MECHANICALLY STRONG POLY (VINYL ALCOHOL)/EPOXY HYDROGELS

By

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(B.Tech, M.S)

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I am the author of the thesis entitled “MECHANICALLY STRONG POLY (VINYL ALCOHOL)/EPoxy HYDROGELS”

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<tbody>
<tr>
<td>AA</td>
<td>Acrylic acid</td>
</tr>
<tr>
<td>AAm</td>
<td>Acrylamide</td>
</tr>
<tr>
<td>AMPS</td>
<td>2-acrylamido-2-methyl-1-propanesulfonic acid</td>
</tr>
<tr>
<td>BC</td>
<td>Bacterial Cellulose</td>
</tr>
<tr>
<td>DN</td>
<td>Double Network</td>
</tr>
<tr>
<td>KGM</td>
<td>Konjac glucomannan</td>
</tr>
<tr>
<td>LCST</td>
<td>Lower critical solution temperature</td>
</tr>
<tr>
<td>$M_c$</td>
<td>Molecular weight between crosslinks</td>
</tr>
<tr>
<td>MMC</td>
<td>Macromolecular microsphere composite</td>
</tr>
<tr>
<td>NC</td>
<td>Nanocomposite</td>
</tr>
<tr>
<td>PAA</td>
<td>Poly (acrylic acid)</td>
</tr>
<tr>
<td>PAAM</td>
<td>Polyacrylamide</td>
</tr>
<tr>
<td>PAMPS</td>
<td>Poly (2-acrylamido-2-methyl-1-propanesulfonic acid)</td>
</tr>
<tr>
<td>PBDT</td>
<td>Poly (benzodithiophene)</td>
</tr>
<tr>
<td>PDMAAM</td>
<td>Poly (N,N-dimethyl acrylamide)</td>
</tr>
<tr>
<td>PDMAPS</td>
<td>Poly (N-(3-sulfopropyl)-N-methacroyloxyethyl-N-N-dimethylammonium betaine)</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly (3.4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly (ethylene glycol)</td>
</tr>
<tr>
<td>PEGDGE</td>
<td>Poly (ethylene glycol) diglycidyl ether</td>
</tr>
<tr>
<td>PEGMA</td>
<td>Poly (ethylene glycol) methyl acrylate</td>
</tr>
<tr>
<td>PNIPAM</td>
<td>Poly (N-isopropylacrylamide)</td>
</tr>
<tr>
<td>PSAPS</td>
<td>Poly (3-sulfopropylacrylate potassium salt)</td>
</tr>
<tr>
<td>PSBMA</td>
<td>Poly (sulfobetaine methacrylate)</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly (styrene sulfonate)</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly (vinyl alcohol)</td>
</tr>
<tr>
<td>PVP</td>
<td>Poly (N-vinyl pyrrolidone)</td>
</tr>
<tr>
<td>SANS</td>
<td>Small angle neutron scattering</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small Angle X-ray Scattering</td>
</tr>
<tr>
<td>TP</td>
<td>Topological</td>
</tr>
<tr>
<td>UPy</td>
<td>2-ureido-4-pyrimidone</td>
</tr>
<tr>
<td>VDT</td>
<td>2-vinyl-4,6-diamino-1,3,5-triazine</td>
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ABSTRACT

This thesis reports a novel hydrogel system using poly (vinyl alcohol) and epoxy with high mechanical performance. The hydrogels were prepared using solution mixing and freeze thaw process to induce covalent bonding, crystallites and interpolymer interactions. The PVA/PEGDGE hydrogels exhibited enhanced mechanical strength and toughness. PVA/PEGDGE hydrogels with 4 wt% epoxy displayed maximum tensile strength and toughness of 1.1 MPa and 2838 KJ/m$^3$ respectively. The fracture toughness of PVA/PEGDGE hydrogels ranged from 160 to 450 J/m$^2$. The enhanced mechanical properties are attributed to the increase in covalent bonding and the decrease in crystallite distribution with an increase in epoxy content.

The structure of the hydrogels was elucidated based on network parameters calculated using the Flory Huggins and Mooney-Rivlin theory. The morphology was analyzed using a combination of SEM and SAXS. An increase in the crosslink density and a decrease in both the molecular weight between crosslinks and mesh size was observed with increasing epoxy concentration. SEM showed a decrease in the pore size of the hydrogels with an increase in the epoxy concentration. Radius of gyration and fractal information of the hydrogels were obtained by fitting the SAXS data to the Guinier and power law models. The obtained results showed a transition from a heterogenous morphology to a homogenous morphology while showing a limiting crosslink for obtaining the highest mechanical properties.

Further, the strain rate-dependant mechanical properties, large strain behaviour and internal fracture mechanism in PVA/PEGDGE hydrogels were investigated. The hydrogels displayed rate-dependant mechanical properties with a higher strain rate showing higher tensile strength and fracture energy in comparison with hydrogels stretched at lower strain rates. The internal fracture process shows a continuous-discontinuous phase transition due to the chemically cross-linked epoxy network. Crystallite orientation/fracture and the epoxy sacrificial bond contribute to the
mechanism for energy dissipation in hydrogels formed by covalent/crystallite networks. The large strain behavior in PVA/epoxy double network hydrogels has been well described by the Mooney-Rivlin model.

The compositional effects of PVA/PEGDGE hydrogels on the mechanical properties were investigated. The hydrogels were analyzed with regard to the influence of water, salt, PVA content and short-term strain on the mechanical properties of the hydrogel. The analyses showed enhanced mechanical properties with a decrease in water content and by the increase in salt content (0.3 moles). The results were interpreted based on the change in the crystallite structure and the role of epoxy covalent crosslinks and hydrogen bonding.

Finally, the role of a multifunctional amine as a hydrogen bonding crosslinker for PVA/PEGDGE hydrogels have been investigated. It has been shown that a small amount of amine addition improved the tensile stress and strain by two and three times respectively. It can be concluded that the hydrogen bonding moieties play a vital role in systems such as PVA/epoxy hydrogels due to its suitability in forming inter and intramolecular hydrogen bonds.
CHAPTER ONE

INTRODUCTION

1.1 Thesis Objective

Polymer science and technology has developed significantly and plays a major role in engineering applications. Hydrogels are a new class of materials capable of absorbing large amount of water. Water absorption of the hydrogels is attributed to the three dimensional network structure formed by cross-linking polymer chains. Due to this interesting phenomenon, they have found application in biomedical industry as drug delivery materials, wound dressing and as scaffolds for cell cultures [1]. However, hydrogels are soft and mechanically weak materials hindering their wider applications in engineering applications.

