Effect of unidirectional freezing using a thermal camera on polyvinyl (alcohol) for aligned porous cryogels

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Abstract

Unidirectional freeze casting for polymers and ceramics has been performed extensively; however, the mechanisms involved in unidirectional freezing is not thoroughly understood and therefore, in this study, polyvinyl (alcohol) hydrogels were freeze-thawed by unidirectional freezing and the resultant freezing profile was investigated using thermal imagery to comprehend the physical mechanism involved in the production of these aligned cryogels. The approach used follows a slight variation from what is currently used in literature, by enclosing the mould with insulating materials and leaving one side with a metal encasing for a fast freezing flow from the direction of the desired aligned of the structure. This method was cost-effective and simple; however, it was able to induce unidirectional freezing resulting in two distinct structures. These structures exhibited a cellular region interspersed with a fibrous and porous morphology. The method developed without the need of a freeze-dryer was confirmed to produce a unidirectional freezing which can be used for future studies.

Keywords: unidirectional-freezing, freeze casting, polyvinyl (alcohol) cryogels

1. Introduction

The general idea within the usage of unidirectional freezing technique is that by controlling the parameters of growth from ice crystals it is possible to create aligned porous materials; this is achieved by the fact that when freezing, ice crystals act as templates and, after melting, produces an anisotropic porous structure of a continuous 3D network [1–3].

Research on the freeze-drying method have been carried out on water soluble polymers [4,5], ceramic suspensions [6,7] and composite materials [8,9]. In the case of water-soluble polymers, the process of unidirectional freezing also produces scaffolds and the variation on the morphology – size of the pores, surface area and thickness can be adjusted by the averaged molecular weight, concentration and the freezing rate of the water-soluble polymer, such as Polyvinyl(alcohol) (also known as PVA) [10]. These polymer scaffolds have been shown to be well suited to drug delivery – due to the morphology and structure of the scaffold, the drug entrapped can be released up to several days [11]– and this technique can mimic the structure of bone tissues, due to the freezing mechanism in one direction, resulting in uniform structures that can improve its mechanical properties [10,12]. The usage of highly porous aligned scaffolds from PVA can exhibit high strength. Zhou et al., (2019) created an aerogel with microfibrillated cellulose, PVA and graphene which in compressive stress at 80% strain reached 0.22 MPa [13].

The field of unidirectional freezing for aligned porous ceramic scaffolds have also been gathering considerable attention [14], containing Hydroxyapatite [15] or silk fibroin [16], to be used as a bone replacement for biomaterials and adsorption of heavy metal ions for water treatment. By controlling the cooling rate on the unidirectional freeze-drying, it is possible to obtain various pore sizes which leads to different ratio of adsorption for heavy metal ions [17]. Such is the case for ceramic scaffolds designed for biomaterials [15], by controlling the cooling rate and concentration of the ceramics, it is possible to obtain suitable porosity and pore size with great biomechanical strength.

Unidirectional freezing technique is usually performed within a metallic container by the usage of liquid nitrogen, that rests at the bottom, and a plastic tube apparatus where the polymer or ceramic sludge would be confined. The apparatus is exposed only at the bottom part with the liquid nitrogen due to a metal piece inserted in between the liquid nitrogen and the apparatus. Subsequently, these materials are freeze-dried and the unidirectional growth of ice occurs from the bottom to the upper part [12,18].

Nonetheless, there are several studies of PVA cryogels modified via unidirectional freezing casting, but all of these works include the necessity of freeze-drying [19] and few examined the effect of the ice crystals in the freezing mechanism to understand their template function for an aligned scaffold [20]. Therefore, this work adds insights to the function of the ice crystals by the usage of a thermal camera where we measured the temperature profile of the polymer soluble PVA in between a unidirectional freezing to study the ice alignment formation within this methodology The PVA produced exhibited a cellular structure via freeze-thawing and drying only in an oven with a low-cost apparatus.

2. Materials and Methods

2.1 Polyvinyl alcohol (PVA) cryogel preparation

PVA powder with an average molecular weight of 195,000 g/mol and a percentage of hydrolysis of 98% (Mowiol 56-98) was dissolved at 5% concentration (w/v) in distilled water (dH2O), at 80 °C with constant stirring until the complete solubilisation of PVA. Subsequently, 20 ml of PVA solution was transferred to a polytetrafluorethylene (PTFE) mould with a size of 5.3 cm x 4.6 cm x 6 cm and insulated with heat insulation tapes and freezer foam, with a working range of -40 °C to +100 °C. The bottom part of the PTFE mould was removed and replaced with an aluminium board of 0.5 cm thickness. In addition, one side of the mould was also removed, and insulation tapes were added around its sides and glued so that it was possible to expose this side to the thermal camera analysis at specific time intervals. The scheme of this methodology used to uni-direct the cryogels described herein is presented in Figure 1.

