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Influence of processing parameters on the macroscopic mechanical behavior of PVA hydrogels

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This paper investigates the influence of three different processing parameters on the global mechanical behavior of PVA (Polyvinyl alcohol)/DMSO (Dimethylsulfoxide) hydrogels: the initial concentration of PVA, the DMSO:H₂O ratio and the number of freeze/thaw cycle applied to the material. A specific thermo-regulated testing apparatus for hydrophilic materials is presented, along with the performed cyclic and rupture tests. The observed mechanical responses are explained by an in-depth analysis of the cross-linking phenomenon. Using the Neo-Hookean hyperelastic model, the experimental data is fitted and a link between the density of macromolecular chains in the material and its mechanical behavior is established. Strong differences are observed and discussed.

1. Introduction

Poly(vinyl alcohol) (PVA) hydrogels are used for various pharmaceutical [1] and biomedical [2] applications. It is a polymer of great interest since it is non-toxic, non-carcinogenic, bioadhesive and easy to process [3]. The elastic behavior of the hydrogel, its lifetime and the simplicity of its chemical composition result in its acceptance by the human body. Its stiffness, which can easily be controlled by adjusting its chemical composition, can compare well to the one of soft tissues. PVA is used in drug delivery systems [4], contact lenses [5], and substitutes tendons [6], ligaments [7], cartilage [8], and more.

PVA hydrogels can be prepared by various methods which impact their mechanical and optical properties. They can be cross-linked through the use of cross-linking agents, resulting in residual amounts of potentially toxic agents in the PVA gel [9]. Another method of chemical cross-linking includes the use of electron beam or γ -irradiation [10]. These methods have the advantage of not leaving behind potentially toxic agents but often result in bubble formation [10]. A “physical” cross-linking of the hydrogel is also possible [11] due to crystallite formation upon repeated freezing and thawing cycles. This method results in a high degree of swelling in water and an elastic nature. In addition, the properties of the hydrogel are influenced by the molecular weight of the polymer, the concentration of the aqueous PVA solution, the temperature and time of freezing and thawing and by the number of freezing/thawing cycles [12]. An improvement of mechanical properties

when using a gelation process using an aqueous solution of dimethylsulfoxide (DMSO) has been reported [13]. This study aims at quantifying the effect of the processing parameters of this last process on the mechanical behavior of the ensuing hydrogel. To this day, the available information is limited to the evolution of the mechanical properties with aging [14], the effect of processing parameters on the structure [12] and basic tensile testing [13].

The correlation between the molecular weight and the size of crystallites in PVA polymers has already been established [15]. It is also known that there is a minimum PVA chain length necessary for crystallization [3]. For these reasons, it was chosen to study a PVA of specific molecular weight instead of evaluating the impact of the polydispersity of the polymer. This paper aims at studying the influence of the processing parameters on the mechanical behavior of specific PVA hydrogels. Section 2 presents the materials and the experimental setup. Section 3 gives the results obtained for different processing parameters. The evolution of the mechanical behavior is discussed in Section 4. Finally, concluding remarks close the paper.

2. Experimental setup

This section focuses on the presentation of the elaboration parameters of the hydrogel, its preparation, the experimental setup of this study and the description of the mechanical tests performed.

2.1. Preparation of PVA hydrogels

The polymer used in this study is a PVA (Mw 85,000–124,000, 99 + % hydrolyzed) from Sigma Aldrich. It was stored in a dry

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environment to prevent moisture absorption. DMSO (ACS reagent, $\geq 99.9\%$) was also obtained from Sigma Aldrich. Solutions were prepared by heating a mixture of PVA in an aqueous medium of ultra-pure water and DMSO for 2 h at 120 °C on a magnetic stirrer. DMSO is used to regulate the freezing of the aqueous medium, which would otherwise lead to phase separation and prevent the large formation of PVA crystallines [13]. The beaker used was covered to avoid loss of water and DMSO vapors. After the heating step, the PVA solutions were placed in a vacuum bell at room temperature to facilitate the release of air bubbles. The solutions were then injected into 2 mm thick rectangular molds and placed in a cooling oven in which freeze/thaw (10 h at -20 °C followed by 2 h at 20 °C at a constant rate) cycles were achieved. The solutions' dosages and the number of applied cycles are listed in Table 1. Since a physical cross-linking process is used to synthesize the polymers, no covalent bonds are formed between the hydrogel and the DMSO. The latter can thus be evacuated by repeated rinsing. The 2 mm rectangular hydrogel sheets were rinsed by exposing them to a flow of water for 5 min, 3 times per day the first week following synthesis. The polymers were then stored for 4 months in containers filled with distilled water, which was renewed every day. This ensured the extraction of any residual DMSO [12,13] and limited aging effects [14].

2.2. Mechanical testing of the hydrogel

Rectangular samples of 40 mm width and 10 mm height were then cut from the rinsed hydrogel sheets for pure shear testing and inserted in the sample holders. The resulting area of interest (AOI) is a 40 mm width and 2 mm height rectangle, as shown in Fig. 1.

Fig. 2 shows the tested sample in both its initial and deformed states. It is supposed that the sample stays rectangular and border effects are neglected [16]. The material deformation gradient tensor \bar{F} describes the motion of a continuum. It characterizes the transformation of a material point from the reference configuration to a deformed one. The material is considered incompressible, which translates into $\det(F) = 1$. This implies that \bar{F} can be written as:

$$F = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \lambda^{-1} \end{bmatrix} \quad (1)$$

where $\lambda = \frac{l}{l_0}$ is the stretch (l and l_0 are the initial and instantaneous height of the specimen, as presented in Fig. 2). The tests are analyzed by measuring the nominal stress defined as:

$$\pi = \frac{F}{A_0} \quad (2)$$

where F is the applied force and A_0 the initial cross section.

