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Article

Preparation and Characterization of Novel Poly(Vinyl Alcohol) (PVA) and Poly(Acrylic Acid) (PAA) Hydrogels for Sensitive Hydrogels

Gabriel G. de Lima[1,*]; Declan Devine[2]; Caroline M. de Alencar Amanda Junqueira[2]; Ramon Emanuel[2]; Michael J.D. Nugent[2]

[1] Athlone Institute of Thechnology, Polymers Department, Dublin Rd, Athlone, Co. Westmeath; E-mail: ggoetten@research.ait.ie (Gabriel Goetten) ddevine@ait.ie (Declan Devine); amandajunqueiraunifal@gmail.com (Amanda Junqueira); ramon_sejan@yahoo.com.br (Ramon Emanuel); carolinemirandalencar@gmail.com (Caroline de Alencar); mnugent@ait.ie (Michael Nugent)
* Author to whom correspondence should be addressed; E-mail: mnugent@ait.ie (Michael Nugent). Tel.+353 – (0)90 646 8000

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Abstract: Stimuli Sensitive hydrogels have enormous potential in various applications. Various environmental variables are found in the body, such as low pH and elevated temperatures. For this reason, either pH-sensitive and/or temperature-sensitive hydrogels can be used for site-specific controlled drug delivery. For many applications hydrogels require a very rapid time-response in terms of their sensitivity to either pH and/or temperature. Rapid time-responsive sensitivity is a research field which is still in development. In this research pH-sensitive hydrogels have been made varying the composition and molecular weight of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA). After total dissolution of the PVA/PAA the hydrogel was freeze/thawed. The swelling responses were investigated as well as the drug release profile with varying pH. The drug release was studied with a model drug theophylline. The characteristic properties were examined with ac impedance. The results showed that the optimum formulation to be used as a stimulus sensitive hydrogel is found with lower concentration of PVA and a higher concentration of PAA. These PVA/PAA hydrogels have potential in biomedical applications.

Keywords: Hydrogels; pH sensitivity; Poly(vinylAlcohol); Freeze-Thaw

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1. Introduction

pH sensitive hydrogel have in common a group pendant that is either acidic or basic. These groups are the responsible for the response pH condition, accepting or releasing protons. For this category of hydrogels composed by polyelectrolytes, the swelling ability is related to the pH environment [1]. The main application of hydrogels is drug delivery systems because pH is useful to control the area that the drug would be delivered and also the speed of release rate can be controlled with pH sensitive hydrogels.

Moreover, hydrogels created with PAA in the composition are protein resistivity, and this property makes the PAA useful in the medical field [2]. The purpose of this work is to compare different concentrations of the PVA with PAA and examine their swelling properties and conduct impedance tests to verify if there is any correlations between their different hydrogels.

2. Results and Discussion

Hydrogels made with PVA/PAA displays different aspects with different molecular weights (M.W.) of PAA. With a lower molecular weight of PAA the hydrogels displays a very weak gel even after the freeze-thaw process, the strongest gel possible with a lower M.W. is the composition of 5% PAA. However, with a higher M.W. of PAA, and an increase concentration a stronger gel is possible.

2.1. Swelling behavior

Figure 1 and 2 displays the swelling behavior of the manufactured hydrogels. It is shawn that the concentration of the PVA affects the swelling results. In addition, the concentration of PVA also affects the swelling results of PAA as well. At 5% of PVA and between the low molecular weights (Figure 1a) there is negectable difference with the swelling. However, on high molecular weights (Figure 1b) it can be observed that the results vary slightly. This can maybe due by the fact that some samples react more to a low pH than others. Alternatively, the samples with the condition of 7% of PVA with a low molecular weight (Figure 1c) present some differences on the reaction of the swelling in comparison with the 5% PVA samples. In fact, the 7% PVA samples reaches the swelling equilibrium earlier than the samples with 5% of concentration of PVA. Higher concentration of PVA improves the gel strength and increases the crosslink on the structure [3]. However, increasing the crosslinking density leads to lower swelling ratios [4]. This can be verified in both conditions of PVA (5% and 7%) that an increase of PAA concentrations can compromise the ratios of swelling.