Mechanically strong hydrogels have the potential to be used in engineering application such as molecular filters, actuators, soft robotics, water purification [2-5]. Significant amount of work has been devoted to improve the mechanical properties of hydrogels in the past few decades. A well-recognized strategy is the incorporation of a two or more cross-linked networks to strengthen the hydrogels. The toughness can be improved significantly by using a combination of different types of networks such as covalent and ionic networks[6] or by using a sequential combination of a tightly cross-linked network with a lightly cross-linked network [7]. Conventionally, extensive studies have been undertaken on use of polyacrylamide as the first network. Recently polysaccharides as the second network has shown to improve the fracture toughness. However, newer combination of polymers are being investigated for the preparation for strong hydrogels.

Epoxy based materials signify one of the most important thermosetting polymers extensively used in engineering applications. Epoxy hydrogels represent a new class of hydrogels with huge potential as functional materials. Poly (vinyl alcohol) is a commercially available biocompatible, biodegradable, highly crystalline, toxicologically safe and inexpensive polymer. The hydroxyl group of poly (vinyl
alcohol) is well suited for forming covalent network or physical hydrogen bonded networks.

The objective of the thesis is to report experimental results of attempts to develop mechanically strong hydrogels using epoxy and poly (vinyl alcohol). The study is based on the fundamental knowledge that the combination of two different types of networks exhibit a marked increase in the mechanical properties. The combination of physical, covalent bonding and inter polymer interaction have a significant improvement in mechanical properties by initiating diverse toughening mechanisms during crack propagation. This work demonstrates the pathway towards novel network topologies in the field of tough hydrogels.

1.2 Thesis Outline

This thesis consists of eight chapters including introduction (Chapter one), literature review (Chapter two) and conclusions (Chapter eight). The format of each chapter includes an introduction section followed by experimental section and then by results and discussion sections. Each chapter consists of a reference section for citations in that chapter.

Chapter two reviews the recent literature on the types of mechanically strong hydrogels and their diverse toughening mechanism based on network design. The review focusses on double network hydrogels, nanocomposite hydrogels, topological hydrogels, ionic-covalent hydrogels, hydrogen bonded hydrogels, hydrophobic hydrogels, macromolecular microsphere hydrogels and poly (vinyl alcohol) hydrogels.

Chapter three illustrates the design, synthesis and mechanical characterization of poly (vinyl alcohol)/epoxy hydrogels using crystallite/covalent networks. The role of epoxy on the design and mechanical properties of the hydrogels were investigated extensively.
Chapter four examines the structure and morphology of poly (vinyl alcohol)/epoxy hydrogels. The structure parameter such as crosslink density, molecular weight between crosslinks and mesh size were obtained from swelling, mechanical and rheological data. The morphology was studied using a combination of scanning electron microscopy and small angle X-ray scattering.

Chapter five focuses on the fracture behaviour and large strain behaviour of poly (vinyl alcohol)/epoxy hydrogels. The continuous/discontinuous phase transition occurring in these hydrogels have been investigated from hysteresis measurements. The large strain behaviour was further analysed using the Mooney- Rivlin hyperelastic model.

Chapter six examines the compositional effects of poly (vinyl alcohol)/epoxy hydrogel on the mechanical properties. The epoxy content was fixed at 4 wt% and the effect of water content, PVA content and multivalent salts on the mechanical properties were investigated.

Chapter seven illustrates the mechanical properties of poly (vinyl alcohol)/epoxy in the presence of hierarchical hydrogen bonding. Hydrogen bonding was induced between poly (vinyl alcohol) and 4,6-diamino-2-hydroxy-1,3,5-triazine while covalent bonding was present between epoxy and poly (vinyl alcohol). The mechanical properties of combination of networks were extensively investigated.

Chapter eight draws conclusions from the previous five chapters on the design, mechanical properties and fracture mechanism in poly (vinyl alcohol)/epoxy hydrogels. Recommendation for further work on the synthesis of tough hydrogels using epoxy and poly (vinyl alcohol) have been proposed.
1.3 References


CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Hydrogels are three dimensional polymer networks capable of retaining a large amount of water due to the presence of crosslinks [1]. The similarity of hydrogels and soft natural tissues had resulted in great interests in applying them to biomedical applications. Therefore, extensive studies have been conducted on the swelling[2], diffusion characteristics[3] and physical and mechanical properties[4, 5] of hydrogels towards biomedical applications. Moreover, hydrogels have the ability to respond to external stimulus such as temperature [6-9], pH[10-12], light[13, 14], electric field[15, 16] and certain chemicals [17, 18]. Hydrogels respond with a change with release of water resulting in variation of size or stress generation. Such responses are extremely useful in applications such as artificial muscles [19-21] and biomedical systems [7, 22]. Hydrogels have been extensively studied towards applications in a plethora of fields such as food industry[23], tissue engineering[24, 25] and electronics engineering[26-33].

The fracture energy of conventional hydrogels range from 0.1 J/m$^2$ to 100 J/m$^2$ and are not sufficient for load bearing mechanical devices [34]. The low fracture energy is attributed to the solution-like nature and heterogeneities during the formation of hydrogel. The ability to absorb large amount of water and the non-uniform crosslinking of monomers provides inhomogeneity in the hydrogel and are believed to be the prime reason for the origin of low mechanical strength. Hence, stress is accumulated on the shortest chain leading to failure at low stresses. Typically, conventional synthetic single network hydrogels have a failure tensile stress and strain of few 100 kPa and 100% respectively. Thus, conventional hydrogels, typically consisting of single network are soft, weak, and brittle. It is of interest that a good number of biological hydrogels possess exceptional mechanical toughness, shock absorption, low sliding friction and contraction [35]. A classic example is cartilage, which has a compressive fracture stress as high as 36 MPa [36]. Gel scientists in the past decade have been trying to bridge the gap between man-made and biological gels. Figure 2.1 shows the number of papers published
pertaining to robust hydrogels in the past decade. Figure 2.2 illustrates application of robust hydrogels.

**Figure 2.1** Number of journal articles for keywords hydrogel, nanocomposite hydrogel and double network hydrogel (data obtained from Scopus).

**Figure 2.2** Proposed Applications of Tough Hydrogels.
The context of the thesis relates to the development of mechanically strong and tough hydrogels and this chapter will describe the relevant literature on mechanically strong and tough hydrogels developed in the past decade. The chapter lays emphasis on the various network topologies employed to achieve high toughness, their mechanical properties and the corresponding fracture mechanism in these systems. The hydrogel systems described include double network hydrogels, topological hydrogels, nanocomposite hydrogels, hydrogen bonded hydrogels, macromolecular microsphere hydrogels, poly (vinyl alcohol) hydrogels, click chemistry based hydrogels and hydrophobic association hydrogels.

