Effects of Hydration on the Mechanical Response of a PVA Hydrogel

Fan Cui, Jikun Wang, Alan Zehnder, Chung-Yuen Hui

Mechanical and Aerospace Engineering
Cornell University
Ithaca NY 14853

ABSTRACT

The effect of drying on the tensile behavior of a dual cross-linked poly(vinyl alcohol) (PVA) hydrogel is studied here. This gel contains about 90% water when fully hydrated. The mass-volume relationship of the gel is measured using a microbalance with a density kit. Our results show that as the gel dries the volume is linearly proportional to the mass. The impact of drying on the gel's mechanical properties is measured in uniaxial tension tests, which include loading-unloading tests at three different constant stretch rates, a complex loading history test and a stress-relaxation test. Data from specimens with different hydration levels can be described by a constitutive model of the gel. The results show that the model parameters are strongly dependent on hydration level and that as the gels dry, the gels are much stiffer than those in the fully hydrated state.

Keywords: Viscoelasticity, Hydration, Large strain, Dual crosslinked hydrogel

INTRODUCTION

A hydrogel is essentially a network of polymer chains swollen in water. Typical single chemical crosslinked hydrogels have poor mechanical strength limiting their applications. One method to overcome this is to introduce non-covalent, transient crosslinks as a sacrificial network that can fail and then reform [1]. Hydrogels are prone to drying, leading to shrinkage and poor mechanical properties such as enhanced stiffness and reduced toughness. However, there is very little work on how dehydration affect mechanical properties. In this work, we focus on a dual-crosslinked PVA hydrogel developed by Mayumi at el.[2]. This hydrogel has both chemical and physical crosslinks. The chemical crosslinks form a permanent network. The physical crosslinks form a temporary network which can break and reattach. For a fully hydrated gel, we and our coworkers have established a constitutive model which accurately predicts its behavior [3][4]. Liu at el. [5] demonstrated the mechanical properties of this PVA hydrogel over a range of temperatures can also described by this constitutive model. Meacham at el. [6] studied the effect of hydration on the tensile response this PVA hydrogel. Here we report on an experimental study of the effects of drying on the constitutive response of the PVA hydrogel. We find that the same constitutive model can be used to explain our experimental results.

EXPERIMENTAL METHODS

Experiments were performed with a dual-crosslinked PVA hydrogel which contained approximately 12% PVA and the balance an ionic solution. The gel was synthesized in three steps: making a 16% PVA solution, adding chemical crosslinks, then adding physical crosslinks. First, PVA powder was added to distilled water at 5 ºC. The mixture was stirred and heated to 95 ºC to dissolve the PVA in the water. Then the PVA solution and glutaraldehyde cross-linker were mixed with hydrochloric acid. The solution was injected in mold and held for 24 hours to form the chemical crosslinks. Finally, the chemically crosslinked gel was washed to neutralize the pH by soaking in distilled water for 24 hours. It was then soaked in an ionic solution made of water, sodium chloride and borax to form the ionic (physical) crosslinks. After 3 to 4 days, the physical bonds have completely formed, and the gel is ready to be used in experiments.

The sample was then allowed to dry in lab air. Hydration levels were characterized by the amount of mass loss during drying. We also measured mass-volume relationship at different hydration level. The mass and volume of a fully hydrated sample were measured initially. We then measured its mass every 5-10 minutes until it reached 95%, 90%, 85%, 80%, 75%, 70%, 65% and 60% of the initial mass. For each of these hydration levels we also measured its volume. The mass was

measured by a microbalance with an accuracy of 0.01 mg. The volume was measured by weighing the sample in air and in mineral oil using a density kit on the microbalance. The difference between these two values is the buoyancy which allows us to calculate the volume of the sample via Archimedes principle and the oil density.

The mechanical tests were performed with a custom-built tester using a stepper motor driven translation stage, a 1 N load cell, an oil container, LVDT and DVM based data acquisition system [7]. Samples were cut into strips 2 mm thick, 10 mm wide initially and clamped between a pair of sandpaper lined aluminum grips separated by a gauge length of approximately 30 mm. All tests were performed in mineral oil to prevent the sample from further drying.