Figure 2 illustrates the swelling behavior of PVA-PAA in buffer solution of 7.4. For all samples, swelling ratio of the hydrogels is found to increasing with pH. The samples which attained the maximum swelling ratio also reached swelling equilibrium earlier than others samples.

Figure 1. Swelling kinetics on deionized water for 5% of PVA and 5%PVA/PAA **(a)** with lower molecular weight and **(b)** higher molecular weight, 7%PVA and 7%PVA/PAA **(c)** with lower molecular weight and **(d)** higher molecular weight.

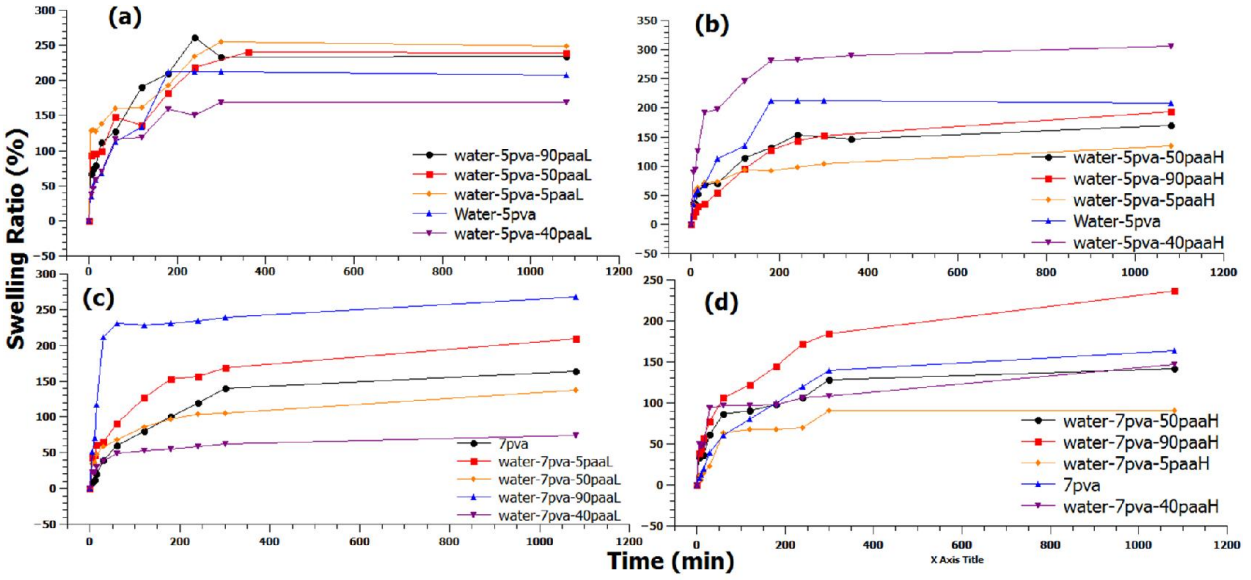
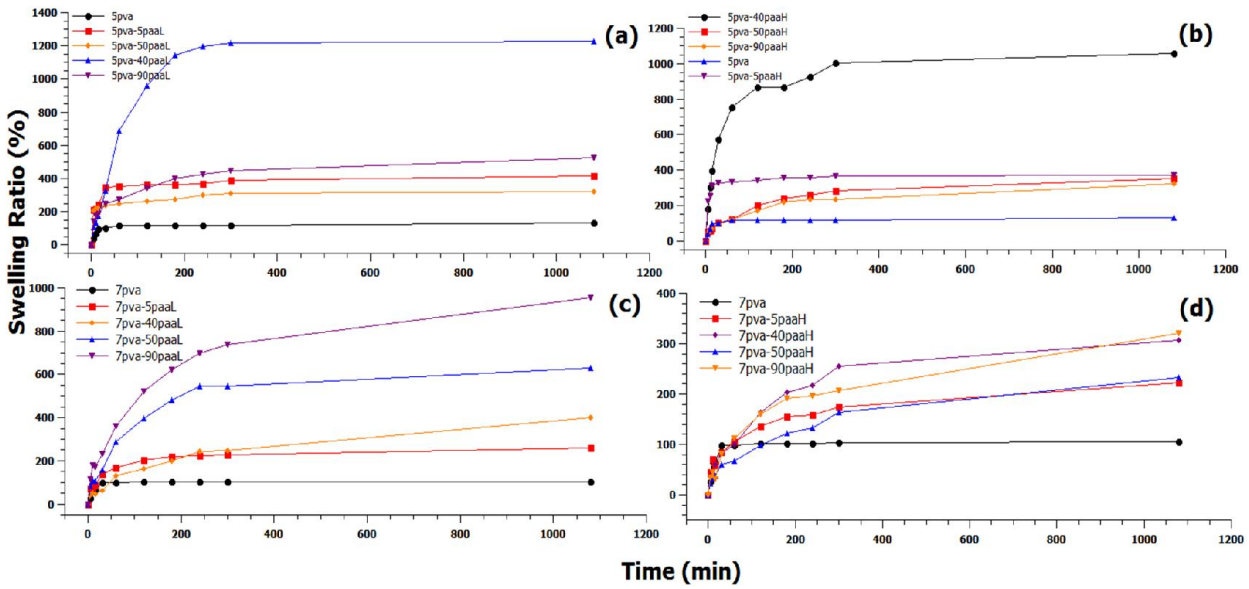