2.2 Topological Hydrogels

Topological hydrogels (TP) are characterized by a network design of cyclic molecules laced on to linear polymer chains which are terminated by bulky groups. A classic example is polyrotaxane entities which contain many cyclic molecules threaded along a single linear polymer chain end capped by bulky end groups. Okumura and Ito pioneered in the synthesis of strong hydrogels using polyrotaxane molecules consisting of high molecular weight polyethylene glycol as the linear chain and α-cyclodextrin cyclic molecules threaded on the PEG chains [37]. In the next step cyanuric chloride was used to chemically cross-link the α-cyclodextrin in an aqueous solution of polyrotaxane to achieve a network design as shown in Figure 2.3. Such network design facilitates the crosslinkers to slide along the linear polymer chain and thereby shows exceptional elongation strains and high swelling ratios of 2000% and 400% respectively.

TP gels are visually clear, transparent and of low viscosity. The internal structure of TP gels are formed with bulky end groups by topologically interlocking by figure of eight crosslinks. The fracture behaviour in TP gel is distinctly different from chemical gels formed by covalent bonding or physical gels formed by ionic crosslinking. Figure 2.4 shows a schematic model of chemical gel and a topological gel on uniaxial tensile stretching. In the chemical gel, the polymer chains are broken gradually by distribution of the tension among the polymer chains because of the heterogeneous polymer length between fixed crosslinks. In a topological gel, however, the figure of eight crosslinks can slide along the polymer chains freely to equalize the tension of the threaded polymer chain. Okumura and Ito called this
equalization of tension the “pully effect” [38]. Through the pulley effect the mechanical properties of TP gel increase and the gel can stretch to approximately 20 times its original length without fracture. SAXS of TP hydrogels showed a normal butterfly pattern under uniaxial elongation indicating of spatial homogeneity of the hydrogel due to the pulley effect.

**Figure 2.3** (a) Schematic illustration of topological hydrogel. (b) Polyrotaxane linear chain consisting of PEG backbone chain and circles are a-cyclodextrin. (c) Chemical cross-linking in topological gels [37].

**Figure 2.4** Schematic illustration of fracture in chemical gel and the TP gel under uniaxial tension. (a) In the chemical gel, tension of chains is unequal, and short chains are cut first. (b) In the TP gel, the chains and the figure-of-eight cross-linkers can slide each other. Due to this motion, the tension can be regulated [37].
2.3 Double Network Gels

Double Network (DN) gels are another class of mechanically strong hydrogels [24-42]. DN gels are formed by sequential crosslinking of two different types of polymers namely a polyelectrolyte and a neutral polymer. The first mechanically strong DN gels reported consisted of a rigid network of poly (2-acrylamido,2-methyl, 1-propanesulfonic acid) (PAMPS) and neutral polyacrylamide which served as the second network [39]. A combination of a tightly cross-linked first network with a loosely cross-linked second network proved to be the ideal combination for strong DN hydrogels. Another feature of DN hydrogels is the apparent variation in the molar ratio of individual polymers. The molar ratio of the second polymer should be more than ten times that of the first polymer. The classical DN hydrogel showed a tensile strength of ~ 1.1 MPa and elongation of ~1000% characterized by a large necking zone. The schematic illustration of sequential preparation of double-network gels is shown in Figure 2.5.

Figure 2.5 Schematic illustration of two step sequential polymerization for the preparation of double network hydrogel [40].
As shown in Figure 2.5, the first sequence involves the use of strong polyelectrolytes to form a covalently cross-linked brittle network via conventional chemical/UV photo-polymerization. The obtained single network gel is then immersed and swelled in an aqueous solution of neutral monomer along with the initiator and crosslinking agents. The strong polyelectrolytes swell enabling the neutral monomer to diffuse into the first network. Later the polymerization is initiated to form a loosely crosslinked second network within the first network. Such methods have been adopted to prepare a wide range of DN hydrogel with both the networks chemical crosslinked. In general, enabling diffusion of the second monomer necessitates the use of a large excess of the second monomer typically 20-50 times greater than the 1st monomer. Moreover, the mechanical properties were sufficiently high when the molar ratio was atleast 10 times higher than the first monomer molar ratio[39]. Time is another factor and the two stage DN process typically takes more than two days to complete the synthesis. However, in the recent past one pot synthesis of DN hydrogels have also been reported. The design of using a physically crosslinked network and a chemical crosslinked network have also been reported to form strong DN hydrogels. Several different combinations of polymers have been employed and reported as DN hydrogels. Table 2.1 shows the various DN hydrogels developed using both classical DN and modified DN hydrogel approaches.

**Table 2.1** Mechanical properties of double network hydrogels using various combination of polymers.

<table>
<thead>
<tr>
<th>Polymer Combination</th>
<th>Tensile Properties</th>
<th>Compressive Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_b$ (kPa)</td>
<td>$\varepsilon_b$ (%)</td>
</tr>
<tr>
<td>PAAMPS-PAAM DN</td>
<td>600</td>
<td>1000</td>
</tr>
<tr>
<td>PVA-PAMPS-PAAM DN[41]</td>
<td>1200</td>
<td>1400</td>
</tr>
<tr>
<td>PAAM-PEDOT-PSS DN[42]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAAM-BC DN[43]</td>
<td>2500</td>
<td>100</td>
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<tr>
<td>Material</td>
<td>2250</td>
<td>1200</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------</td>
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</tr>
<tr>
<td>Silica gel – PAAM DN[45]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA-PEG[46]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBDT-PAAM DN[47]</td>
<td>450</td>
<td>2000</td>
</tr>
<tr>
<td>PHA-PDMAAM DN[48]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSBMA-PSBMA DN[49]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEG-PAA DN[50]</td>
<td>3400</td>
<td>105</td>
</tr>
<tr>
<td>PDMAPS-PAAM DN[51]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC–Gelatin DN[52]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC–Gellan gum DN[52]</td>
<td>1200</td>
<td>30</td>
</tr>
<tr>
<td>BC–Sodium Alginate [52]</td>
<td>2200</td>
<td>30</td>
</tr>
<tr>
<td>BC-Carrageenan DN[52]</td>
<td>500</td>
<td>26</td>
</tr>
<tr>
<td>PAAM-Agar DN[53]</td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>PAAM – PVA[54]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEG-PVA[55]</td>
<td>1200</td>
<td>380</td>
</tr>
<tr>
<td>PVA–KGM – PAAM[56]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chitosan – TPT-block PEG -block TPT[57]</td>
<td></td>
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</tr>
</tbody>
</table>
Several interesting choices of polymers have been employed to improve biocompatibility or strength. Bacterial cellulose has been used as the first network while a synthetic or natural polymer was used as the second network[58-61]. Thin hydrogel films based on PAMPS and PAAM with thickness ranging from ~30 to 110 µm fully swollen in water were developed[44]. These thin film hydrogels showed high tensile strength of ~ 2MPa, tensile elongation of ~1000% and fracture energies as high as 600J/m². Recently an interesting DN has been developed using agar as the physically crosslinked first network while Polyacrylamide was used as the neutral second network[53]. The DN gels showed exceptional compressive strength of ~38 MPa, tensile elongation of 1500 – 2000%, fracture energies of 100 to 1000 J/m² and fast recovery.

