4$   $\text{g} \cdot \text{mol}^{-1}$  for -AM and  $8.38 \times 10^2$ ;  $2.62 \times 10^3$ ;  $4.05 \times 10^3$  and  $3.79 \times 10^3$   $\text{g} \cdot \text{mol}^{-1}$  for -AT hydrogels respectively. For the Flory-Rehner theory, the samples composed of malic acid obtained the highest average crosslinking indexes, having the maximum crosslinking value ( $\text{g} \cdot \text{mol}^{-1}$ ) for the time of 20 min of reaction. Thus, the decrease in molar mass between the PVOH chemical structure and consequently an increase in the average density between the acids used (higher for malic acid compared to tartaric acid) formed more esterified hydrogels with higher  $G_X$  in a shorter proposed synthesis time [15]. The increase of chemical reactivity induced by malic acid compared to tartaric acid is evidenced from the initial times of the chemical reaction until the 3 h of

reaction with the decrease of  $GX$  of all hydrogels, over the reaction time due to the reagents to consumption (organic acids) from the starting of the reaction. It is observed that with the increase of the crosslinked molar mass of the hydrogel, there is a lower release of the dye over the reaction time in comparison to the migration graphs. This event is shown after the synthesis has been shifted during the reaction and shown in the collated data for the 3 h of the reaction due to the lower degree of crosslinking as seen in Figure 3.

## Conclusions

The dyes used were incorporated, obtaining a good dispersion in the middle of the crosslinked polymeric networks of the hydrogels. With the evaluation of the migration of the dye using UV-VIS spectroscopy, a suitable time and synthesis of 20 min up to 2 h is observed for a controlled release with optimization of the synthesis time. For the Flory-Rehner theory, the samples composed of malic acid obtained the highest average crosslinking indexes, having the maximum crosslinking value (g/mol) for the time of 20 min of reaction. Thus, hydrogels based on malic and tartaric acids can be used to immobilize higher amounts of dyes or essential oils systems and a higher proportion (reaction low times) of them remained mobile after the analysis time.

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