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Polyvinyl alcohol hydrogels for capsules formulation

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ABSTRACT/RESUME

Abstract *: Poly(vinyl alcohol)-based hydrogels were prepared by freeze-thaw cycles (FT) and room temperature (RT) methods, in the presence of increasing proportions of sodium carbonate. Films from these hydrogels were characterized by ATR-FTIR, SEM, TGA/DSC, optical microscopy, and by their mechanical properties. The results of thermal analyses revealed that* T_g*s of the films from hydrogels made from RT were higher than those from FT method. Mechanical tests indicated the creation of significant free volumes between the PVA chains in the hydrogels of FT method. And, their mechanical stretching caused their chains to slip. However, the PVA chains from RT method were arranged in a star-like morphology, leading to their disassembling upon stretching. Overall, the global results of this study are promising for future applications in biomedicals, particularly in capsules making.*

I. Introduction

In the pharmaceutical field, the capsule is one of the oldest galenic forms in the history of biodegradable polymers. Hard pharmaceutical capsules, used for therapeutic purposes, have their origin in the strong interest aroused by the numerous discoveries in the pharmacological field. This has considerably broadened the range of possible formulations. Today, pharmaceutical capsules are mainly based on animal gelatin of porcine or bovine origin.

However, the use of animal gelatine in the food and pharmaceutical industry is subject to increasingly stringent regulations. The precautionary principle applied, for example, to the risk of transmission of bovine encephalopathy (mad cow disease) by animal gelatine has called into question its use. The sources from which gelatine comes can also pose religious or ethical problems for certain populations, many people around the world do not consume pork-based products (vegetarians, Muslims and Hebrews) or beef-based products (vegetarians and Hindus), it is for these reasons that the replacement of gelatine by other texturing agents of non-animal origin has been the subject of much research in recent years such as sucrose and gelatine from marine animals.

PVA hydrogels are of interest both to researchers, for their advantageous functional properties (emulsifying, foaming, gelling properties), and to industrialists who use them in numerous applications, particularly in the pharmaceutical field. PVA hydrogels are used in numerous applications biomedical, pharmaceutical and industrial [1-4]. Their bioadhesive characteristics, ease of forming and biocompatibility make them excellent candidates for biomaterials. Their elasticity, durability and simple chemical formula that can be modified by simple grafting, make PVAs suitable for capsule formulation. PVA hydrogel prepared by the method developed by Peppas (FT method) [5] has the advantage of not using a solvent that may remain in a residual state after gel formation.

The objective of this study is to prepare the PVA hydrogel by two different methods in order to have a polymer that can substitute gelatin and to determine the physicochemical properties of the generated films. Characterization by ATR- FTIR and tensile tests gave interesting results, allowing our samples to be used in biomedical engineering applications.

II. Materials and methods

II.1 Preparation of polyvinyl alcohol hydrogels

A 10% aqueous solution of PVA rhodoviol (4/20, hydrolysis rate, 98.2%; source: Prolabo) is prepared. Different proportions of sodium bicarbonate (SBC) are added to this solution (see Table 1). The different solutions thus prepared are placed in 10 cm diameter Petri dishes which have been subjected to 5 freeze-thaw cycles (FT); freezing at -20°C for 16 h, followed by thawing at 18°C for 8 h. This was the preparation of the PVA hydrogel by physical cross-linking. A second series of solutions with the same proportions was left at room temperature until the film (RT) was formed. Film formation varied between 3 and 7 days depending on the composition of the sodium bicarbonate hydrogel.

Table 1. *Composition of PVA-based hydrogels*

Freeze/thaw method (FT)		Preparation at room temperature (RT)	
Composition	**Designation**	**Composition**	**Designation**
PVA	1**A**	PVA	1**A’**
PVA+1% SBC	2**A**	PVA+1% SBC	2**A’**
PVA+5% SBC	3**A**	PVA+5% SBC	3**A’**

II.2 ATR-FTIR Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was performed using the Attenuated Total Reflectance Mode (ATR) on a 360 FTIR avator nicolet, with a persecution cycle of 32 scans and a resolution of 8 cm^{-1}. Samples were scanned from 400 to 4000 cm^{-1}.

II.3 Mechanical tests

The mechanical tests were performed on a Zwick-Roell Z25 universal machine, equipped with the expert test software V9.0 and a 2.5 KN force sensor (Fig 2). The tests were carried out at 22 °C. A computer was used for control and acquisition. In tensile tests, at least five specimens were loaded for each type of laminate with a test speed of 10 mm/min. The specimens were cut to a length of 100 mm and a height of less than 1 mm according to ISO 527-3 standards.

II.4 Observations by optical microscope

The films before and after stretching were observed by optical microscope type OPTIKA ITALY S-20-2L WF 10X20mm incident and transmitted light tungsten bulbs.