The mechanical properties of DN hydrogels have been extensively investigated both in compression and elongation. Fracture of the hydrogels, Mullins effect, large strain behaviour and necking have been reported based on the design of the hydrogels. The classical DN hydrogels possess exceptional compressive and tensile strength. Recently developed DN hydrogels have surpassed the mechanical properties in comparison with classica DN hydrogels. These impressive properties have alluded to comparison and replacement with natural occurring biological tissues [61] and [62].

2.3 Nanocomposite Gels

Nanocomposite gels were developed by Haraguchi and Takehisa using inorganic clay to form crosslinking junctions [62-70]. The pioneering work demonstrated the use of exfoliated hectorite clay to polymerize NIPAM monomers using free radical polymerization without the addition of any chemical crosslinking agents. The schematic illustration of the structure of NC gels is shown in Figure 2.6. As shown, the NC gels are formed by strong adsorption of the polymer chains (χ) onto the surface of the exfoliated clay sheets. A large number of polymer chains are adsorbed onto different clay sheets that provides the bonds to form a network structure. Using clay sheets as crosslink junctions provides the NC gels with exceptional mechanical properties; in particular, very high extension ratios [62].
Later, a large number of water soluble and modified clays have been employed towards the synthesis of NC gels. In general, acrylamide based monomers have been used as the polymer matrices due to their adequate interaction with the inorganic clays. The mechanical properties of NC gels can be tailored by altering the clay[71] and monomer content[65, 67]. Typically, NC gels possess a tensile strength of 10 – 1000 kPa, elongation at break above 1000% and elastic moduli of 1- 50 kPa. The compressive strength of these gels are significantly higher than the tensile strength (1- 5 MPa) [68]. It has been shown that the addition of small amount of chemical crosslinker enhances the mechanical properties[72].

The high elongation at break of NC gels and their transparency are attributed to the formation of a homogenous network structure. Experimental evidence shows that the multifunctional clay crosslinks provide a more homogenous structure than chemical crosslinked hydrogels [62, 63]. The following facts provide further proof of homogenous structure in NC gels: (i) no significant change in transparency of NC hydrogels prepared above the lower critical solution temperature (LCST) of PNIPAM whereas opaqueness was obtained for chemically crosslinked PNIPAM hydrogels; (ii) extremely high extension ratios and minimal/no hysteresis; (iii) minimal change in glass transition temperature with varying clay composition while a significant change occurs with change in composition in chemically crosslinked hydrogels.

Rubber elasticity theory was first proposed to elucidate the origin of mechanical properties in NC gels where the polymer chains were assumed to be in a rubbery
Equation 2.1 was used to relate the tensile stress to tensile strain according to rubber elasticity theory

\[ \sigma = \phi N^* kT \left[ \lambda - \frac{1}{\lambda^2} \right] \]  

(2.1)

where \( \phi \) represents the front factor and \( N^* \) represents the number of crosslinked chains in the swollen state and is inversely related to the molecular weight between crosslinks (\( M_c \)). \( k \) represents the Boltzmann constant, while \( \lambda \) and \( T \) represent the extension ratio and temperature respectively. \( N^* \) can be approximately related to \( M_c \) as follows [63]:

\[ N^* \sim \rho^* \frac{N_A}{M_c} \]  

(2.2)

where \( \rho^* \) represents the polymer density of the fully swollen polymer and \( N_A \) indicates the Avogadro’s number. The values of \( M_c \) and \( N^* \) can be calculated using mechanical data along with equation 2.1 and 2.2. The total number of crosslinked chains per individual clay platelets can be estimated as \( N^*/n \), where \( n \) is the number of separated clay platelets per unit volume. This is valid for fully exfoliated clay and the value of \( N^*/n \) increases when the clay composition varies, which is direct evidence towards the concept of clay acting as crosslinking sites.

In addition to the rubber elasticity theory, viscoelastic models have been proposed to further elucidate certain discrepancies that could not be addressed by the rubber elasticity theory solely. One such discrepancy was the role of chemical structure of polymer and clay composition on the mechanical properties. For example, a significant hysteresis was noted when NC hydrogels based on PNIPAM homo- and copolymers were stretched to 800% (below the fracture strain) during tensile testing [73, 74]. While PAAM-based NC hydrogels displayed exceptional recovery while displaying very low hysteresis [73]. This difference was shown to originate from the difference in the molecular structure between two polymers. PNIPAM has bulky hydrophobic groups which are not present in PAAM [73], although smaller hysteresis was obtained for PNIPAM NC hydrogels based on the resting time between loading-unloading cycles and by varying the clay content [68]. The recovery time was less than one minute for low clay content with a strain of 900% while the recovery time was vastly prolonged for medium clay content.
However, for high clay content, recovery of the hysteresis did not occur even after a time frame of 14 days. A modified Maxwell model consisting of two springs and two dashpots was used to model these experimental results. The Young’s modulus of the spring component 2 (E₂) and viscosity of the dashpot component 2 (η₂) contribute to the viscoelastic behaviour while the Young’s modulus of spring component 1 (E₁) and the viscosity of the dashpot component 3 (η₃) contribute to the elastic and pseudo strain behaviour respectively. Another model consisting of two springs and a dashpot was also used to model the mechanical properties of these hydrogels [75].

Another theory was proposed based on the orientation of the clay particles upon deformation. It assumes the clay particles align parallel to the direction of applied force when the clay content is higher than the threshold clay content. Upon release of the applied force, the clay particles partially return to their original state due to the high level of clay content and orientation. It also assumes the orientation is insignificant for low levels of clay content and hence hysteresis is minimal; in contrast, at high clay loadings, a hysteresis is present even with higher resting times. Small angle neutron scattering (SANS) was used to verify this theory which showed an abnormal butterfly pattern at very low q values, i.e. an indication of orientation of the platelets [76].