At each hydration level (100, 90, 80, 70 and 60%), six tests were performed. Tests were performed sequentially using the same sample for consistency. Between each test, the sample was allowed relaxed for about 12 minutes to fully recover to its initial state. We carried out three different type of tests. First, we carried out cyclic tests where the sample was loaded to a stretch of $\lambda = 1.3$ at stretch rates of $\dot{\lambda} = 0.003/s, 0.010/s, 0.03/s$ and then unloaded at the same rate. Second, we carried out a complex loading history in which the sample was loaded to a stretch of $\lambda = 1.15$ at a rate of $\dot{\lambda} = 0.003/s$, held for 1 minute and then loaded to $\lambda = 1.3$ at $\dot{\lambda} = 0.030/s$, held for another 1 minute and then unloaded at a rate of $\dot{\lambda} = 0.010/s$. Then the sample was loaded to $\lambda = 1.3$ at $\dot{\lambda} = 0.100/s$ and unloaded at $\dot{\lambda} = 0.001/s$. This is followed by a tensile-relaxation test at a maximum stretch of $\lambda = 1.3$ with an initial stretch rate of $\dot{\lambda} = 0.500/s$.

Results are presented in terms of the nominal stress, i.e. applied force divided by the initial cross-sectional area of the sample. For the fully hydrated gel, the cross-sectional area was $2\ \text{mm} \times 10\ \text{mm}$. For the drying gels, the gel shrinks uniformly in all three dimensions, thus the cross-sectional area is calculated using $2\ \text{mm} \times 10\ \text{mm} \times (V\%)^{2/3}$, where $V\%$ is the volume percentage (volume after drying divided by initial volume at full hydration). This relationship is found from the mass-volume relationship described below.

EXPERIMENTAL RESULTS

The results of mass-volume experiments are shown in Fig. 1. The volume percentage decreases linearly with the mass percentage (mass after drying divided by initial mass). The data in Fig. 1 can be fit using $V\% = 1.03M\% - 3.04\%$. This equation allows us to calculate the cross-section area of the gel at different hydration levels as described above.

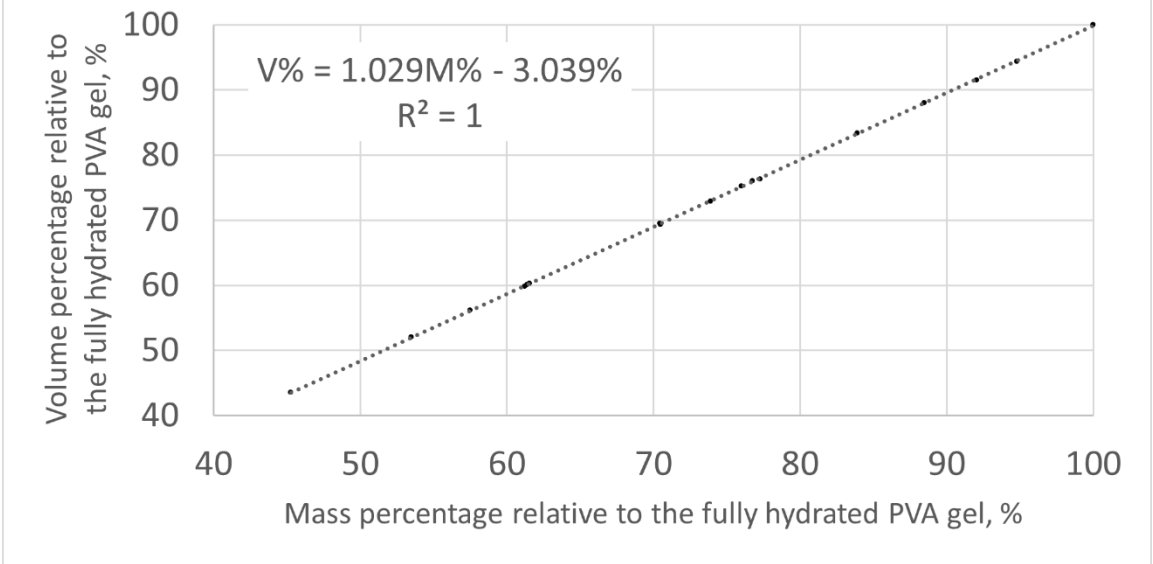

Fig. 1 Mass-Volume relationship of PVA hydrogels as they dry.