III. Results and discussion

III.1 General observations and characterization by FT-IR

Films from PVA hydrogels containing SBC (2A, 3A, 2A', 3A') were found to form more rapidly and become more translucent than those from SBC-free hydrogels. This can be attributed to the weak cross-linking of PVA by HCO3- bicarbonate ions as shown in Figure 1; hydrogen bonds could be established between the hydroxyl (OH) groups of PVA and the oxygen groups of HCO3-, thus ensuring cross-linking.

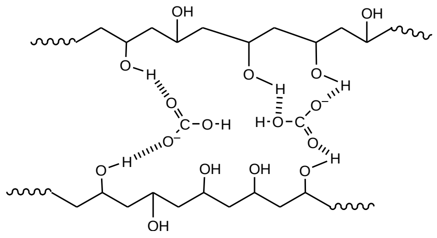


Figure 1. Film structure from PVA hydrogel in the presence of SBC.

On the other hand, it was observed that films from 1A', 2A' and 3A' formulations were smoother to the touch and more transparent than those from 1A, 2A and 3A, proving the effect of the hydrogel preparation method on the texture of the generated film. However, the same hydrogel composition was maintained for both methods. This difference in the external appearance of the films could also be due to the difference in their thicknesses. Indeed, the film thicknesses from 1A' and 2A' were 2.60 and 2.84 mm, respectively, while 1A and 2A films were thicker, reaching 3.36 and 5.05 mm, respectively. In addition, the results of hydrogel film analysis obtained by both methods using ATR-FTIR effectively corroborated this noted difference. As can be seen (Figure 2), their absorption regions of 2500-3000 cm-1 of the spectra indicate a certain nuance of the films due to the difference between FT and RT methods. Indeed, the absorption band at 3262 cm-1 of the FT method films could be attributed to the elongation vibrations of the OH group and the hydrogen bond formed, coupled with that of COO- [6, 7]. The shape of this band is totally different from that observed for RT films. The asymmetrical elongation vibrations of the C-H bonds of the FT method PVA are visible at 2900 cm-1 and are absent in the RT method PVA. However, the presence of the 850 and 916 cm-1 bands in the spectra of all samples is strong evidence of the PVA skeleton. In addition, the weak bands at 1725-1740 and 1630 cm-1 reveal the existence of carbonyl groups, including residual acetyl groups during the hydrolysis of polyvinyl acetate. The 1142 cm-1 band is characteristic of the C-O bond of the polymer.

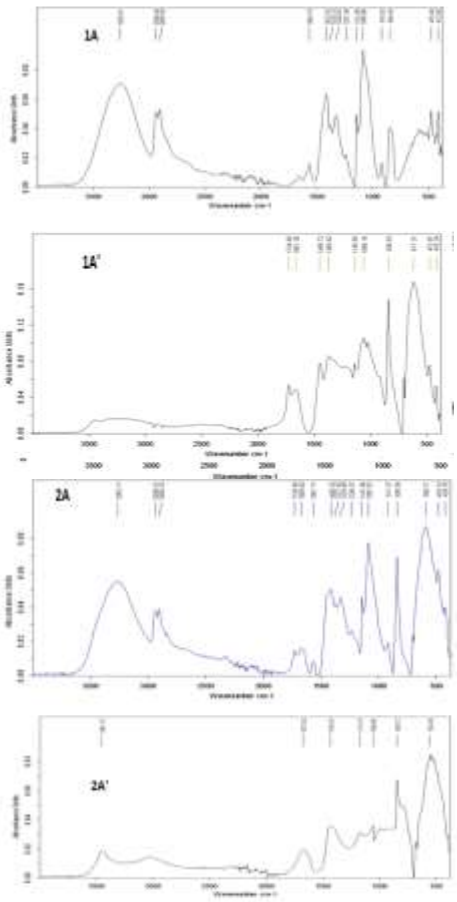


Figure 2. ATR-FTIR spectra of films obtained from hydrogels 1A, 2A, 1A', and 2A'.

III.2 Gel fraction

The gel fraction (GF) is another property of a hydrogel, characterizing its water absorption capacity and the type of morphology of the polymer. To determine this fraction, the hydrogel is first allowed to swell in a certain amount of water until equilibrium (4 days at room temperature). The swollen hydrogel is then dried in an oven for a period of time (6 h). The gel fraction is therefore estimated by the following relationship:

$$GF\ (\%) = \left(\frac{We}{Wo}\right) \times 100$$

where We and Wo are the mass of the initial hydrogel in the dry state and the mass of the hydrogel after drying (removal of absorbed water), respectively. The gel fractions of the different hydrogels are grouped in Table 2. As can be seen, the GFs of hydrogels obtained by RT are higher than those of hydrogels obtained by FT, meaning that the macromolecular chains are arranged in such a way that they allow significant hydration. Hydrogel 2A' would be more interesting because it has the highest GF of hydrogels.