### 2.4 Hydrogen-bonded Hydrogels

As seen in the previous section, the DN hydrogels use a strong polyelectrolyte first network to interact through electrostatic interaction between PAAM and PAMPS. It is shown that PAAM can become charged in a polar solvent such as water and hence lead to electrostatic interactions between PAAM and PAMPS. However, these are very weak interactions in contrast to hydrogen bonding, which has been proved to provide a stronger interaction resulting in much improved mechanical properties. Frank and co-workers synthesized hydrogels using crosslinked PAA within an end-linked PEG network, showing enhanced mechanical properties[50]. The prepared hydrogels showed true strength ranging from 2 MPa to 12 MPa and displayed strain hardening with no evidence of necking. Wang et al prepared purely physically crosslinked hydrogels using cooperative hydrogen bonding[77]. They used a facile strategy of polymerizing acrylamide in the presence of poly (N-vinyl
pyrrolidone) (PVP) without any chemical crosslinkers to create purely physically crosslinked hydrogels using hydrogen bonding. After heating the PVP/acrylamide solution at 56 °C for 36 hours, hydrogels were created by hydrogen bonding. The prepared hydrogel displayed high tensile strength (~1.2 MPa) and exceptional elongation of 3000%. Liu et al synthesized hydrogels with remarkable compressive strength using intermolecular hydrogen bonding by 2-vinyl-4,6-diamino-1,3,5-triazine (VDT) and polyethylene glycol diacrylates [78].

Recently quadruple hydrogen bonding based on 2-ureido-4-pyrimidone (Upy) networks have been used to create hydrogels with high mechanical toughness as well as self-healing function[79]. Figure 2.7 shows the schematic of synthesis of hydrogels using acrylamide monomer and hydrophobic comonomer consisting of Upy tail, acrylate head and a long alkyl chain mid-block (Figure 2.7 a, b). Micellar polymerization was used to synthesize the hydrogel using sodium dodecyl sulphate micelles as solubilisation environment for the hydrophobic environment (Figure 2.7 c, d). The hydrogels did not fracture even after stretching 100 times of its original length, however it had very low tensile strength of around 4 kPa. Self-healing hydrogels have been prepared using hydrogen bonded networks. PVA self-heals autonomously due to the effect of extensive intermolecular hydrogen bonding when the PVA concentration was greater than 25% [80]. Further hydrogen-bonded supramolecular hydrogels based on Upy are able to heal despite the fact that they are extremely weak [81].
Figure 2.7 Schematic of 2-ureido-4-pyrimidone based hydrogels synthesized using micellar copolymerization of acrylamide and 2-ureido-4-pyrimidone comonomer [79].

2.5 Macromolecular Microsphere Hydrogels

These hydrogels are prepared using nano/micro spherical particles that act as functional crosslinkers. Macromolecular microspheres with active surfaces showed enhanced toughness. The first step involved preparation of the microspheres using a mixture of styrene, butyl acrylate and acrylic acid in emulsion followed by gamma irradiation under oxygen atmosphere to produce peroxides on the surface of the microspheres [82]. The microspheres acted both as crosslinker and initiator to polymerize acrylic acid. The maximum compressive strength achieved by these hydrogels was ~ 78 MPa with a water content of 70% while full recovery of the strain was achieved when the compressive stresss ranged from 1 to 20 MPa. Zhu et al., used a cationic nanosphere of polystyrene which acted as a crosslinking agent for PAAM based hydrogel. These hydrogels reported a compressive strength as high as ~ 40 MPa and high swelling ratios. They had high tensile elongation that
is comparable to that of NC gels (~ 5000%) and a maximum tensile stress of 1 MPa. Similarly, nano-sized spheres were synthesized from acrylamide and AMPS monomers and crosslinked using chemical crosslinkers. The amide groups were substituted by double bonds and these double bonds on the surface of the sphere acted as crosslinker for the final hydrogel. The mechanical properties were strongly related to the nanosphere content in the final hydrogel composition. The compressive strength ranged from 2 to 4.6 MPa while the tensile stress and strain reported ranged from 190 – 270 kPa and 420-550% respectively.

A two-network hydrogel was prepared consisting of a first network of a microgel made of grafted copolymer chains of acrylic acid and acryloxyethyl trimethylammonium chloride and acrylamide (AAm) on to PNIPAM – poly (vinyl amine) spheres and a second network of copolymer chains. A compressive strength of 5 – 30 MPa was achieved based on the varying compositions. Another similar hydrogel involved using poly (NIPAM-co-AA) microgels for crosslinking. These hydrogels showed stimuli responsiveness to both temperature and pH.

### 2.6 Tetrahedral PEG Hydrogels

These hydrogels possess homogeneity similar to that of topological hydrogels. They are formed using star polymers with symmetrical arms of same size containing functional groups. The tetrahedron macromonomers react with each other through the functional groups of the arms of the star polymer. The hydrogels made using two PEG based tetrahedral-like macromonomers containing functional groups such as amine and succinimidyl ester displayed a maximum compressive strength of 2.5 MPa. The homogeneity of the hydrogel was further confirmed by SANS measurements and the heterogeneity started when the stoichiometric ratio between the polymers deviated from 1. It was also found that defects such as trapped entanglements, dangling chains and loops are negligible. Mechanical and scattering studies show a structure similar to elastic polymer blobs packed within the hydrogel. These hydrogels display very low hysteresis and can be correlated to the behaviour of rubbers. Another characteristic feature of these hydrogels is the presence of uniform density within the hydrogels.
2.7 Poly (vinyl alcohol) Hydrogels

Poly (vinyl alcohol) (PVA) is a biocompatible, commercial available and cost effective polymer. These properties along with elasticity and high swelling ratios provide exceptional opportunity to be used as an alternative to human tissues in comparison with any other synthetic biomaterials [83]. PVA can be chemically crosslinked by crosslinkers such as aldehydes, borates or physically crosslinked using heat treatment and freeze thaw methods.

PVA was marketed as Ivalon® by using formaldehyde to create a super porous spongy material during 1970’s [84]. Ivalon® was applied as duct replacement, articular cartilage replacement [85], drug release and reconstructive (vocal cord) surgery [86]. Further works on chemically crosslinked PVA hydrogels involved the use glutaraldehyde as the crosslinker [87-91], however this has been criticized due to the toxic nature of glutaraldehyde. Borates have been recently used to create strong hydrogels with self-recovery thermos-reversible and self-healing properties [92, 93]. However, the mechanical properties of chemically crosslinked PVA hydrogels suffered significantly in the mechanical properties.