2.2 Thermal camera specifications

The thermal camera FLIR b50 was used for this work and was calibrated from the company which supplied the instrument – Butler technologies. For the procedure to verify the accuracy of the values it was followed by the usage of Bath fluid Thermal HY (Julabo), this fluid is then frozen at specific temperatures in F81-ME Ultra-Low Refrigerated-Heating Circulator (Julabo). A picture of known emissivity sample is taken from this fluid (amount of infrared emitted) and we compare it with the thermocouple from the freezer, temperatures worked with an accuracy of 2% until -20 °C, values below -20°C gave an accuracy of 4%.

2.3 Unidirectional freezing procedure

For the freezing methodology, the mould was lowered down in height until fully immersed in liquid nitrogen at a speed of 100 mm min $^{-1}$. The frozen sample was then thawed at ambient temperature for 1 h. This cycle was repeated three times.

To analyse the freezing profile and the effect of unidirectional freezing, the apparatus where the sample was initially contained was quickly removed and scanned at different time intervals with a thermal camera FLIR b50 at observation times 3, 10, 20, 30, 40, 50, 60 and 70 minutes. A new PVA solution and so a new experiment was conducted for each observation time.

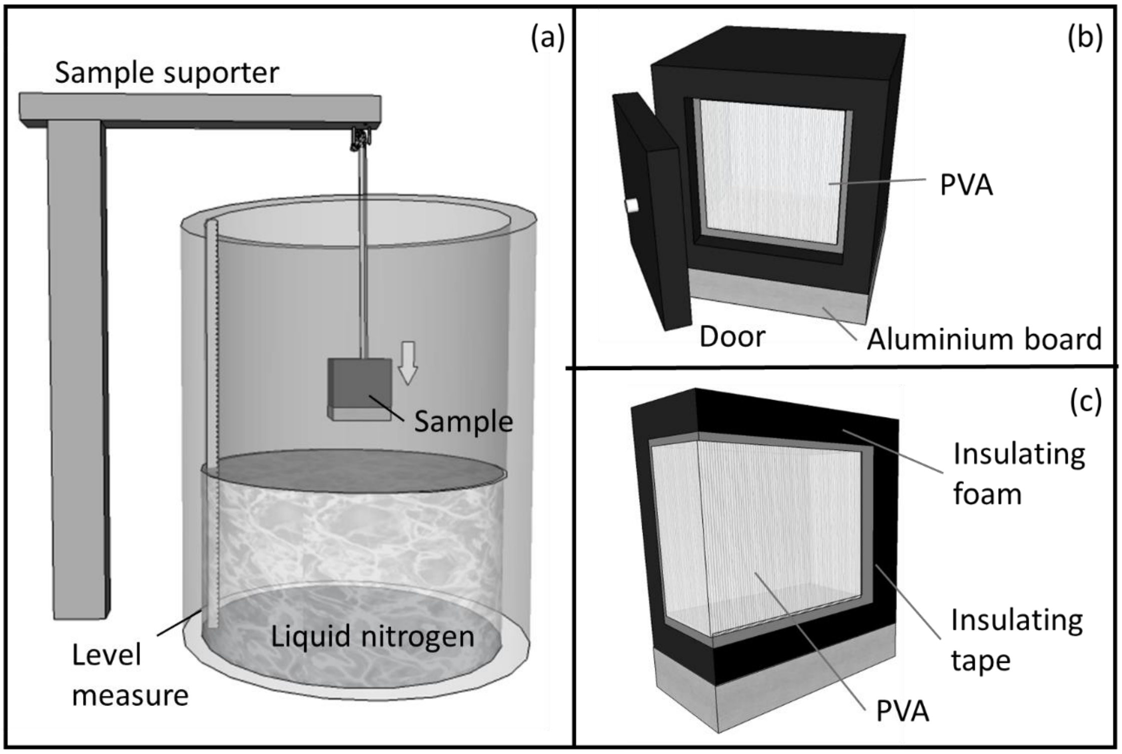

Figure 1. a) Freezing apparatus for unidirectional solidification. The sample box represents where the PVA is contained and is lowered at a constant velocity of 100 mm min $^{-1}$ represented by the down arrow in figure. The white part represents a metal piece connected to the PVA apparatus, inducing a faster cooling rate from the bottom part leading to a unidirectional freezing. b) Sample box and c) Cross-section view.