Being hydrophilic, PVA hydrogels tend to dry up when removed from water. To attend this problem, a thermostatic tank was designed to conduct immersed mechanical tests at a controlled temperature on a Gabo Eplexor 500 N mechanical test machine fitted with a 10 N force transducer. Fig. 3 shows the device that consists of a hermetic steel tank, heat cartridges, a thermocouple sensor and a proportional-integral-derivative closed loop controller to adjust the temperature of

the tank. The tests were performed at a constant temperature of 37 ± 1 °C.

In order to investigate the behavior of the material, different types of mechanical tests are performed. The first consists in a series of 5 load-unload cycles reaching a stretch of $\lambda = 1.25$ to analyze the cyclic behavior of the material. The second type is a load until failure in order to obtain the ultimate strain and stress of the material.

3. Test results

3.1. Cyclic tests

Results obtained on gels processed with a PVA concentration of 10 wt% and 5 wt% are presented in Figs. 4 and 5 respectively. The general shape of the curves is the same for all the tested materials, although the reached values differ. Hence the description of a single curve can apply to all the others. Focusing on A_1 for example, all the loading phases are superimposed except for the first one. This softening phenomenon is often present in polymeric material and is known as stress-softening [17]. In the present case, however, the phenomenon is small and can be neglected. The unloading phases are all overlaid. Also, the difference between the loading and unloading phases, however small it may be, can be associated to hysteresis which is characteristic of the behavior of viscoelastic materials. It can be noted that the hysteresis is very small. The viscoelastic phenomenon is negligible in comparison to the hyperelastic behavior. Nevertheless, a residual strain appears. The evolution of the phenomena mentioned earlier - i.e. stress level reached, hysteresis, residual strain and softening- will be evaluated function of the processing parameters.

Fig. 4a shows the mechanical response of materials composed of 10 wt% PVA and 80% DMSO. The stress level reached for a stretch of 1.25 decreases with the number of freeze/thaw cycles. Residual strain and hysteresis, however, are maximal for 2 freeze/thaw cycles and minimal for 1. Samples A_2 and A_3 , unlike A_1 , exhibit some stress softening.

The results for a DMSO concentration of 60% are presented in Fig. 4b. In this case the highest and lowest levels of stress are observed for 2 and 1 freeze/thaw cycles respectively. Residual strains behave similarly for materials containing 10 wt% PVA and 80% DMSO, even though the hysteresis is slightly more important. Stress-softening, however, does not appear as the first load is confounded with the others.

In general, no significant trend can be extracted concerning the stress level reached achieved by materials containing 10 wt% PVA. Hysteresis and residual strain, however, increase with the number of freeze/thaw cycles. Stress-softening is only observed for 80% DMSO.

Fig. 5 presents the results of the pure shear cyclic tests on hydrogels containing 5 wt% PVA. Since materials B_1 and E_1 are so brittle, inserting them in the sample holders was problematic and a couple of loading cycles were enough to tear them. This explains why no cyclic data is provided for these materials.

For a DMSO concentration of 80% (Fig. 5a), the highest stress is achieved for 2 freeze/thaw cycles, but the variation is very small. Also both samples have the same residual strain, which can reach 10%, and a very similar softening rate. The hysteresis is relatively large for the first load/unload cycle but becomes quasi-null for the following ones.

Table 1
Processing parameters of the PVA hydrogels.

Sample	Initial PVA concentration in solution [wt%]	Initial DMSO:H ₂ O ratio	Number of freeze/thaw cycles
A_1, A_2, A_3	10	80:20	1, 2, 3
B_1, B_2, B_3	5	60:40	1, 2, 3
C_1, C_2, C_3	10	80:20	1, 2, 3
D_1, D_2, D_3	5	60:40	1, 2, 3
E_1, E_2, E_3	5	40:60	1, 2, 3

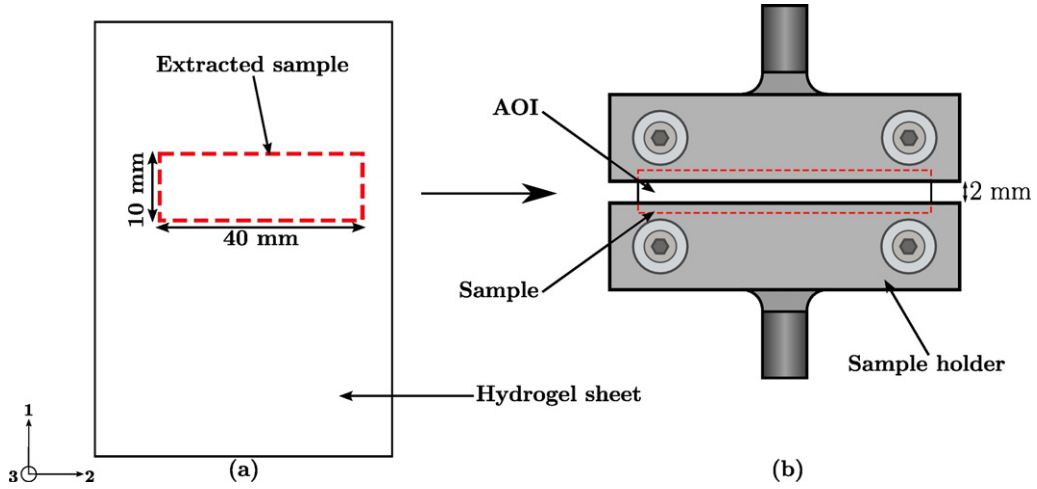


Fig. 1. Sample preparation: (a) extraction of the sample from the hydrogel sheet, (b) insertion of the extracted sample in the sample holders.

Fig. 5b shows that the highest stress level is reached by materials containing 60% DMSO and increases with the number of freeze/thaw cycles, although in this case also, the variation is not very important. The residual strain, however, is maximal for sample D_3 and minimal for sample D_1 . Softening increases with freeze/thaw cycles while hysteresis remains constant.

For material configuration E (Fig. 5c), the highest stress level is reached by sample E_3 . In comparison with material E_2 , only a slightly more important softening can be observed while the residual strain is equivalent. Hysteresis however, does not manifest for a DMSO concentration of 5%.