The majority of physically crosslinked PVA hydrogels are formed using freeze thaw method. The hydrogels show very good mechanical strength and are non-toxic due to the absence of toxic chemical crosslinking agents. The freeze thaw process involves a cyclic process of freezing the PVA solution for a pre-determined time followed by thawing for predetermined time. During the first freezing cycle, the PVA phase separates from water due to the difference in the freezing rates. The phase separation creates regions of high and low concentration of PVA. During the thawing cycle, the regions with high concentration of PVA crystallizes and these crystallites are held together by hydrogen bonding. The crystallites connected by hydrogen bonding form the physical crosslinking and are responsible for the formation of hydrogel. Further freezing and thawing cycles increases the crystallinity of the hydrogels and thereby the mechanical strength increases with the increase in freeze thaw cycles. In general, it is found that the mechanical strength does not increase after 8 or 9 cycles.

The initial work of PVA hydrogels using freeze thaw cycling was carried out in the 1980’s [86, 94, 95]. Nambu et al prepared PVA hydrogels by freeze thaw method.
and found an significant increase in the modulus of the hydrogels. The inference was that the gelation occurred during sustained thawing due to the formation of fine crystals which could act as knots responsible for the hydrogel structure[86]. Yokoyama et al., studied the structure and morphology of 15 wt% PVA hydrogels using XRD, microscopy and tensile tests[94]. They concluded that the hydrogels could consist of three regions: (i) namely a water phase with low PVA concentration (ii) PVA amorphous phase that is hydrogen-bonded with water and (iii) PVA crystals. They showed that the mechanical properties improved with the increase with the freeze thaw cycles, which was directly related to the increase in crystallinity. The maximum tensile stress achieved was 1.2 MPa after 10 freeze thaw cycles. Further, Stauffer and Peppas investigated the influence of freezing and thawing times and number of cycles on the swelling and compressive properties of the hydrogels [95]. They reported that strong hydrogels formed by freezing and thawing for around 24 hours. The hydrogels with higher number of freeze thaw cycles exhibited higher compressive stress, which was inferred as a consequence of the densification of the structure.

Wilcox et al., undertook a comprehensive study on the microstructure of hydrogel to understand the shape and size of crystallite created [96]. Characterization techniques such as NMR, XRD, SEM, SAXS and DSC were used to ascertain the percentage of crystallites and their shape and size. They inferred that the network formation was due to kinetically frustrated crystallization. They further showed that the percentage of rigid segments increased from 5% to 12% with increasing freeze thaw cycles. The crystallite size and gel mesh size range from 3~8 nm to 20~35nm respectively. Hassan and Peppas studied the structure and morphology of as-prepared hydrogels and hydrogels aged up to 6 months [97]. The effect of freeze thaw cycles, initial PVA concentration and PVA molecular weight on the swelling, crystallinity and long-term stability of hydrogels were investigated. They concluded that the increase in concentration of PVA resulted in the increase in crystallinity while higher molecular weight induced larger crystal size and broadening in lamellar thickness distribution. The stability of PVA hydrogels with molecular weight of 64,000 (Mn) and hydrogels synthesized using higher freeze thaw cycles showed excellent stability in swelling for six months. Ricciardi et al. carried out a series of investigation on the crystallization and structure of PVA
hydrogel using various characterization techniques [98-101]. They investigated the structure of as-prepared, aged and rehydrated PVA hydrogels made using D$_2$O as the solvent with the help of XRD measurements [100]. Their results supported the idea of porous morphology with the pores occupied by water and the pore walls consisting of amorphous PVA. They proposed that the crystallites could act as knots and are responsible for the elastic properties of the hydrogel. Further, the group tried to analyse the crystallinity of as-prepared and aged PVA hydrogels using XRD, DSC and NMR [101]. They predicted that NMR results are more accurate in as-prepared hydrogels than DSC due to the smaller crystallites. However, the crystallinity of aged PVA hydrogels provided similar results for both DSC and NMR due to the well-formed crystallite structure.

Although PVA hydrogels prepared by freeze thaw cycling displayed elastic properties, tensile stress of around 1MPa was attained merely with freeze thaw cycles greater than 7 or more. This limits its feasibility due to the excessive long time-frame that could be around 14 days considering a freezing time of 24 hours and thawing time of 23 hours as the optimal conditions by various groups. Thus anisotropic PVA hydrogels were prepared using directional freezing method by applying oriented stress to the hydrogels during freeze thaw drying [102] or by the application of magnetic field [103]. These anisotropic PVA hydrogels exhibit higher mechanical strength along the crystal orientation the compared to PVA hydrogels produced by normal freeze thaw drying. Zhang et al. showed that the tensile strength varied from 0.28 MPa after three cycles to 0.62 MPa after nine cycles when measured in the parallel direction. However, a difference was obtained when measured in the perpendicular direction; tensile strength varied from 0.4 MPa after three cycles to 0.63 MPa after five cycles [104].

In order to enhance the mechanical strength, freeze thaw hydrogels have been prepared with PVA and other polymers/nanomaterials. Significant improvements in both tensile and compressive strength were shown for PVA/graphene oxide hydrogels [105-107]. Tong et al used carbon nanotubes with PVA to prepare freeze thaw PVA/carbon nanotube hydrogels [108]. Higher swelling ratio and ~94% increase in tensile strength were achieved for these hydrogels. PVA was blended with biopolymers such as chitosan, starch and gelatin to study the structure,
mechanical and swelling properties [109]. Chitin/PVA hydrogels were also prepared by freeze thaw drying which exhibited compressive strength as high as ~2.1MPa [110]. The improvements were purely due to the reinforcing effect of PVA on chitin resulted from formation of PVA and chitin crystallites. The improvement in mechanical properties was purely due to the presence of two physical networks in the case of PVA/biopolymer hydrogels. While in the case of PVA/nanomaterial hydrogels, the improvements were caused by the reinforcing effect of nanomaterials.

PVA hydrogels can be prepared using theta-gel method (physical crosslinks) or by radiation such as electron beam or γ-irradiation to induce chemical crosslinks. The theta-gel method involves using a polymer such as low molecular weight PEG to reduce the quality of solvent so that phase separation of PVA can take place. This method induces crystallization without the use of freeze thaw cycles. Radiation induced crosslinking is preferred in biomedical application due to the absence of cytotoxic agents. The minimum dosage needed for hydrogel synthesis depends largely on the molecular weight and PVA concentration in solution. [95].

2.9 Toughening Mechanism in Hydrogels

The above-mentioned hydrogels dissipate energy based on the network topology. Extensive works have been carried out for understanding the toughening mechanism in DN hydrogels. Due to this fact, the toughening mechanism in DN hydrogels have been used to draw parallels to the toughening phenomenon in a wide range of hydrogels. Henceforth, this section will provide insight on the role of first/second network structures and network interactions on the toughening mechanism in DN hydrogels.