2.4 Thermal images analysis

The images obtained by the thermal camera at specific time-points were further analysed with the help of the software FLIR Tools 5.x from the same company to obtain a spot and a line measurement at three specific regions from the sample. The line measurement was obtained by the procedure followed from the thermal camera manual. The software takes each pixel from the thermal image and correlates it to a calibrated temperature, these temperature values can then be further exported for further analysis in external software. We exported the line measurement to be able to obtain mean and standard deviation values from these three specific regions.

3. Results and Discussion

3.1 Thermal camera analysis

The PVA freeze-thawed by unidirectional freezing was evaluated using a thermal camera during the whole freezing experiment. Figure 2 exhibits the effect of freezing at different time points, whereas the thermal camera images were obtained perpendicular to the freezing direction and it was possible to observe the whole thermal behaviour and that unidirectional freezing was achieved.

The sequence of images presents the freezing occurring first at the bottom of the sample, due to the fact that it is approaching the liquid nitrogen, and the freezing gradually occurring upwards until reaches the top part. The spots, labelled as sp, in figures shows the gradual drop in temperature over time and at three distinct heights. This is another evidence that proves the efficiency of this mould in freezing the sample unidirectionally. As the mould decrease towards the liquid nitrogen, the temperature decreases and a linear upward freezing occurs.

To confirm if this mould was successful and unidirectional freezing was obtained, temperature lines were drawn at each specific temperature spot measurements of Figure 2, labelled as sp, and the dashed lines represent the limits extremities of the line measurement performed. Figure 3 shows further that it was possible to obtain a linear downward freezing against time for the first 0-50 min which then leads to a faster freezing from 50-70 min; also, the three regions from the apparatus exhibits the same freezing profile whereas the top part of the mould was the last one to reach -40 °C. It is important to clarify that the limit of this camera is -40 °C, and if the result is too close to its limit it could be unreliable. Nonetheless, it is possible to observe the faster freezing occurring from 50-70 min in the thermal camera images as well – Figure 2.