In general, for materials containing 5 wt% PVA, highest stresses are achieved for a DMSO concentration of 60% while the residual strain is maximal for 80% DMSO. These two statements compare well with the observations made on materials containing 10 wt% PVA. Softening can be observed for all material configurations except D_1 , and hysteresis can almost be neglected.

To sum up, the initial PVA concentration has a consequent influence on the yielded stress by the material: on average, for a given DMSO:H₂O ratio and a given number of freeze/thaw cycles, the maximum achieved stress is 3 times higher for a PVA concentration of 10 wt%. The effect of DMSO seems maximal for a concentration of 60%. The effect of the number of freeze/thaw cycles depends on the other two parameters.

3.2. Ultimate values

The analysis of the evolution of the ultimate stress and strain of the material gives a general overview of the effect of the processing parameters. Tables 2 and 3 show the results of the tests. Materials containing 10 wt% of PVA, i.e. A and C compositions, reach higher ultimate strains and stress than gels containing 5 wt% of PVA.

Table 2 presents the results for hydrogels containing 10 wt% PVA. Its analysis shows that the ultimate strain seems to be increasing with the number of freeze/thaw cycles in an almost linear manner for materials containing 80% DMSO. The ultimate stress however, is maximal for 2 freeze/thaw cycles and quasi-equal for 1 and 3 cycles.

For hydrogels containing 60% DMSO, the ultimate strain is maximal for C_1 and minimal for C_2 , even though the difference in their values is relatively small, i.e. 21%. The ultimate stress however, is maximal for 2 freeze/thaw cycles and minimal for 1, albeit the difference between C_1 and C_3 being of 18 kPa only.

Table 3 shows that the ultimate stress and strain increase with the number of freeze/thaw cycles for all three compositions. In this case also, materials containing 60% DMSO achieve the highest ultimate stress for a given amount of freeze/thaw cycles, except for material D_1 which is slightly lower than B_1 . Hydrogels containing 80% DMSO having undergone 1 or 2 freeze/thaw cycles reach the highest strains before breaking,

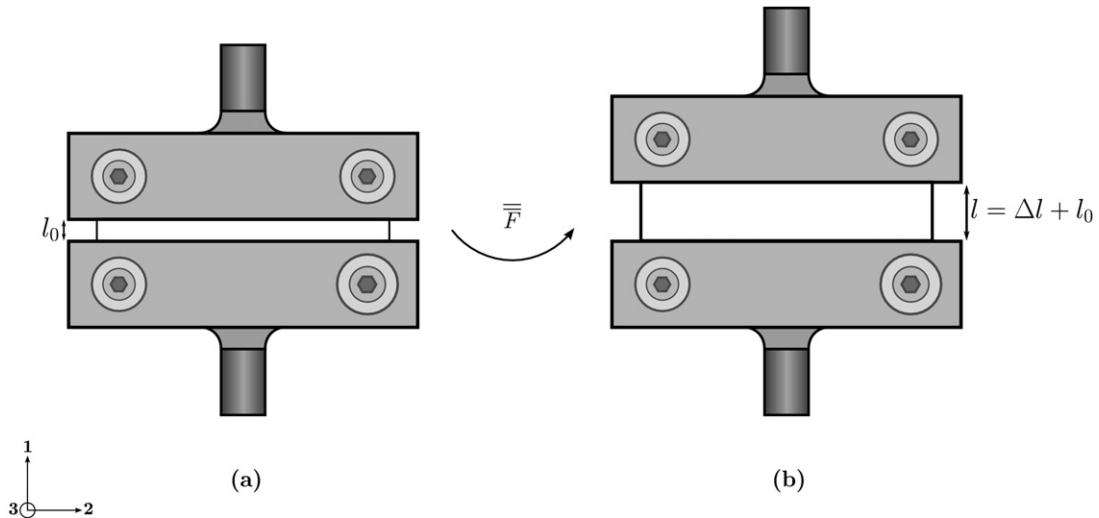


Fig. 2. Pure shear test: (a) initial configuration of the material, (b) deformed configuration of the material.

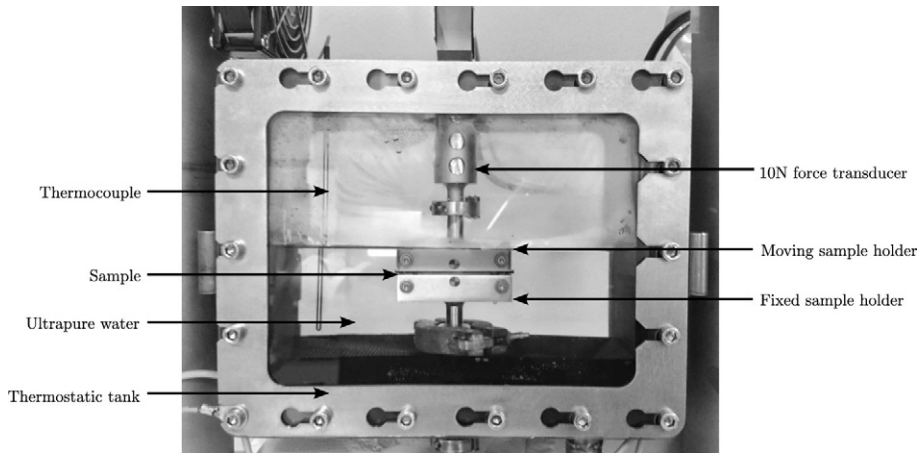


Fig. 3. The mechanical testing apparatus: the sample and its holders are inserted in a stainless steel tank containing a thermostatic aqueous medium.

while D_3 , which contains 60% DMSO, achieves the highest ultimate strain for materials made with 3 cycles.

Fig. 6 shows a scatter of hydrogel compositions based on ultimate strain and stress. Higher PVA concentration clearly improves mechanical behavior. On average, a hydrogel containing a concentration of PVA of 10 wt% can yield ultimate stresses four times larger than hydrogels containing 5 wt%. The number of freeze/thaw cycles, however, seems to improve the ultimate strain achieved by materials. A DMSO concentration of 60% produces materials that yield the highest stress for a given PVA dosage while ultimate strain seems to improve with freeze/thaw cycles.