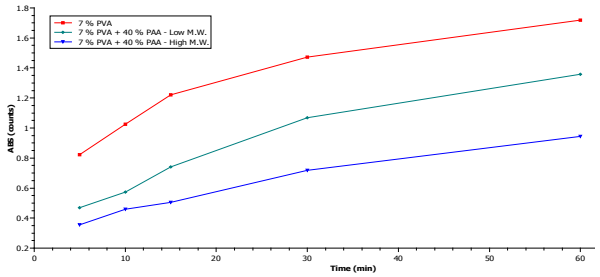
Figure 2. Swelling kinetics on buffer solution of pH7.4 for 5% of PVA and 5%PVA/PAA **(a)** with lower molecular weight and **(b)** higher molecular weight, 7%PVA and 7%PVA/PAA **(c)** with lower molecular weight and **(d)** higher molecular weight.



2.1. Drug release studies

Figure 3 shows the drug release profile for the 7% PVA/PAA (40%L and 40%H) at pH 7.4. The amount of released drug gradually increases as the time over by and the samples containing PAA lowered the concentration release in relation to samples containing only PVA.

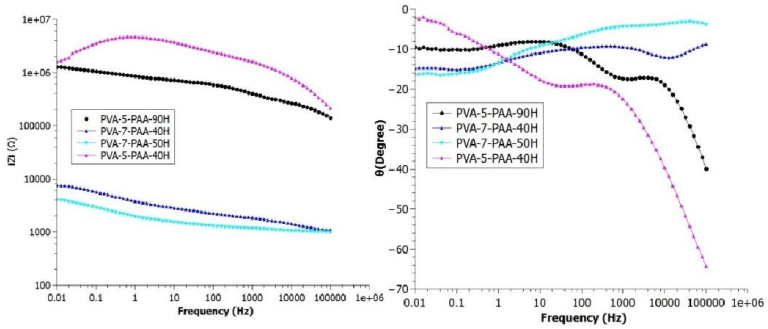
Figure 3. Drug release behaviors of PVA/PAA hydrogels at pH 7.4



2.2. Electrochemical impedance spectra (EIS)

Some hydrogels electro-sensitivity are increased by additional components with PVA and PAA. Therefore, measure of the impedance can be useful under low interface impedance to minimize electrode polarization and power consumption, as it is in neural stimulation [5]. The impedance of a neural electrode at the frequency of 1 kHz is an important characteristic parameter, as it correlates to the power consumption during electrical neural stimulation [6]. The EIS results of PVA/PAA samples are given in Figure 4. The samples with 5% of PVA show higher impedance than the samples with 7% of PVA. However, higher concentrations of PAA shows a decrease in impedance.