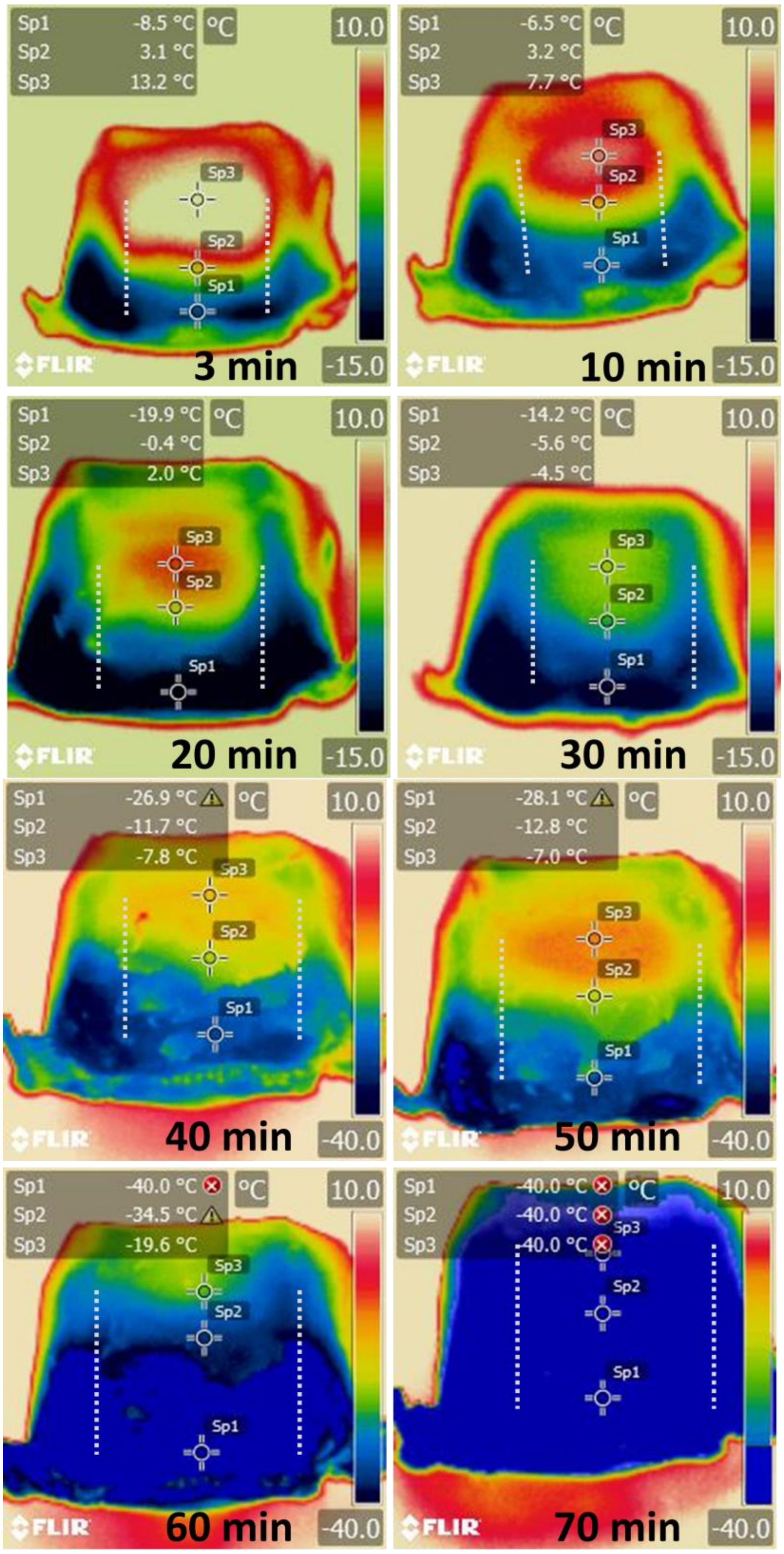

Figure 2. Thermal camera images obtained from the PVA samples while subjected to unidirectional freezing from 0-70 min. The white dashed lines represent the limits of the line temperature measurement performed in FLIR software that were further used to construct a new graph (Figure 3).

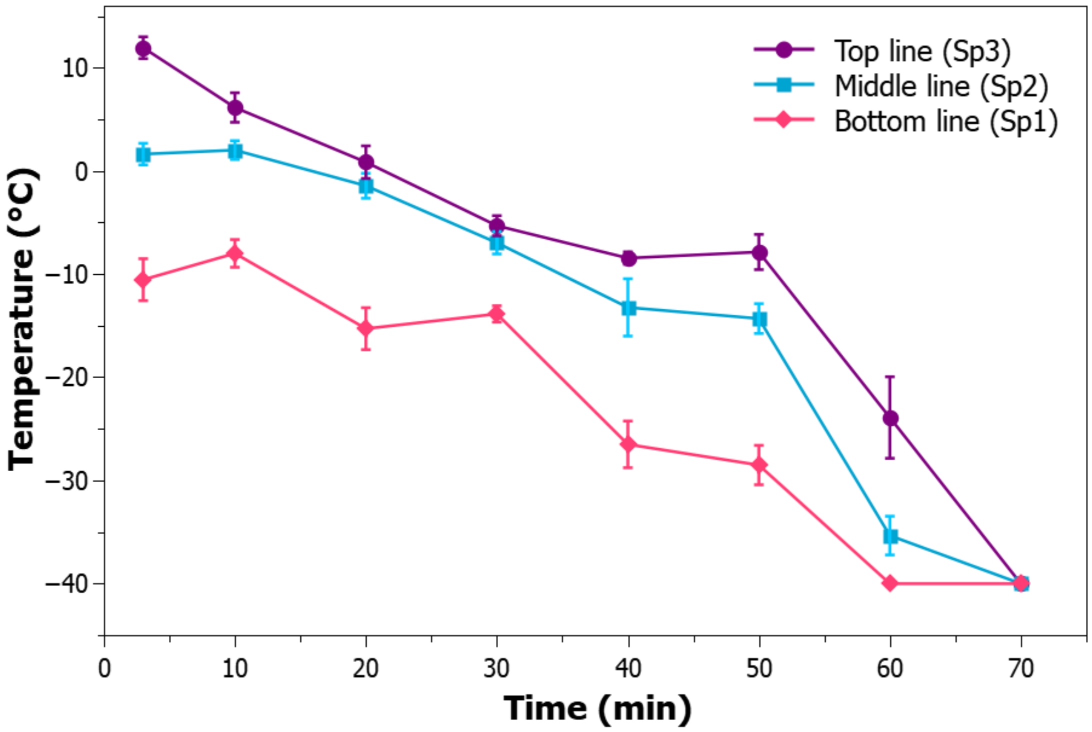

Figure 3. Plotted values from the line temperature measurement obtained at different times using the FLIR software at three distinct regions, specified in Figure 2 by Sp spots.