In summary, cyclic tests and failure tests lead to the same conclusion. Higher PVA concentration improves the mechanical behavior of the hydrogel. This trend was already observed by [12], even though the ultimate stresses for different materials measured in this study are significantly lower. The ultimate strains, however, are consistent.

The DMSO's influence varies with the quantity of PVA in the initial solution, but hydrogels containing 60% DMSO yield the highest stresses.

The influence of the number of freeze/thaw cycles is difficult to assess for the cyclic tests as it did not seem to have much effect on

hydrogels containing 5% PVA and no clear trend could be extracted for materials made of 10% PVA.

4. Discussion

In this section, the cross-linking mechanism is first described in order to evaluate its impact on the mechanical behavior of the hydrogels when submitted to different tests. An explanation of the observed results is then proposed accordingly. Finally, the impact of the processing parameters on the mechanical properties of the hydrogel will be quantified by considering the Neo-Hookean model.

4.1. Description of the cross-linking mechanism

According to Yokoyama et al. [18], the hydrogel is composed of three kind of phases: the solution phases with a very low concentration of PVA, which corresponds to the crystal phases of ice in the frozen gel; the amorphous phases, in which every PVA chain is associated with water; and the PVA crystal phases, which restrain gross mobility of the amorphous chains.

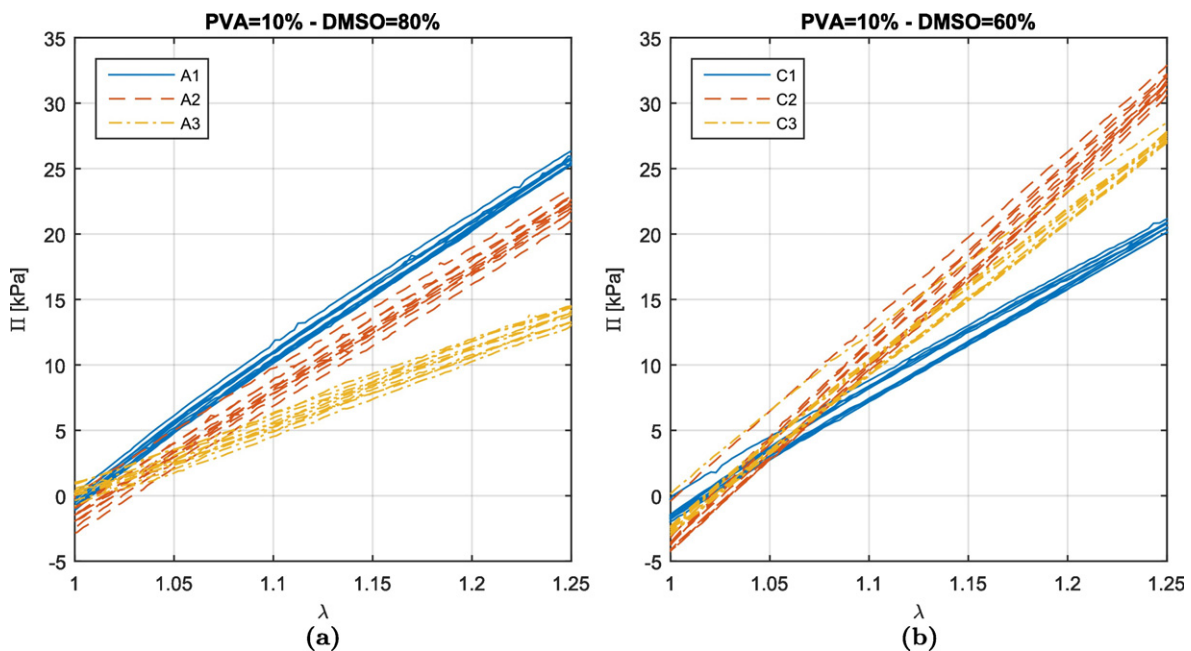


Fig. 4. Cyclic pure shear test results for a concentration of 10% PVA and (a) 80% DMSO and (b) 60% DMSO.

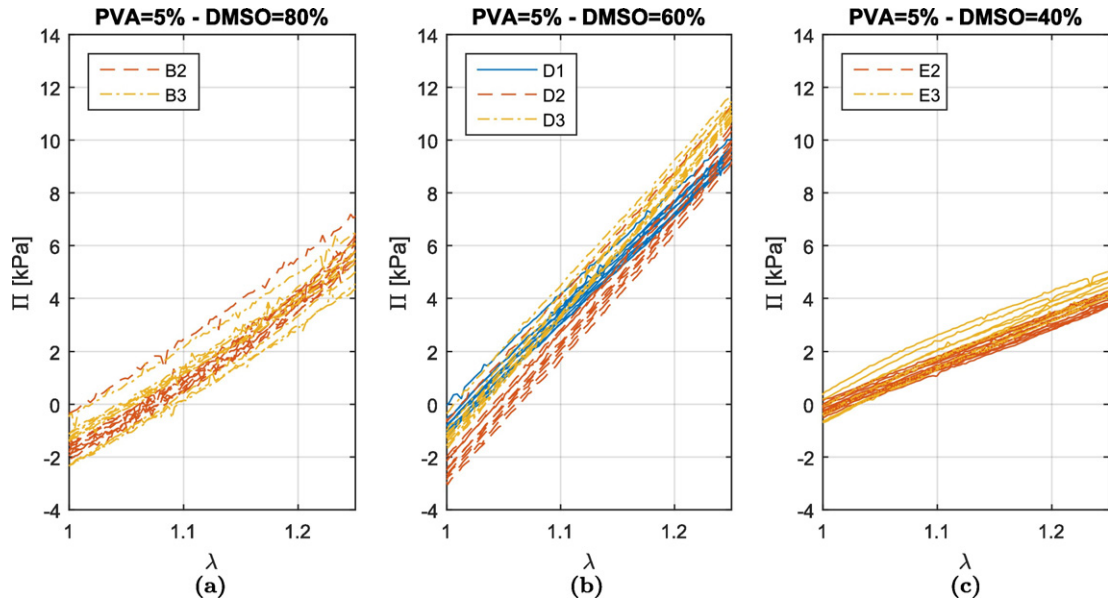


Fig. 5. Cyclic pure shear test results for a concentration of 5% PVA and (a) 80% DMSO, (b) 60% DMSO and (c) 40% DMSO.

