

# Effect of annealing on the strength of poly(vinyl alcohol) hydrogels for cartilage resurfacing

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## Statement of Purpose:

Poly(vinyl alcohol) (PVA) hydrogels are candidate materials for use as synthetic articular cartilage due to their viscoelastic nature, high water content, and biocompatibility. Our aim was to investigate the use of PVA hydrogels in interpositional devices. Most forms of PVA hydrogels lack the strength and toughness to be used as an interpositional device, which requires stronger and stiffer materials. Most researchers used the dehydration and annealing to increase the mechanical strength of PVA hydrogels; yet this process collapses the pores and subsequently decreases the equilibrium water content (EWC) of the gels. It has been shown that a highly crystalline, high creep resistant PVA hydrogel with improved crystallinity can be prepared by the combination of theta gel method and dehydration followed by high temperature annealing in the presence of a non-volatile gelling agent such as poly(ethylene glycol) (PEG)<sup>1</sup>. The increase in crystallinity after annealing is presumably due to increased hydrogen bond formation between the OH groups of PVA caused by the increase in chain proximity and the chain mobility at the annealing temperature. In this study, we investigated the effect of dehydration (heat vs. vacuum), annealing environment (dry vs. humid) on the crystallinity and creep resistance, tear strength and EWC of PVA theta gels.

## Materials and methods:

PVA-PEG gels were prepared by mixing 25% (w/w) PVA solution at 90°C with 28% PEG. The solution was molded and gelled by cooling down to room temperature. The resulting gels were divided into 3 groups: (i) control, (ii) vacuum dried, and (iii) heat dried (dried in a convection oven at 25°C for 14h, ramped to 80°C in 8h, then kept at 80°C for 20h prior to annealing). The control gels were immersed in deionized (DI) water until equilibrium with no further treatment. The vacuum dried gels were divided into 5 subgroups: (i) annealed in vacuum under a 500mmHg argon partial pressure at 160°C (vacuum annealed) for 1h, (ii) vacuum annealed for 20h, (iii) annealed in self-pressurizing vessel (bomb annealed) under argon for 1h, (iv) bomb annealed immersing in PEG for 1h, (v) bomb annealed in the presence of water vapor for 1h. The heat dried gels were investigated after either (i) vacuum annealing for 1h at 160°C or (ii) annealing by ramping from 80°C for 20h to 160°C and holding at 160°C for 1h in a pressure vessel under argon, while immersed in PEG, or in the presence of 20 ml of water in a container which was placed in the chamber purged with argon and allowed to pressurize to about 200psi at annealing temperature. Subsequent to annealing, all gels were rehydrated in DI water until equilibrium. The equilibrium water content (EWC) was measured using a Thermogravimetric Analyzer (TGA). Creep behavior was determined at 40°C by applying a 100N load for 10h followed by a relaxation period under a 10N load for 10h on cylindrical samples. The Instron Insight 2 (MTS) pulling at a rate of 50cm/min was used to determine the tear strength of the gels. The crystallinity was measured using the X'Pert PANalytical powder diffractometer. True PVA crystallinity was calculated by normalizing measured crystallinity values by the PVA content.

## Results:

EWC of the PVA-PEG hydrogels decreased after annealing compared to the control (Table 1). The gels dried under vacuum showed higher EWC compared to their air and heat dried counterparts. Crystallinity of PVA-PEG theta hydrogels markedly increased after all types of annealing (Fig 1 and Table 1).

