



# Covalent/crystallite cross-linked co-network hydrogels: An efficient and simple strategy for mechanically strong and tough hydrogels

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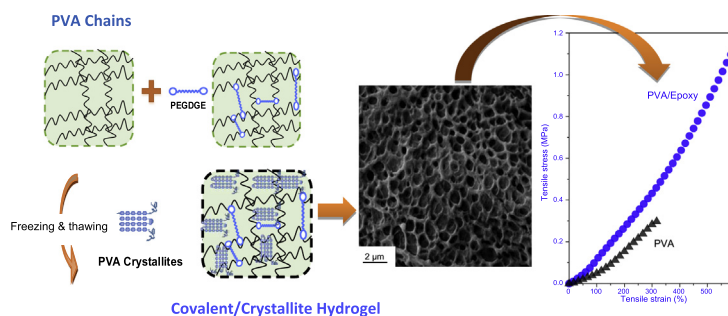
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## HIGHLIGHTS

- Co-network hydrogels of covalent epoxy and crystallite PVA are synthesized.
- Incorporating epoxy into PVA network greatly improves its mechanical properties.
- Hysteresis is shown for PVA/epoxy hydrogels due to the structural transition.

## GRAPHICAL ABSTRACT

Covalent/crystallite co-network hydrogel with high strength and toughness was prepared using epoxy and PVA. The epoxy network led to a change in structure, morphology and acted as sacrificial bonds leading to an increase in mechanical strength.



## ARTICLE INFO

### Article history:

Received 7 January 2016

Received in revised form 24 March 2016

Accepted 5 April 2016

Available online 23 April 2016

### Keywords:

Hydrogel  
Poly(vinyl alcohol)  
Epoxy  
Network

## ABSTRACT

Covalent/crystallite cross-linked co-network hydrogels have been prepared using epoxy and PVA through a cyclic freezing-thawing process. The PVA/epoxy hydrogels show enhanced mechanical strength and toughness. PVA/epoxy hydrogels with 4 wt% epoxy loading display maximum tensile strength and toughness of 1.1 MPa and 2838 kJ/m<sup>3</sup> respectively. The fracture toughness of PVA/epoxy hydrogels ranges from 160 to 450 J/m<sup>2</sup>. Radius of gyration and fractal information of the hydrogels were obtained by fitting the SAXS data to the Guinier and power law models. The enhanced mechanical properties are attributed to the increase in covalent bonding and decrease in crystallite distribution with an increase in epoxy content. However a larger hysteresis is shown for PVA/epoxy hydrogels due to irreversible destruction of covalent bonds between epoxy and PVA.

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## 1. Introduction

Hydrogels are classified as superabsorbent materials that can retain large amount of water (>50%) [1,2]. Due to this interesting phenomenon, they have found broad applications in biomedical industry as drug delivery and wound dressing materials and also

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as scaffolds for cell cultures. In addition, hydrogels can be used in various engineering applications such as molecular filters, actuators and soft robotics [3–6]. The idea of developing novel hydrogels with high mechanical strength has been the research focus of gel scientists in the past decade. Double network gels [7,8], nanocomposite gels [9], slide ring gels [10], tetra arm polyethylene glycol gels [11] and macromolecular microsphere gels [12] have been developed to address the issue of low mechanical strength and low toughness in hydrogels.

Hydrogels can be chemically cross-linked such as in the case of double network hydrogels and macromolecular microsphere gels. They can also be physically cross-linked through heat treatments [13], phase separation using theta-solutions [14], freeze–thaw cycling [15] and by using cationic salts [16]. The polymerization of hydrophilic monomers in the presence of exfoliated clay lead to the development of nanocomposite hydrogels. Slide ring hydrogels have a linear polymer chain end capped with bulky end group while cyclic molecules are threaded on linear polymer chain. Chemically cross-linked hydrogels such as double network gels have high mechanical strength but suffer significantly under fatigue loading. Physically cross-linked gels have inherent weakness in their mechanical strength. The cyclic freeze thaw method is a promising and simple technique for preparing hydrogels with improved mechanical properties. Much research has focused on poly (vinyl alcohol) (PVA) hydrogels using the freeze thaw method in relation to its structure, morphology and mechanical properties [15,17–22]. Three different phases exist in such hydrogels, namely “free water”, crystallized PVA aggregates and swollen amorphous PVA [23]. The primary crystalline phase is involved in network formation while the swollen amorphous PVA forms porous structure with water occupying the pores. PVA hydrogels prepared using freeze thaw hydrogels have shown enhanced mechanical properties [15]. Anisotropic PVA hydrogels have been prepared using directional freezing method, by applying oriented stress to the hydrogels during freeze thaw drying [24] or by the application of magnetic field [25]. These anisotropic PVA hydrogels exhibit higher mechanical strength in the direction of orientation of the crystallites compared to PVA hydrogels produced by normal freeze thaw drying. PVA can be chemically cross-linked using aldehydes, acids, silanes and isocyanates [26]. Chemically cross-linked PVA hydrogels have been synthesized and characterized using glutaraldehyde [27,28] and borates [29], however they are limited by their low mechanical strength.