Figures 2-4 show the stress-strain curves for PVA hydrogels at different hydration levels for the first two types of tensile tests (cyclic and complex loading). Figure 5 shows the stress-time curves for PVA hydrogels at different hydration levels in tensile-relaxation tests.

These figures show that for all stretch rates the stress is significantly higher rate as the gel dries. Exceptions are gels at 70% and 60% mass. Fig. 2 shows that the stress increases slowly at the initial part of loading for these hydration levels. One

possible reason is that gel samples with mass percentage less than 70% have not had sufficient time to recover after the previous experiment. Even with this initial dip, the maximum nominal stress of the drier gels is higher and across all tests we see that the gel stiffens as it dehydrates.

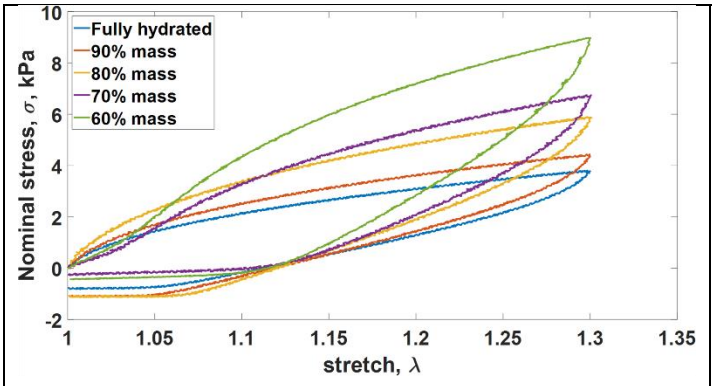

Fig. 2, Nominal stress vs. stretch at five hydration states. Load-unload at stretch rate of $\dot{\lambda} = 0.003/s$.

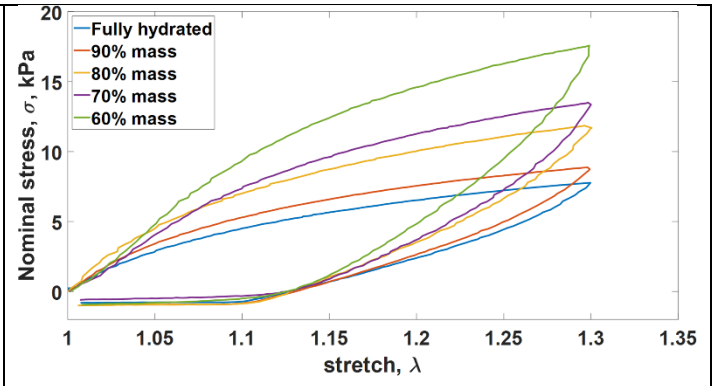

Fig. 3, Nominal stress vs. stretch at five hydration states. Load-unload at stretch rate of $\dot{\lambda} = 0.030/s$.

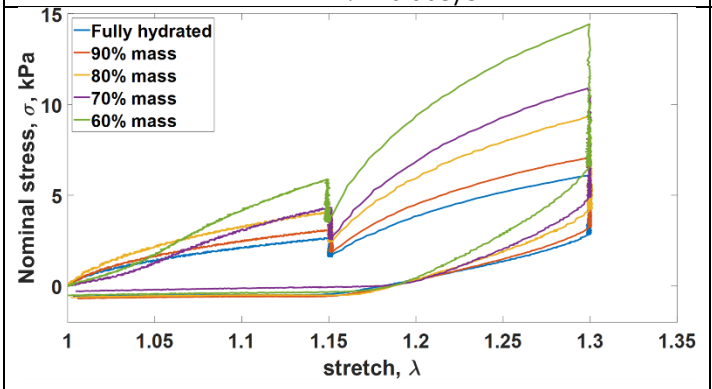

Fig. 4, Nominal stress vs. stretch at five hydration states. A complex loading history.