2.9.1. Effect of the first network

As seen in DN hydrogels, the first network is highly crosslinked by the use of strong anionic monomers such as PAMPS and poly (3-sulfopropylacrylate potassium salt) (PSAPS). The first network has a large swelling ratio on immersion in aqueous solution containing the second neutral monomer and hence absorbs a large amount of the neutral monomer due to its ionic character. The first network becomes brittle and rigid after swelling and attributed to be the most important feature for effective
dissipation of energy. The type of the first monomer has been changed by using neutral polymers, weak polyelectrolytes, or physically linked polymers; PAMPS has been used predominantly among them.

There have been considerable interests in understanding the fracture dynamics of the first network upon deformation due to its relation to the mechanical strength of the DN hydrogels. This is due to the formation of large damage zones in the first network which further can accumulate more stress till macroscopic failure of the hydrogels [111-116]. Another critical point to consider based on the network structure for the origin of high mechanical strength in DN gels is the inhomogeneity of the first network. This was further verified by the use of various types of first networks. Kawauchi et al. introduced a large degree of heterogeneity into the PAMPS first network to prepare DN hydrogels [117]. The DN hydrogels showed high mechanical strength (tensile modulus of 0.1 ~ 0.5 MPa and tensile stress of 1MPa) with a larger necking region. Nakajima et al. showed that the addition of spherical voids in the first network increases the tearing energy two folds than that of DN gels without voids [118]. Spink et al. further verified the role of the first network by using PVP to create first network and poly(acrylic acid) to create the second network [119]. The crosslink density was manipulated by varying the first network monomer and the crosslinker concentration. They showed that the toughness increased by a factor of 150 with the increase in crosslink density, indicating the role of the first network on determining the overall toughness of the DN hydrogels. Wang and Hong used a quantitative mathematical model to predict the damage process in DN hydrogels[120]. Their model predicted significant energy dissipation (toughness) as a result of necking and the Mullins effect. Eshaghi et al. studied the necking phenomenon in semi-interpenetrating PSAPS–PAAm DN gels by varying the molecular weight [121]. They performed uniaxial tensile tests after the DN hydrogels were compressed to understand the influence of the first network. They predicted that the first network is essential for the onset of necking while molecular weight of the second network is important to attain sufficient entanglement for the propagation of necking. However, Gong et al. provided a contrasting theory to the viewpoint of heterogeneity of the first network as a criteria for high toughness [111]. They synthesized a homogenous first network (T-PEG) using tetra arm PEG with amine-terminated groups and ester-
terminated groups while PAAM served as the second network. They found similar mechanical strength for both conventional DN gels and the T-PEG/PAAM DN hydrogel, illustrating that inhomogeneity of the first network is not critical for high strength. However, the T-PEG/PAAM DN hydrogels showed varying yielding behaviour with different level of inhomogeneity.

2.9.2 Effect of network entanglement and interaction

The origin of high mechanical strength and toughness in DN has been studied based on the chain entanglement between the two networks [112]. Theoretically the polymer chain entanglement can be related to the “ratio of densities of elastically effective polymer chains of the two networks” \( \frac{\nu_{e,2}}{\nu_{e,1}} \), corresponding to the role of the second network and chain entanglement, the latter being the more prominent contributor. \( \frac{\nu_{e,2}}{\nu_{e,1}} \) is directly related to the ratio of the fracture stress ratio of the two networks \( \frac{\sigma_{f,2}}{\sigma_{f,1}} \). Thus when \( \frac{\nu_{e,2}}{\nu_{e,1}} \) is less than the value of \( \frac{\sigma_{f,2}}{\sigma_{f,1}} \) of 2.5-4.5, brittle fracture occurs since the fracture of the second network happens well before the first network fracture happens. When \( \frac{\nu_{e,2}}{\nu_{e,1}} > 4.5 \) \( \frac{\sigma_{f,2}}{\sigma_{f,1}} \), the DN hydrogels display high toughness. This is because propagation of initial fracture of first network leads to microcracks that are prevented by the second network. The ductile and soft second network transfers the force back to the first network. The polymer chain entanglement primarily determines the stress transfer dynamics between the ductile second network and the first brittle network. Another factor for consideration is the inter-network interactions. Depending on the type of network topology, the inter-network interaction could be between covalent or physical in nature. The inter-network interaction involves the molecular level interaction and associations between the networks. In order to understand the internetwork interactions on the mechanical properties, Gong et al. synthesized two different types of DN gels named as truly independent DN gel (t-gel) without any covalent crosslinker for the second network [122]. The t-gel did not have any covalent interaction with the first and second networks. The t-gel was mechanically stronger than the conventional DN gels when the second network had a crosslinker density of 0.01 mol%. Similarly, DN hydrogels synthesized using hyaluronan and poly(N,N-dimethylacrylamide) showed similar results when the second network was lightly crosslinked or non-crosslinked [48]. Grafting of polymer chains also
had effects on the mechanical properties as shown by Es-haghi et al [123]. They synthesized poly(3-sulfopropylacrylate)–polyacrylamide (PSAPS–PAAm) DN gels with varying graft content. The hydrogels with higher grafting content displayed enhanced toughness in comparison with gels with lower graft content. The literature does infer that internetwork interaction is important for achieving tough hydrogels.

2.9.4. Sacrificial bond concept

Sacrificial bond concept is the most widely reported mechanism for toughening in DN hydrogels [61, 124, 125]. Covalent and noncovalent approaches have been used widely in fabrication of tough hydrogels while one of the networks served as the sacrificial bonds to provide enhanced energy dissipation. The sacrificial bond theory involves specific yielding, necking and softening during hysteresis measurements as shown in Figure 2.8. The breaking of the first network leads to higher energy dissipation and irreversible stress softening during the hysteresis measurements. The necking region takes place after the yielding point that is symbolised by a flat and propagating plateau afterwards in the stress-strain plots. The appearance of yielding followed by necking generally indicates the fracture of the first network. A sharp decrease in the initial elastic modulus is experienced following the first loading unloading cycle.

Gong et al. was the pioneer in preparing DN hydrogels while proposing the concept that the first brittle network served as sacrificial bonds break into clusters to effectively dissipate energy [124]. They further proposed that the polymer chains break with varying chain length, wherein the shorter chains are prone to be the least strong junctions and fail by the applied stress to dissipate more energy. The concept of energy dissipation as a result of sacrificial bonds has been applied to various types of hydrogels such as lamellar bilayers [126], microgels [127, 128] and physical gels[41]. The mechanism was also applied to the case of elastomeric systems. Creton et al synthesized a triple network elastomeric system consisting of butane diol diacrylate crosslinked poly (ethyl acrylate) as the first network, PMMA served as the second and third networks [129]. The elastomers achieved elastic modulus of 4.2 MPa, tensile stress of 29 MPa, and tearing energy of 5000 J/m².
The concept of introducing sacrificing bonds into hydrogels and elastomeric systems have significant impact on the enhancing the toughness of these materials.