3.2 Morphology analysis

The sample produced in this work exhibits through macroscopic visual observation (Figure 4) two different zones, this has been reported by Deville at al., (2006) that depending on the processing condition, three zones can be found – a lamellar, cellular and dense region [21]. In the case of our sample, we macroscopically identified two zones. The second zone obtained with this technique (Figure 4) could be due to the formation of a denser structure which was in direct contact with the metal piece apparatus, also exhibiting a more rigid structure than the overall cryogel.

Figure 4. Macroscopic evaluation of the cryogel after production. The dashed line represents the two different regions perceived.

The cross-section of the cryogels submitted to unidirectional freezing was divided into two different portions, the left side (1), and the middle region (2) in figure 5; whereas region 1 is the left part of the cryogel, region 2 is at its centre. It was possible to confirm that these materials obtained a cellular structure oriented within the direction of the dashed arrows, presented in figure 5, which is similar to findings reported by other authors [18,22]. The dashed line corresponds to the different regions observed in this dried cryogel and is similar to what has been macroscopically observed in figure 4. In region 1, the oriented cellular structure can be seen from the top part of the dashed line and a fibrous structure is observed at the bottom part. However, when approaching the middle region of the cryogel, these fibrous structures superimpose the dashed line and are also present in the top part region, almost completely surrounding the whole middle region. Based on this result we tried to cut the cryogel with a knife as a simple test to investigate if the interior of the cryogel before drying also exhibits the same structure that one at the bottom, and we also obtained the same integrity structure confirming that at the middle a new region was formed.

We deduce that this effect could have occurred due to the freezing mechanism, as discussed from the thermal camera results. Since the freezing occurred at a slower rate in the centre region, the fibrous pattern – presented in the dense region migrated through the whole area due to the equilibrium energy obtained in the freezing reaction.

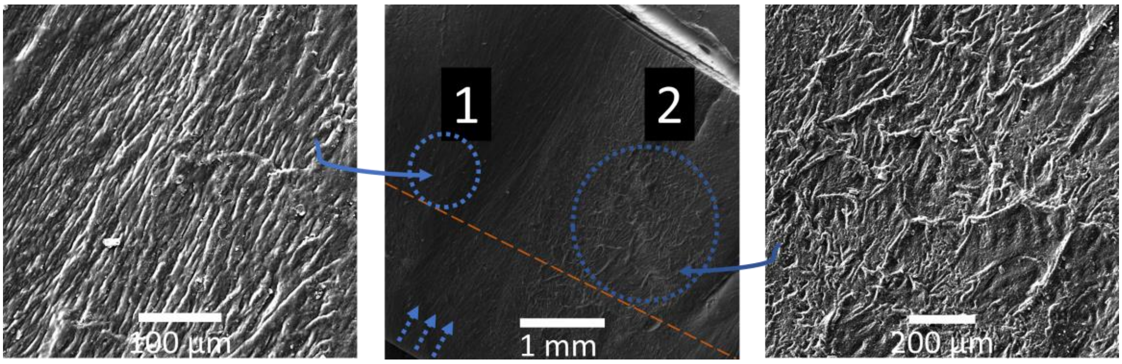

Figure 5. SEM image of the interior PVA cryogel, the dashed circle represents two different morphologies obtained while these images were magnified as represented by the arrows. The dashed line corresponds to the different zones perceived within this cryogel, according to figure 4, and the dashed arrow at the bottom of the middle image indicates the direction of the freezing.

A defined orientation due to the freezing mechanism can be seen in both regions (Figure 5) and the cellular structure is more evidenced in the zoomed image of region 1. Nonetheless, region 2 exhibits a somewhat fibrous structure with varying sizes and also appears to exhibit some porous structure in between these fibrous patterns. This porous structure was only identified in this middle region, not seen on the bottom part of the sample. This could be due to the unidirectional freezing mechanism and the effect of drying in an oven, where the slow evaporation of water leads to the weak polymer chains shrinking and occurrence of material deformation.

4. Conclusion

The directional freezing process presents a directional arrangement of crystalline regions along the direction perpendicular to the freezing, which was confirmed with the help of a thermal camera. Temperature measurements from thermal images exhibited a linear freezing profile and it was possible to obtain different distinct structures in the cryogel such as a cellular and a fibrous as well as a porous zone similar to what found in literature. The technique presented is easy, low-cost and can potentially be used for further research to produce unidirectional structure in cryogels.

Acknowledgements

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001 and Science Without Borders.

Conflicts of Interest

No conflicts of interest regarding this manuscript.

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