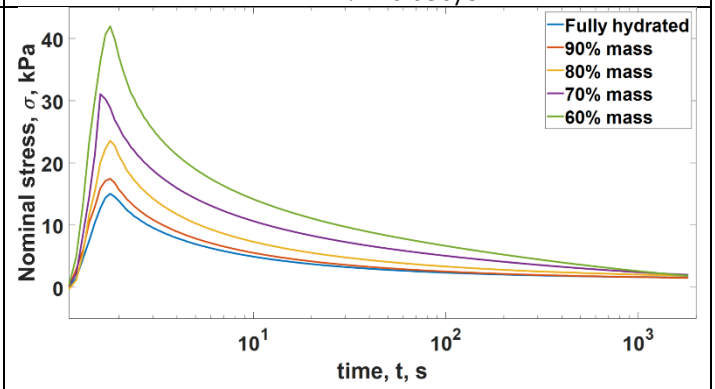

Fig. 5, Nominal stress vs. time in log scale at five hydration states. Loading rate is 0.5/s. Maximum stretch is 1.3.

DATA FITTING AND DISCUSSION

The constitutive model of PVA dual crosslinked hydrogel was developed by Long et al.[2] and Guo et al.[3]. For uniaxial loading the nominal stress σ is related to stretch λ by

$$\sigma = \mu(\rho + n(t))\left[\lambda(t) - \frac{1}{\lambda^2(t)}\right] + \mu\bar{\gamma}_\infty \times \int_0^t \phi_B\left(\frac{t-\tau}{t_B}\right)\left[\frac{\lambda(t)}{\lambda^2(\tau)} - \frac{\lambda(\tau)}{\lambda^2(t)}\right] d\tau, \quad (1)$$

where

μ is the small strain shear modulus of neo-Hookean model,

ρ is the molar fraction of the chemical crosslinks,

$\bar{\gamma}_\infty$ is the steady state reattachment rate of the temporary chains, i.e., molar fraction of the temporary chains reattached per unit time, and

$$\phi_B\left(\frac{t-\tau}{t_B}\right) = \left(1 + (\alpha_B - 1)\frac{t}{t_B}\right)^{\frac{1}{1-\alpha_B}}, \quad (2)$$

which denotes the probability of breaking of physical crosslinks, where t_B is the characteristic time for breaking; $2 > \alpha_B > 1$ is a material constant that specifies the rate of decay of ϕ_B.

$n(t)$ is the fraction of physical bonds present at $t = 0$ and still attached at t, which is

$$n(t) = \bar{\gamma}_\infty \int_{-\infty}^{0} \phi_B\left(\frac{t-\tau}{t_B}\right) d\tau = \bar{\gamma}_\infty \frac{t_B}{2-\alpha_B}\left(1 + (\alpha_B - 1)\frac{t}{t_B}\right)^{\frac{2-\alpha_B}{1-\alpha_B}}, \quad (3)$$

The constitutive model has four independent parameters, $\mu\rho$, $\mu\bar{\gamma}_\infty$, α_B and t_B.

We use a machine learning algorithm to determine material parameters. Figure 6 shows that these parameters provide very accurate predictions which fit the experimental results for a fully hydrated PVA dual-crosslinked hydrogel. For other hydration levels, the agreement between the model prediction and experiment are just as good. The best fit model parameters for the PVA hydrogel at different hydration levels are given in table 1.