Freeze thaw hydrogels have been prepared with PVA and other polymers/nanomaterials to further improve the mechanical properties. Significant improvements in both tensile and compressive strength were shown for PVA/graphene oxide hydrogels [30–32]. Tong et al. used carbon nanotubes with PVA to prepare freeze thaw PVA/carbon nanotube hydrogels [33]. Higher swelling ratio and increase in tensile strength of ~94% were achieved for these hydrogels. PVA was blended with biopolymers such as chitosan, starch and gelatin to study the structure, mechanical and swelling properties [34]. Chitin/PVA hydrogels were also prepared by freeze thaw drying which exhibited a compressive strength as high as ~2.1 MPa [35]. The improvements were purely due to the reinforcing effect of PVA on chitin as a result of formation of PVA and chitin crystallites. The improvement in mechanical properties was purely due to presence of two physical networks in the case of PVA/biopolymer hydrogels. While in the case of PVA/nanomaterial hydrogels, the improvements were a result of reinforcing effect of the nanomaterials. Nevertheless, purely dual cross-linked networks with both covalent bonding and crystallite network have rarely been studied.

Thermosets and their blends have been extensively investigated due to their significant industrial applications [36–38]. Epoxy hydrogels have been studied for their use in load bearing applications [39,40]. The formation of ionic–covalent entanglement has been established to form sufficiently strong hydrogels. Carrageenan and gellan gum biopolymers were used to form the ionic links using calcium ions and poly (ethylene glycol) diglycidyl ether (PEGDGE) with amine terminated cc served as covalent bonding in forming ICE hydrogels [39]. Carrageenan biopolymers showed substantial mechanical strength when entangled with epoxy–amine systems, while the gellan gum did not behave similarly. Qiao et al. synthesized ultrathin hydrogel films using chitosan and PEGDGE

while cystamine acted as the branching [40]. However, to our best knowledge, epoxy/PVA hydrogels prepared using freeze thaw method have not been reported in literature.

Here we report the synthesis and characterization of strong PVA/epoxy hydrogels. These hydrogels were formed from PEGDGE and PVA using three freeze thaw cycles with a freezing time of 20 h at  $-18^{\circ}\text{C}$  and a thawing time of 5 h at room temperature. PEGDGE forms brittle covalent bonding with PVA macromolecules while PVA forms crystallite networks. The hydrogels formed exhibited enhanced mechanical properties and toughness.

## 2. Materials and methods

### 2.1. Hydrogel preparation

PVA with a molecular weight of 89,000–98,000, 99% hydrolyzed was obtained from Sigma Aldrich. PEGDGE with a molecular weight of 500 was obtained from Sigma Aldrich. 15 wt% PVA solution with varying PEGDGE contents were mixed at  $95^{\circ}\text{C}$  for 1 h to initiate the ring opening reaction of the oxirane group. The solution was then transferred to a Teflon mould for the preparation of tensile and compressive testing samples. The mould was kept at  $-18^{\circ}\text{C}$  for 20 h and then thawed for 5 h at room temperature. Three freeze thaw cycles were conducted for preparing the samples. PVA and PVA/epoxy hydrogels were prepared according to the same procedure.

### 2.2. Water content of the epoxy/PVA hydrogels

The water content of the as-prepared hydrogels were measured by drying the hydrogels to a constant weight using a vacuum oven, i.e.  $W_d$ . The water content was calculated as follows:

$$\text{water content (\%)} = \frac{(W_a - W_d)}{W_a} \times 100$$

where  $W_a$  and  $W_d$  are the weight of the as-prepared and dried hydrogel respectively.

### 2.3. Swelling ratio

The dried hydrogels ( $W_d$ ) were placed in deionized water and the swollen weight ( $W_s$ ) was recorded every 24 h by removing the hydrogels and by gently blotting the excess water using a filter paper. The swelling ratio is expressed as:

$$\text{Swelling ratio (\%)} = \frac{W_s - W_d}{W_d} \times 100$$

### 2.4. FTIR spectroscopy

Infrared spectrum was recorded using a Bruker FTIR spectrometer at a resolution of  $4\text{ cm}^{-1}$ . Data was collected over a wavelength of  $400\text{--}4000\text{ cm}^{-1}$  with 64 scans. The hydrogels were dried in an air circulating oven at  $40^{\circ}\text{C}$  for 48 h and later using a vacuum oven at  $40^{\circ}\text{C}$  for 48 h before testing. ATR-FTIR accessory using a diamond point was used to obtain the spectrum.

### 2.5. Rheological measurements

The PVA and PVA/epoxy solutions were characterized using a stress controlled rheometer (TA Instruments, HR-3). Both PVA and PVA/epoxy solutions were stirred for 1 h at  $95^{\circ}\text{C}$ , allowed to cool to room temperature and immediately tested. Care was taken to avoid bubbles. Flow measurements were carried out at  $25^{\circ}\text{C}$  within a shear rate range of 10–1 to 102 s<sup>-1</sup> using a 40 mm parallel plate equipped with a solvent trap.

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