**Table 1. Tear strength, water content (EWC), total creep strain (TCS) and crystallinity for various annealing types.**

Annealing Type	Dehydration Type	Tear Strength (N/mm)	EWC (%)	TCS (%)	Crystallinity (%)	Color
Control	None	5 ± 0.2	84 ± 0.1	69 ± 1.1	7 ± 0.9	White
Bomb annealed under argon	Vacuum	10 ± 0.4	78 ± 0.6	60 ± 5.7	21 ± 3.6	White
	Air and heat	18 ± 0.6	68 ± 1.3	21.4 ± 1	42 ± 3.7	Light yellow
Bomb annealed with water	Vacuum	15 ± 0.2	70 ± 0.2	47	24 ± 5.8	White
	Air and heat	21 ± 1.1	68 ± 1.7	18 ± 1.1	41 ± 1.6	White
Bomb annealed in PEG	Vacuum	8 ± 0.3	80 ± 0.1	63	19 ± 1.6	White
	Air and heat	18 ± 0.7	67 ± 0.9	22 ± 2.3	22 ± 2.9	Orange
	Vacuum	12 ± 0.4	75 ± 0.6	34 ± 6.8	18 ± 2.9	White
Vacuum annealed 1h	Vacuum	12 ± 0.4	75 ± 0.6	34 ± 6.8	18 ± 2.9	White
	Air and heat	13 ± 0.6	73 ± 0.2	48 ± 4.6	15 ± 0.3	Yellow
Vacuum annealed 20h	Vacuum	18 ± 0.6	69 ± 0.7	19 ± 1.9	26 ± 3	Dark orange

The gels that were air and heat dried and annealed in the pressure vessel under argon as well as the ones annealed in the presence of water showed the highest crystallinity. Regardless of the drying type, all vacuum annealed gels showed lower crystallinity values with the exception of 20h

annealed gels than pressure vessel annealed counterparts (Fig 2 and Table 1). There was a strong negative correlation between crystallinity and EWC ( $\gamma = -0.8$ ). Annealing in general markedly increased the total creep strain (TCS) of the hydrogels; air and heat dehydrated hydrogels exhibited better creep resistance when annealing was carried out in a pressure vessel (Fig 2 and Table 1). However the vacuum dried hydrogels showed lower TCS when the annealing was carried out under vacuum (Fig 2 and Table 1). We found a strong positive correlation ( $\gamma = 0.9$ ) between TCS and EWC and a strong negative correlation ( $\gamma = -0.8$ ) between the TCS and the crystallinity. The gels that were air and heat dried and annealed in the pressure vessel in the presence of water showed the highest tear strength, whereas the gels that were vacuum dried and bomb annealed in PEG showed the lowest tear strength (Table 1). There was a strong negative correlation ( $\gamma = -1.0$ ) between EWC and tear strength and a strong positive correlation between crystallinity and tear strength ( $\gamma = 0.8$ ). The air and heat dried gels resulted in discoloration when they were annealed with the exception of annealing in pressure vessel with water.

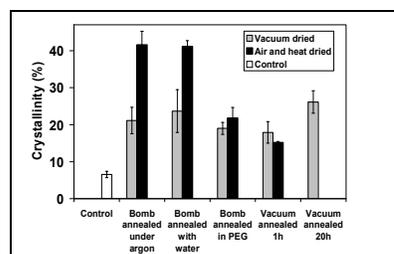


Figure 1. Tear strength for annealing types

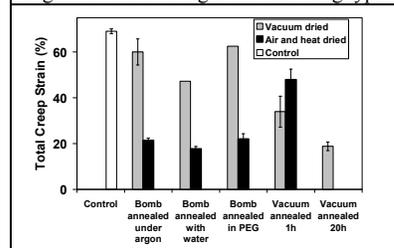


Figure 2. Crystallinity values for annealing types

also increased the crystallinity and mechanical strength of PVA theta hydrogels. The increase in crystallinity likely arose from the plasticizing effect of water vapor at the annealing temperature. The presence of PEG increased the mechanical strength of the air and heat dried hydrogels as well but did not increase the crystallinity. This result suggests that the plasticizing effect of the PEG may be more dominant in the amorphous region. This is possibly because water vapor is highly mobile and volatile, providing energy and creating more interactions between PVA chains whereas non-volatile PEG would presumably act as a space filler between the chains, compromising their ability to interact with each other. The discoloration in the air and heat dried samples during annealing is likely due to the interaction between air and PEG molecules in PVA-PEG network which is blocked in the presence of water.

## Conclusion:

The mechanical strength and the crystallinity of the PVA hydrogels can be optimized by changing the drying and annealing method; a highly crystalline and mechanically strong PVA hydrogel with high water content can be prepared by pressure vessel annealing in the presence of water. Mechanically strong PVA hydrogels are promising candidates as a load bearing cartilage substitute for the treatment of early stage lesions.

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**References:** 1) Bodugoz-Senturk, H et al. Biomaterials, 2008, 29(2): 141-9.