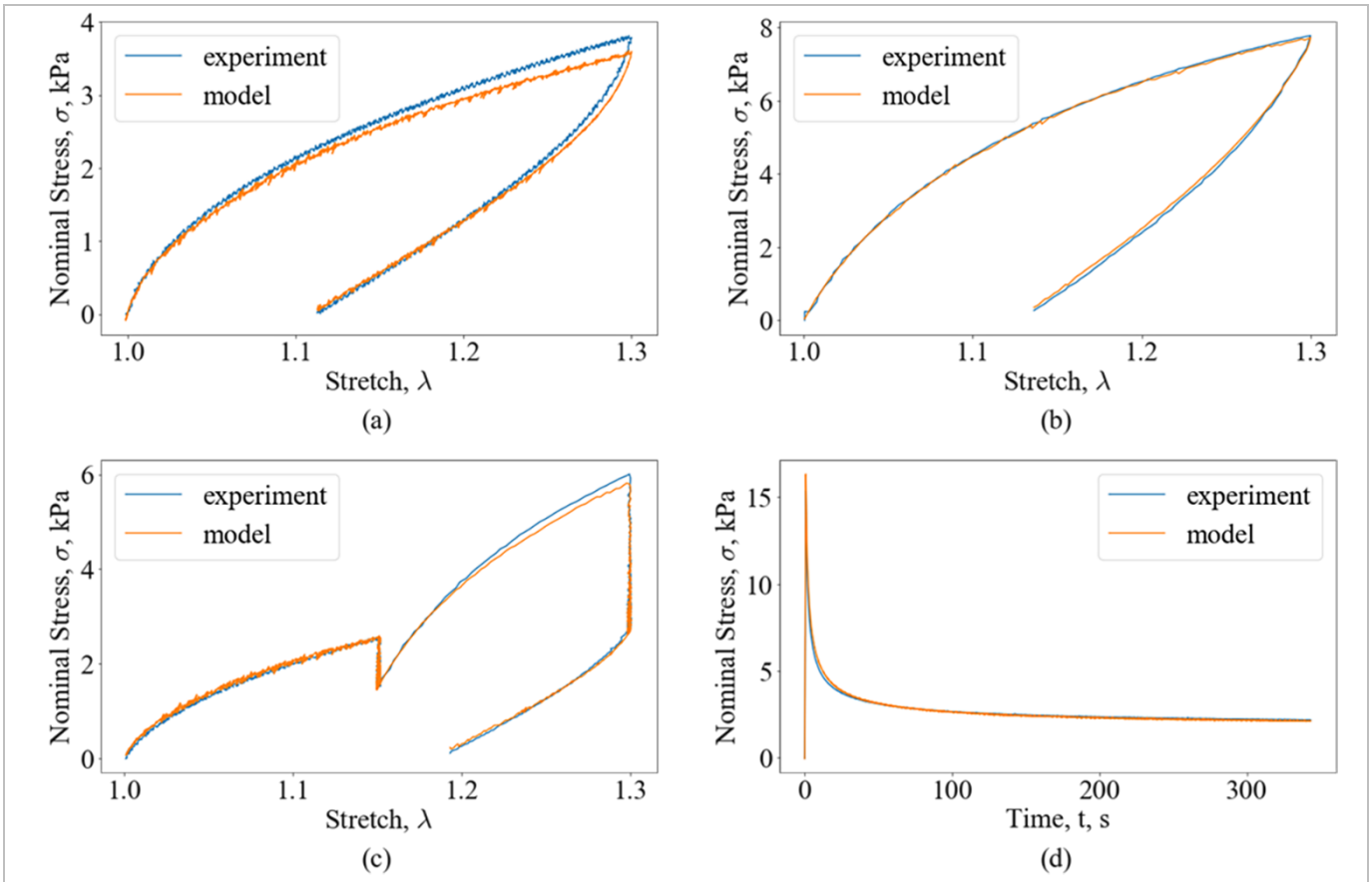

Fig. 6, Fitting results for fully hydrated (100% mass) PVA hydrogel. Nominal Stress vs. Stretch for
(a) Loading-unloading to stretch $\lambda = 1.3$ at stretch rate 0.003/s,
(b) Loading-unloading to stretch $\lambda = 1.3$ at stretch rate 0.03/s,
(c) A complex loading history which was mentioned above,
and (d). Nominal Stress vs. Time for loading at stretch rate 0.5/s to a stretch of $\lambda = 1.3$ and then holding as the stress relaxes.