During the freezing process, the ice crystals formed by the solution phases force the amorphous chains - which are initially free and distributed homogeneously in the solution (water and DMSO in this study) - to become constricted in whatever space is not crystallized. The amorphous chains, associated with water through hydrogen bonds, maintain a fraction of the PVA in its amorphous state, which prevents complete crystallization of the polymer thus giving it a rubbery texture. The crystal phase consists of a high concentration of polymer chains linked to each other and excluding any trace of solution. By restraining the mobility of certain points of the structure, it ensures cross-linking. Repeating the freeze/thaw process should push more and more amorphous chains to the previously established amorphous phase, thus increasing its molecular concentration, while also increasing the size of the crystallines.

DMSO is used to prevent the freezing of the PVA solution by bonding to water molecules, thus preserving the amorphous phase and achieving cross-linking faster. Hoshino et al. [19] showed that at 23 °C, approximately 800, 50 and 1100 min were needed to form gels containing 40%, 60% and 80% DMSO respectively and 5 wt% PVA. Although cross-linked differently - at room temperature vs. -20 °C - this might explain the fact that hydrogels containing 60% DMSO exhibit better mechanical properties than others: the amorphous phase starts forming quicker which leads to denser polymer chains and crystallines.

The cross-linking mechanism is thus responsible for the cyclic response of the hydrogels: the amorphous chains being randomly organized, the first tensile load applied to the material is expected to unfold them to a certain measure. After unloading, the chains recover their initial state through elasticity, but are unable to retrieve their tangled configuration. Due to this new configuration of the amorphous phase, a smaller effort is needed to reach the desired strain thus explaining the difference between the first load and all the following loads. This explanation also accounts for the residual strain observed on the tested materials. The hysteresis, however small in the loading

range, is a result of the viscous behavior of the polymer chains of the amorphous phase. Stress softening might be caused by the rupture of some polymer chains during loading. Being fragile, the crystal phase might have also been damaged during cyclic loading, thus explaining the failures of materials B_1 and E_1 .

For hydrogels containing 5 wt% PVA, the results concur with the observations of Hoshino et al. [19], i.e. the stress level reached is highest for a DMSO concentration of 60% and lowest for one of 80%. The effect of freeze/thaw cycles is less obvious at this stretch level, but the fact that materials B_1 and E_1 did not achieve the cyclic test while materials $B_{2,3}$ and $E_{2,3}$ did, suggests that the resistance to tearing during cyclic loading is improved.

For hydrogels containing 10 wt% PVA also, the highest stress levels are also most important for the configuration containing 60% DMSO except for material made by a single freeze/thaw cycle.

The response of the material to rupture tests can be explained by the fact that a larger PVA concentration ultimately leads to denser amorphous and crystal phases. More amorphous polymer chains increase the resistance to strain and lead to a larger yielded stress. This is easily visible on Fig. 6: on average, configurations A and C yield ultimate stresses four times larger than materials B , D and E and ultimate strains twice as big. For configurations A , B , D and E , the ultimate strain achieved by most tested hydrogels improves with the number of freeze/thaw cycles. This can be explained by the increase of PVA chains in the crystal phase with the number of freeze/thaw cycles, resulting in an improvement of resistance to rupture of the hydrogels. For configuration C , achieved ultimate strains remain constant regardless of the number of freeze/thaw cycles. This might be due to a fully cross-linked structure after a single cycle. The variation of ultimate stress increases with the number of cycles for materials containing 5 wt% PVA. For hydrogel compositions A and C , however, no clear trend can be extracted.

Table 2

Ultimate stress and strain of the material for different processing parameters at a fixed PVA concentration of 10%.

Sample ID	A_1	A_2	A_3	C_1	C_2	C_3
Ultimate strain [%]	222	310	434	358	337	349
Ultimate stress [kPa]	188	230	189	198	292	216

Table 3

Ultimate stress and strain of the material for different processing parameters at a fixed PVA concentration of 5%.

Sample ID	E_1	E_2	E_3	D_1	D_2	D_3	B_1	B_2	B_3
Ultimate strain [%]	154	218	261	84	187	323	72	117	200
Ultimate stress [kPa]	38	48	77	31	81	95	10	31	56

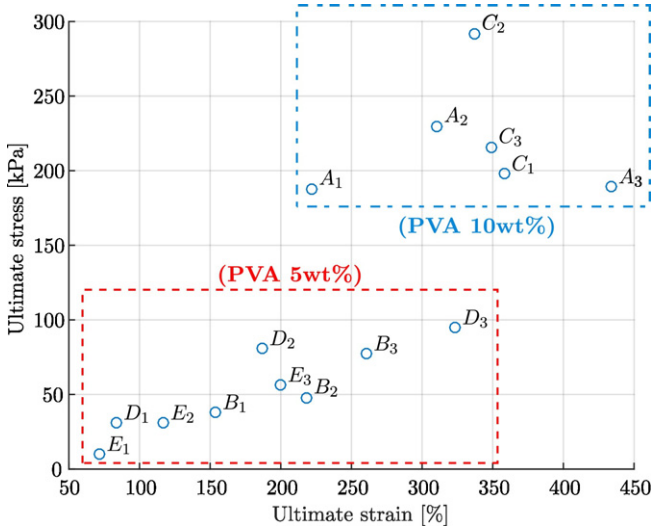


Fig. 6. Repartition of hydrogel compositions based on ultimate strain and ultimate stress.