50%. In any case, the addition of SBC increases the gel fraction of the hydrogel, because some hydrogen bonds (interchains) between the hydroxyl groups of the PVA chains would be broken, thus allowing hydration of the OHs; the OHs would be much more accessible to water molecules. However, an optimal percentage of SBC above 1% but below 5% could give better results because a drop in GF is noted at the latter percentage (33.35%).

Table 2. Gel fractions of different samples

Hydrogel	1**A**	1**A’**	2**A**	2**A’**	3**A**	3**A’**
GF (%)	18,00	24,75	16,65	50,00	23,10	33,35

III.3 Mechanical properties

To enhance the performance of hydrogels in particular applications, the study of their mechanical properties is of paramount importance [6]. The behavior of PVA hydrogels prepared by the RT method has been shown to be viscoelastic. Indeed, the viscoelastic curves of the different hydrogels shown in Figure 3 indicate a ductile (thermoplastic) behavior, clearly showing the linear elastic behavior followed by a viscous behavior. The fact that the curves have the same shape suggests that the viscoelastic behavior of the hydrogel does not depend on the method of its preparation.

Table 3. *Results of stress-strain tests*.*

Hydrogel	σ_B (MPa)	ε_B (%)	ε_{max} (%)	σ_{max} (MPa)	E (MPa)
1A	14.49	122.52	116.67	21.26	14.51
1A'	8.44	161.34	136.21	23.04	14.28
2A	12.18	21.22	20.08	12.72	1.47
2A'	10.91	209.74	187.03	19.38	0.33

*σB : Stress at break; εB = Elongation at break; σmax = Maximum stress
εmax: Maximum elongation; E = Young's modulus

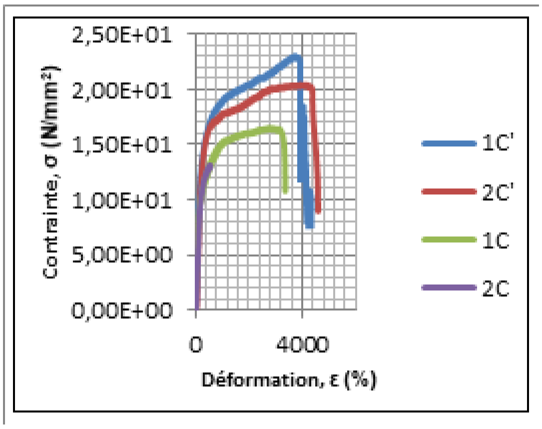


Figure 3. Stress-strain curves of different hydrogels.

The different mechanical parameters of these hydrogels deduced from their viscoelasticity curves are presented in Table 3. It is evident that the mechanical parameters are strongly influenced by the addition of 1% sodium bicarbonate. The increase in elongation (εB and εmax) and the decrease in stress (σB and σmax) when incorporating 1% SBC reflect the plasticizing role of the latter. A small amount of plasticizer can be easily inserted between polymer chains, increasing their mobility and free volume, thus decreasing the mechanical resistance of the polymer and improving their extensibility. However, the addition of a large amount of plasticizer could weaken the polymer. It can also be seen that the higher the gel fraction (Table 2), the higher the free volume will increase, giving better mechanical properties up to a threshold SBC concentration. The 1A and 1A' hydrogels have a high elasticity with a Young's modulus of 14.50 and 14.28 MPa, respectively.

III.4 Microscopic observations

Optical microscope images (Figure 4) reveal that the texture of the films prepared by the two methods before and after stretching shows a noticeable difference. This is probably due to a particular rearrangement of the macromolecular chains during stretching. By the FT method, the macromolecules take on a sheet structure (c'), while those formed by the RT method take on a star shape (d'), as shown in Figure 5. These results have been consolidated by the images revealed by SEM (Figure 6), highlighting the near difference between the two systems in morphology. The SEM images highlight the existence of pores in the internal structure of the hydrogel obtained by the FT method, whose diameter increases with stretching. On the other hand, the hydrogel obtained by the RT method is in the form of intertwined needles which are transformed into a homogeneous sheet by stretching.