Hydration	$\mu\rho(kPa)$	α_B	$t_B(s)$	$\mu\bar{\gamma}_\infty(kPa/s)$	$\frac{\mu\bar{\gamma}_\infty t_B}{2-\alpha_B}(kPa)$
100% mass	2.347	1.634	0.4618	19.91	25.15
90% mass	2.567	1.633	0.4335	26.72	31.53
80% mass	2.640	1.664	0.4250	31.62	40.05
70% mass	2.994	1.674	0.3383	48.76	50.62
60% mass	3.439	1.687	0.2338	101.2	75.55

Table 1, Data fitting results for PVA hydrogels at different hydration levels.

According to the constitutive model, $\mu\rho$ describes the long-time response of the chemical network in a relaxation test. When the PVA gel dries from 100% mass to 60% mass, $\mu\rho$ increases by about 47%. This means the chemical network carries more load when the gel dries. Table 1 shows that α_B changes little when the gel dehydrates while t_B decreases and $\mu\bar{\gamma}_\infty$ increases. This suggests physical bonds break and reattach faster when the gel loses water. The last column in the table, $\frac{\mu\bar{\gamma}_\infty t_B}{2-\alpha_B}$, can be seen as a parameter that describes the short-time response of physical bonds at small strains. It grows three times higher when the PVA gel dries from 100% mass to 60% mass. Thus the short time modulus of the gel, which involves both the physical bonds and chemical network, increases strongly with drying. The drier PVA gels are stiffer and water content has a much more significant influence on the physical crosslinks than chemical crosslinks as evidenced by the far greater increase in $\frac{\mu\bar{\gamma}_\infty t_B}{2-\alpha_B}$ relative to $\mu\rho$.

ACKNOWLEDGEMENTS
This material is based upon work supported by the National Science Foundation, under Grant No. CMMI-1903308.

REFERENCES
[1] Gong, J., Y. Katsuyama, T. Kurokawa, and Y. Osada. "Double-Network Hydrogels with Extremely High Mechanical Strength." *Advanced Materials* 15(14), pp. 1155-1158, (2003).
[2] K. Mayumi, A. Marcellan, G. Ducouret, C. Creton, and T. Narita. "Stress Strain Relationship of Highly Stretchable Dual Cross-link Gels: Separability of Strain and Time Effect." *ACS Macro Letters* 2(12), pp. 1065-1068, (2013).
[3] Long, R., K. Mayumi, C. Creton, T. Narita, and C.-Y. Hui. "Time Dependent Behavior of a Dual Cross-Link Self-Healing Gel: Theory and Experiments." *Macromolecules* 47, pp. 7243–50, (2014).
[4] Guo, J., R. Long, K. Mayumi, and C.-Y. Hui. "Mechanics of a Dual Cross-Link Gel with Dynamic Bonds: Steady State Kinetics and Large Deformation Effects." *Macromolecules* 49, pp. 3497–3507, (2016).
[5] Liu, M., J. Guo, C.-Y. Hui, C. Creton, T. Narita, and A. Zehnder. "Time-Temperature Equivalence in a PVA Dual Cross-Link Self-Healing Hydrogel." Journal of Rheology 62(4), pp. 991-1000, (2018).
[6] R. Meacham, M. Liu, J. Guo, A. Zehnder, and C.-Y. Hui. "Effect of Hydration on Tensile Response of a Dual Cross-linked PVA Hydrogel." *Experimental Mechanics* 60(8), (2020).
[7] Liu, M., J. Guo, C.-Y. Hui, and A. Zehnder. "Crack Tip Stress Based Kinetic Fracture Model of a PVA Dual-Crosslink Hydrogel." *Extreme Mechanics Letters* 29, (2019).