4.2. Modeling the mechanical response

As presented in Section 3, the mechanical behavior of the PVA presents few viscoelastic effects. This means that it can be modeled by a pure elastic model. It is proposed to fit a hyper-elastic model on the first loading curve of the cyclic tests of the material. For this purpose, the Neo-Hookean constitutive law [20] is used to predict the experimental results previously presented. The Neo-Hookean equation is written as:

$$W = C_1^{NH} (I_1 - 3) \quad (3)$$

Where W the strain energy, I_1 is the first invariant of the left Cauchy-Green strain tensor, and C_1^{NH} is a material parameter that can be linked to the initial modulus. C_1^{NH} can also be considered equal to nkT [20] where n is the density of macromolecular chains of the amorphous phase by unit of volume (mm^{-3}), k the Boltzmann constant (JK^{-1}) and T the temperature (in K). In the case of pure shear deformation, the evolution of nominal stress is written with the stretch λ as follows:

$$\pi = 2C_1^{NH} \left(\lambda - \frac{1}{\lambda^3} \right) \quad (4)$$

The material parameter C_1^{NH} was fitted on the first load of the cyclic tests issued on all hydrogel compositions. As an example, Fig. 7 shows the Neo-Hookean fit corresponding to the cyclic tests performed on material A_1 . The model fits the data perfectly.

Tables 4 and 5 show the mean values of material parameter C_1^{NH} for all the proposed compositions of the hydrogel in the [1; 1.25] stretch range. 10 samples of each configuration were tested. The initial moduli are also shown, as they can be deduced from the nominal stress π : during infinitesimal deformations, one can assume that the deformed and initial configurations coincide. The Cauchy stress σ , in pure shear test, can consequently be written as:

$$\sigma = \frac{\pi}{\lambda} \quad (5)$$

In the small deformation framework, the Cauchy stress is written:

$$\sigma = \frac{E}{\varepsilon} \quad (6)$$

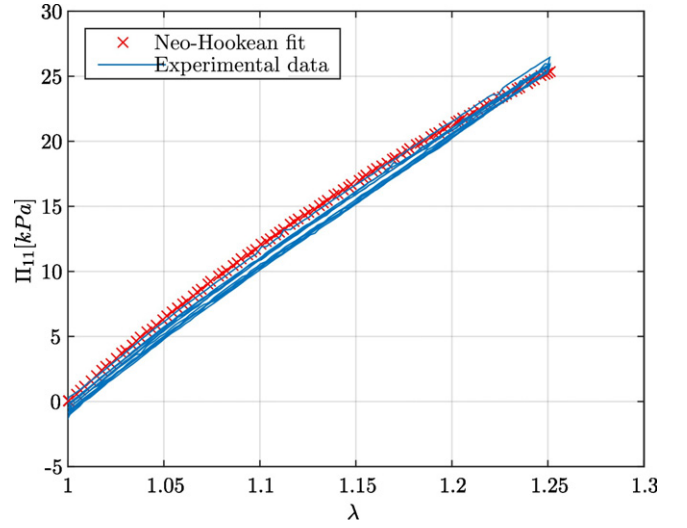


Fig. 7. Comparison of the cyclic behavior of material A_1 with the corresponding Neo-Hookean fit.

where ε is the engineering strain measured by the testing device and E the initial modulus.

Since $\lambda = 1 + \varepsilon$, by combining Eqs. (4) and (5), σ can be written as:

$$\sigma = 2C_1^{NH} \left(\lambda^2 - \frac{1}{\lambda^2} \right) = 2C_1^{NH} \left((1 + \varepsilon)^2 - \frac{1}{(1 + \varepsilon)^2} \right) = 8C_1^{NH} \varepsilon + o(\varepsilon) \quad (7)$$

Using Eqs. (5) and (7), the link between the C_1^{NH} material parameter and the initial modulus $E = 8C_1^{NH} = 8nkT$ is deduced. The calculated values of n for a temperature of 37 °C are also presented in Tables 4 and 5.

The evolution of the mean values of C_1^{NH} and their standard deviation for a given PVA concentration function of the DMSO:H₂O ratio is represented in Figs. 8a and 8b) for all the freeze/thaw cycles. For the sake of comparison, materials having undergone a single freeze/thaw cycle are chosen as references. Normalizing the values obtained for 2 and 3 cycles in relation to 1 cycle allows for the evaluation of the influence of the number of freeze/thaw cycles. Fig. 8c and d show the normalized data of each material configuration.

For hydrogels containing 10 wt% PVA, Fig. 8a and c show an increase of C_1^{NH} with DMSO concentration for a single freeze/thaw cycle. Also C_1^{NH} goes from being the lowest value for a DMSO concentration of 60% to being the highest for 80% DMSO. Materials having undergone more than 1 cycle present a decrease in C_1^{NH} with the increase of DMSO.

Fig. 8b, shows that C_1^{NH} is maximal for a DMSO concentration of 60% and almost twice larger than the values calculated for DMSO concentrations of 40% and 80%, which are almost equal. Also a general increase of C_1^{NH} is observed with the increased number of freeze/thaw cycles. This is more obvious in Fig. 8d: for DMSO concentrations of 40% and 80%, C_1^{NH} increases with the number of cycles, while for the gel containing 60% DMSO, the structure seems to have stabilized after 2 freeze/thaw cycles.

For hydrogels containing 10 wt% PVA, Fig. 8a and c show an increase of C_1^{NH} with DMSO concentration for a single freeze/thaw cycle. Materials having undergone more than 1 cycle present a decrease in

Table 4

Values of the C_1^{NH} material parameters, the initial moduli E and the densities of macromolecular chains by unit of volume n of hydrogels containing a PVA concentration of 10%.

Sample ID	A_1	A_2	A_3	C_1	C_2	C_3
C_1^{NH} [kPa]	16.92	13.86	5.03	13.74	21.23	19.47
Initial modulus [kPa]	135.39	110.92	40.29	109.92	169.84	155.75
n [10^{14} mm^{-3}]	39.53	32.38	11.75	32.10	49.60	45.49

Table 5

Values of the C_1^{NH} material parameters, the initial moduli E and the densities of macromolecular chains by unit of volume n of hydrogels containing a PVA concentration of 5%.