Figure 4. Bode plot of electrochemical impedance of PVA/PAA samples.



3. Experimental Section

3.1 Materials

PVA with average molecular weight of 4,500 and a degree of saponification of 56-98% and PAA with two molecular weights of 45,000 and 3 000,000 are used as supplied by Aldritch.

3.2 Preparation of the PVA-PAA

The PVA was dissolved on deionized water. The concentration of the PVA was varied according to the relation of weight / volume (w/v). The solution was maintained at 75°C with constant agitation until the complete solubilization of the PVA. Following the solubilization of PVA, the PAA was added in concentration of weight / weight (w/w) in relation to PVA. The samples were cooled to room

temperature and kept continuous agitation until the complete solubilization of the PAA. The table 1 indicates the samples conditions.

Table 1. Ratio and preparation conditions of PVA/PAA hydrogels

Codes	PVA	PAA Low M.W.	PAA High M.W.	Codes	PVA	PAA Low M.W.	PAA High M.W.
5PVA	5%	-	-	**7%PVA**	7%	-	-
5PVA - 5PAAL	5%	5%	-	**7PVA - 5PAAL**	7%	5%	-
5PVA - 40PAAL	5%	40%	-	**7PVA - 40PAAL**	7%	40%	-
5PVA - 50PAAL	5%	50%	-	**5PVA - 50PAAL**	7%	50%	-
5PVA - 90PAAL	5%	90%	-	**7PVA - 90PAAL**	7%	90%	-
5PVA - 5 PAAH	5%	-	5%	**7PVA - 5PAAH**	7%	-	5%
5PVA - 40PAAH	5%	-	40%	**7PVA - 40PAAH**	7%	-	40%
5PVA - 50PAAH	5%	-	50%	**7PVA - 50PAAH**	7%	-	50%
7%PVA - 90%H	5%	-	90%	**7PVA - 90PAAH**	7%	-	90%

After total solubilization of the PVA/PAA the samples were subjected to one cycle of freeze-thawing, the samples were held at 5 hours at -80°C and then thawed at room temperature for 24h. After this stage, the samples were dried in an oven for 12 hours at 80°C.

3.3 Swelling behavior and pH dependence on the swelling kinetics

For the swelling tests, initially it was measured gravimetrically [7].To measure the swelling kinetics, the preweighted samples were immersed in distilled water. The excess surface water was gently removed with paper and the swollen samples were measured at various time intervals. The swelling ratio percentage of a hydrogel can be defined as:

$$\mathrm{SR}(\%) = ((\mathrm{Ws} - \mathrm{Wd})/\mathrm{Wd} \times 100 \quad (1)$$

where Ws represents the weight of the swollen hydrogel at an specific time and Wd is the hydrogel dried mass.

3.4 Drug loading and release studies

To conduct the drug release studies solution were added 35 µg/mL of theophylline the PVA/PAA. The drug-loaded hydrogels were added into 900 mL solution and vibrated at 37◦C in pH 7.4, respectively. Subsequently, 5 mL solution was taken out to calculate their drug concentration and 5 mL original solution was added to supplement the release solution.

3.5 Characterization of the hydrogels.

The electrochemical impedance spectrum (EIS) of the test samples was measured at 25 ºC with an impedance gain-phase analyzer (Solartron 1290, UK) using 10-mV (rms). AC sinusoid signal at a

frequency range from 100 kHz to 1 Hz at the open-circuit potential (vs. SCE). Zplot and Zview software (Scriber Associates Inc.) were used for the measurement and curve fitting analyses

4. Conclusions

A series of PVA/PAA hydrogels with pH sensitivity were prepared with PVA and PAA of different molecular weights. Of these, the 5% PVA/50%PAA hydrogel exhibited the highest swelling ratio and promising response in terms of EIS. Therefore, the pH-sensitive PVA/PAA hydrogels have potential candidate to be used as a feasible drug controlled release system in particular where the sensitivity may be tailored by the application of an external electrical field.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest

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