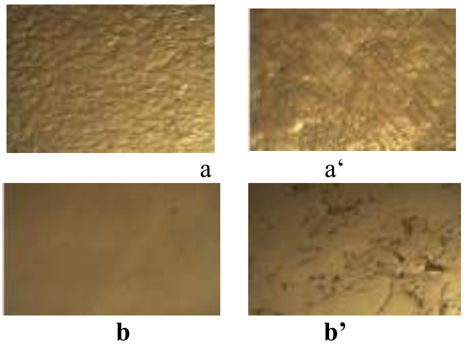


Figure 4. *Images of optical microscope films:* ***a*** *and* ***a'****, films from the FT method, before and after stretching;* ***b*** *and* ***b'****, films from the RT method, before and after stretching.*

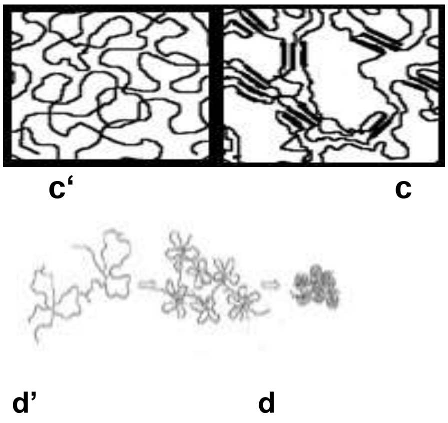
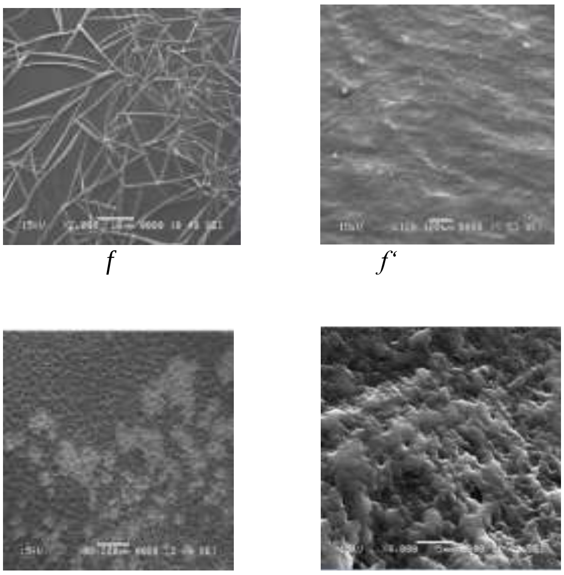


Figure 5. *Leaf* ***(c')*** *and star structure* ***(d')*** *after stretching* ***c*** *and* ***d.***



f *f'*

.e e'

Figure 6. *SEM images of films:* ***e*** *and* ***e'****, films from the* ***FT*** *method, before and after stretching;* ***f*** *and* ***f'****, films from the* ***RT*** *method, before and after stretching.*

III.5 Thermal properties

The thermal properties of the VAPs obtained by the two methods were determined using DSC (Figure 7). The glass transition temperatures (Tg) and melting temperatures (Tm) of these PVAs are presented in Table 4. The measured Tgs are significantly higher than the Tg of a regular PVA (82 °C). For RT PVAs, the Tg and Tm temperatures are higher than those of PVAs obtained by the FT method for hydrogels without SBC and with 1% SBC.

Table 4. *Glass Transition Temperatures Tg and fusion Tm of PVAs*

PVA	Tg (°C)	Tm (°C)
1A	88,5	220,33
1A’	96,8	226,37
2A	86,4	244,96
2A’	95,2	240,34
3A	94,6	247,53
3A’	91,6	238,25

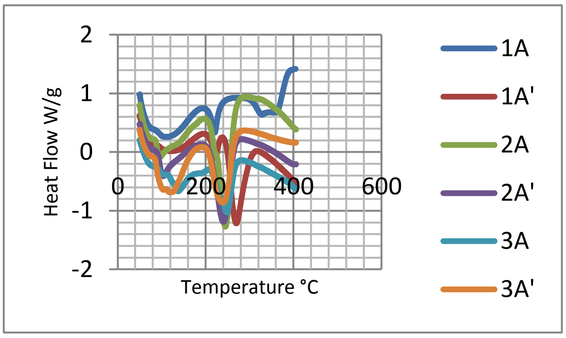


Figure 7. *DSC thermograms of the different PVAs obtained by both* ***FT*** *and* ***RT*** *methods.*

It seems that the effect of freezing (-20°C) remains even after thawing, causing a restriction in the mobility of the macromolecular chains, resulting in a relatively lower Tg. For hydrogel with 5% SBC, on the other hand, these temperatures are lower than those of the PVAs of the FT method. The effect of SBC, as a physical cross-linking agent, on Tg only occurred at a rate of 5%; it was 88.5°C in the absence of SBC (1A) and increased to 94.6°C for 5% SBC (3A). A high level of crosslinker leads to a decrease in the free volume and mobility of the macromolecular chains [8-9] as shown in Figure 1.

VI. Conclusion

In this study, the properties of hydrogels prepared by the freeze/thaw (FT) method and the room temperature method were found to be different. This is only a consequence of the difference between the morphological structures of the PVAs obtained by these two methods. The addition of a physical cross-linking agent, namely sodium bicarbonate, clearly improves certain properties, while ensuring the correct choice of the level of this agent.

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