Sample ID	E_1	E_2	E_3	D_1	D_2	D_3	E_1	E_2	E_3
C_1^{NH} [kPa]	2.94	3.35	4.24	3.06	7.23	6.93	2.27	3.43	3.74
Initial modulus [kPa]	23.54	26.80	33.94	48.49	57.84	55.46	18.20	27.49	29.95
$n[10^{14} \text{ mm}^{-3}]$	6.89	7.82	9.90	14.16	16.89	16.19	5.30	8.01	8.73

C_1^{NH} with the increase of DMSO. Also C_1^{NH} goes from being the lowest value for a DMSO concentration of 60% to being the highest for 80% DMSO.

Fig. 8b, shows that C_1^{NH} is maximal for a DMSO concentration of 60% and almost twice larger than the values calculated for DMSO concentrations of 40% and 80%, which are almost equal. Also a general increase of C_1^{NH} is observed with the increased number of freeze/thaw cycles. This is more obvious in Fig. 8d: for DMSO concentrations of 40% and 80%, C_1^{NH} increases with the number of cycles, while for the gel containing 60% DMSO, the structure seems to have stabilized after 2 freeze/thaw cycles. In general, it is safe to say that the number of freeze/thaw cycles imposed on a material does have an influence, but from a mechanical point of view their effect varies with the initial composition of the material.

Tables 4 and 5 show the mean values of material parameter C_1^{NH} , the deduced initial moduli and the density of macromolecular chains of the amorphous phase by unit of volume n for all the proposed compositions of the hydrogel. Analysis of Table 4 shows that C_1^{NH} decreases for materials containing 10 wt% PVA and 80% DMSO with the number of freeze/thaw cycles. This translates into a decrease of the density of macromolecular chains of the amorphous phase, which might be due to crystal phase outgrowing the amorphous phase. For hydrogels containing 60% DMSO however, C_1^{NH} , as well as n , are maximal for 2 freeze/thaw cycles

and minimal for a single one. This is due to the fact that the gelation time is smallest for 60% DMSO, which might lead to a fully accomplished amorphous phase by the second cycle and an increase of the crystal phase during the third cycle.

For materials consisting of 5 wt% PVA, C_1^{NH} increases with the number of freeze/thaw cycles for all the compositions except for sample D_2 which is slightly larger than D_3 . It is also highest for material D that contains an initial DMSO concentration of 60%. n behaves in a similar way thus the explanation proposed for material C also applies for materials B, D and E .

5. Conclusion

This study investigated the effects of the initial processing parameters of PVA/DMSO hydrogels on their mechanical behavior. A mechanical study in a controlled environment consisting of cyclic and failure tensile tests was made. A tank containing a thermostatic aqueous medium was developed specifically to account for the hydrophilic behavior of the material. This allowed for the observation of different phenomena such as hyperelasticity, softening and residual strain. The results show an influence of the number of freeze/thaw cycles applied to each material configuration but a strong dependence on the initial solution, especially for materials containing larger concentrations of PVA. In general, a

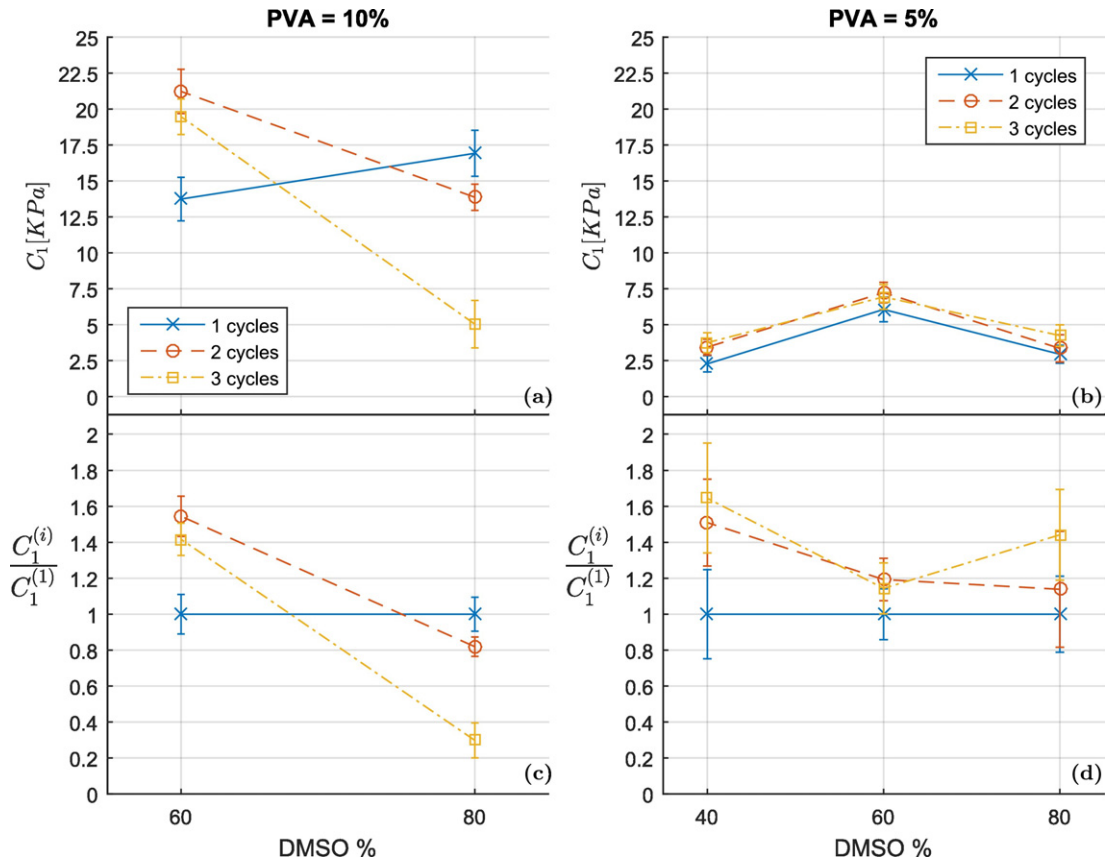


Fig. 8. Evolution of the C_1^{NH} parameter function of the DMSO concentration for hydrogels containing (a) 10 wt% PVA and (b) 5 wt% PVA. Evolution of the normalized C_1^{NH} parameter in relation to the C_1^{NH} parameter of hydrogels prepared by one freeze/thaw cycle function of the DMSO concentration for materials containing (c) 10 wt% PVA and (d) 5 wt% PVA.

loss of mechanical properties was observed with decreasing PVA concentrations. In the tested strain range, the hydrogels exhibited very little visco-elasticity which motivated the use of the Neo-Hookean hyperelastic model to reproduce the results. This was achieved with great success and allowed for the measurement of the elastic modulus of the different materials function of their respective elaboration parameters. The strongest hydrogel was obtained for a PVA concentration of 10 wt%, a DMSO:H₂O ratio of 60:40 and two freeze/thaw cycles. It is worth noting that the elastic behavior of PVA hydrogels compares well with soft tissue, thus making them excellent candidates for producing phantoms with controlled mechanical behaviors. In perspective, a link between the mechanical properties of PVA hydrogels and their crystallinity would allow for a general description of their behavior, independently of the processing parameters.

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References

- [1] V.G. Kadajji, G.V. Betageri, Water soluble polymers for pharmaceutical applications, *Polymer* 3 (4) (1972–2009) 2011.
- [2] S. Jiang, Z. Su, X. Wang, S. Liu, Y. Yu, Development of a new tissue-equivalent material applied to optimizing surgical accuracy, *Mater. Sci. Eng. C* 33 (7) (2013) 3768–3774.
- [3] C.M. Hassan, N.A. Peppas, Structure and Applications of Poly(vinyl alcohol) Hydrogels Produced by Conventional Crosslinking or by Freezing/Thawing Methods, 2000 153.
- [4] N.A. Peppas, N.K. Mongia, Ultrapure poly(vinyl alcohol) hydrogels with mucoadhesive drug delivery characteristics, *Eur. J. Pharm. Biopharm.* 43 (1) (1997) 51–58.
- [5] S.H. Hyon, W.I. Cha, Y. Ikada, M. Kita, Y. Ogura, Y. Honda, Poly(vinyl alcohol) hydrogels as soft contact lens material, *J. Biomater. Sci. Polym. Ed.* 5 (5) (1994) 397–406.
- [6] M. Kobayashi, J. Toguchida, M. Oka, Development of the shields for tendon injury repair using poly(vinyl alcohol) - hydrogel (PVA-H), *J. Biomed. Mater. Res.* 58 (4) (2001) 344–351.
- [7] J.S. Bach, F. Detrez, M. Cherkaoui, S. Cantourmet, D.N. Ku, L. Corté, Hydrogel fibers for ACL prosthesis: design and mechanical evaluation of PVA and PVA/UHMWPE fiber constructs, *J. Biomech.* 46 (8) (2013) 1463–1470.
- [8] Z.Q. Gu, J.M. Xiao, X.H. Zhang, The development of artificial articular cartilage PVA-hydrogel, *Biomed. Mater. Eng.* 8 (2) (1998) 75–81.
- [9] N.A. Peppas, *Hydrogels in Medicine and Pharmacy*, Vol. I, CRC Press Inc., Boca Raton, Florida, 1986 (1987 (Vols. 2 and 3). Volume 21. John Wiley & Sons, Ltd., 1989).
- [10] A. Danno, Gel formation of aqueous solution of poly(vinyl alcohol) irradiated by gamma rays from cobalt-60, *J. Phys. Soc. Jpn.* 13 (7) (1958) 722–727.
- [11] S.R. Stauffer, N.A. Peppas, Poly(vinyl alcohol) hydrogels prepared by freezing-thawing cyclic processing, *Polymer* 33 (18) (Sep 1992) 3932–3936.
- [12] H. Trieu, S. Qutubuddin, Poly(vinyl alcohol) hydrogels: 2. Effects of processing parameters on structure and properties, *Polymer* 36 (13) (Jan 1995) 2531–2539.
- [13] S.H. Hyon, W.I. Cha, Y. Ikada, Preparation of transparent poly(vinyl alcohol) hydrogel, *Polym. Bull.* 22 (2) (1989) 119–122.
- [14] T. Tanigami, K. Murase, K. Yamaura, et al., *Polymer* 35 (12) (1994) 2573–2578.
- [15] L. Mandelkern, The effect of molecular weight on the crystallization, melting, and morphology of long-chain molecules, *Journal of Polymer Science Part C: Polymer Symposia* 15 (1967) 129–162.
- [16] D.J. Charlton, J. Yang, K.K. Teh, *A Review of Methods to Characterize Rubber Elastic Behavior for Use in Finite Element Analysis*, 2012.
- [17] J. Diani, B. Fayolle, P. Gilormini, A review on the Mullins effect, *Eur. Polym. J.* 45 (3) (2009) 601–612.
- [18] F. Yokoyama, I. Masada, K. Shimamura, T. Ikawa, K. Monobe, Morphology and structure of highly elastic poly(vinyl alcohol) hydrogel prepared by repeated freezing-and-melting, *Colloid Polym. Sci.* 264 (7) (1986) 595–601.
- [19] H. Hoshino, S. Okada, H. Urakawa, K. Kajiwara, Gelation of poly(vinyl alcohol) in dimethyl sulfoxide/water solvent, *Polym. Bull.* 37 (2) (Aug 1996) 237–244.
- [20] L.R.J. Treloar, The elasticity of a network of long-chain molecules I and II, *Trans. Faraday Soc.* 36 (1942) 36–41.