**Figure 2.8** (A) Hysteresis cycles for the first and second loading curve and the photographs representing necking in conventional DN hydrogels. (B) Schematic representation of network before and after necking in DN hydrogels [124].

**2.9.5 Brown–Tanaka model**
Brown and Tanaka proposed two independent models based on the occurrence of damage zone to understand the fracture behaviour occurring in DN hydrogels composed of a tightly crosslinked brittle first network and loosely crosslinked second network [130, 131]. The Brown-Tanaka model is based on a two-step crack propagation and the resulting failure. The first step involves the breakage of the first network and formation of a damage zone (soften zone) around the primary crack along with much lower elastic modulus which is largely from the loosely crosslinked second network. The second step involves the growth of the multiple cracks and formation of individual damage around the cracks in the second network. This further softens the materials and creates a large necking region with largely reduced initial elastic modulus. In this case, the energy required to rupture the strands and lead to crack propagation is equal to the elastic energy in that particular damage zone. They therefore introduced two mathematical parameters,
Δb and λm-1 to illustrate the crack initiation in the first network and the crack propagation which contains both strands from the first and second networks.

The presence of damage zones has been confirmed by optical and atomic force microscopy. Tanaka et al. investigated the Young’s modulus of the region below fracture surface immediately following fracture and around the molded surface using atomic force microscopy [132]. The approximate 10 times’ difference in elastic moduli corroborated the fact that yielding deformation occurred locally around the crack tip. Yu et al. visually observed the presence of damage zone around crack tips in conventional DN hydrogels by using a combination of optical microscope and a color3D violet laser scanning microscope (Figure 2.9 a,b,c) [133]. They showed that the damage zone around the crack is distinctly different from the rest of the regions. The results corroborate the Brown-Tanka model by showing the enlarged damage zone by the increased strain rate. The damage zone thickness increased from 150 to 700 μm when the strain rate increased from 0.1 to 500 mm·min⁻¹. These results indicate the presence of large damage zones for DN hydrogels possessing high toughness. Ultrathin DN hydrogel films were also analysed using phase contrast microscope around the crack tip region to understand the damage zone [134]. (Figure 2.9 d). They reported three distinct damage zones namely Y-zone, H-zone and P-zone. The Y-zone represents the yielding region characterised by a homogenous and well connected wrinkle-like structure occurring parallel to the direction of the applied stress. The H-Zone is correlated to the strain hardening region which is closer to the damage zone without any distinct structural features. However, the damage experienced in the H-zone is much more than that in the Y-zone. The thickness of both the H and Y-zone are much smaller.
than the damage zone. The P-zone acts as the pre-yielding region wherein the actual damage starts while the propagation takes place in the H and Y-zones.

Figure 2.9 (a) Schematic presentation of the different network structure in the damage zone and far away from the damage zone [124]; Observation of the damage zone by (b) conventional optical microscope [133], (c) color 3D violet laser scanning microscope [133] and (d) phase contrast microscope [134].

The Brown-Tanaka model claims to well address the origin of most of the mechanical properties in DN hydrogels. The model explains that the decrease in the second network crosslinking leads to enhanced toughness and lower elastic moduli. It also explains increasing first network inhomogeneity leads to higher crack density of the second network which directly relates to higher energy dissipation and toughness. The model also predicts a critical molecular weight for the second network to achieve high toughness in DN hydrogels. Although Brown-Tanaka model explains the fracture behaviour in conventional DN hydrogels, it cannot be applied to DN hydrogels with both physical and chemical crosslinks.

2.9.6 Internal fracture process
The internal fracture processes in DN hydrogels are different based on the network structure and network interactions. The internal fracture process is also different in chemically crosslinked DN hydrogels from DN hydrogels having both physical and
chemical crosslinks. Nakajima et al. studied the internal fracture process in conventional DN hydrogels consisting of PAMPS-PAAM chemically crosslinked network[116]. They proposed a two-stage internal fracture process wherein during application of low strains, the stress is borne by the connecting PAMPS chains and larger strain causes the chains to rupture preferentially. The PAMPS network undergoes a transition from continuous to a discontinuous phase until the chains cannot bear any further application of stress and the PAMPS forms clusters in the second network. The second stage involves the necking and hardening regions in the stress strain curve. During this stage, the applied stress is borne by the second network and transferred to the PAMPS clusters as a result of the strong chain entanglement. Figure 2.10 represents the pre-necking, necking and strain hardening regions with corresponding depictions of the internal fracture process. The analysis of the initial elastic modulus shows a clear decrease with the increase in strain and hence can be inferred that the elastically effective chains of the PAMPS network are ruptured into clusters with the increase in strain.

The presence of wrinkled morphology as evidenced in ultrathin DN hydrogels supports the conclusion of the first network breakage. More polymer chains broke and oriented along the stretching direction in the hardening region with the PAMPS clusters further broken into isotropic clusters as verified by the swelling anisotropy. The ratio of the hysteresis and work of extension \( \frac{U_{hys}}{W} \), illustrates the amount of irreversible work. The \( \frac{U_{hys}}{W} \) shows an increasing trend in the pre-necking region and almost remains constant after the yielding point which is inferred as the phase transition of the PAMPS network from continuous to discontinuous. Although similar results were obtained for chemically crosslinked DN gels, this is not the case for chemical – physical crosslinked DN hydrogels.

Dissimilarities were clearly seen in the case of Agar-PAAM DN hydrogels which consist of physically crosslinked Agar helix and chemically crosslinked PAAM network [53, 125]. The \( \frac{U_{hys}}{W} \) shows a gradual increase with the increase in strain, which is different from that shown for conventional DN hydrogels. Therefore no phase transition occurred in Agar-PAAM DN hydrogels, indicating different internal fracture behavior of these hydrogels. A chain-pull out mechanism was proposed to understand the internal fracture mechanism in Agar-PAAM DN hydrogels.
hydrogels. The Agar helical bundles are in an aggregated state and start to separate upon application of small strain, which is responsible for the decrease in initial elastic modulus and increase in the energy dissipation evidenced by hysteresis measurements.

![Figure 2.10](image)

**Figure 2.10** Schematic showing the internal fracture process in the pre-necking, necking and hardening regions [116].

This chain pull-out mechanism of the physically crosslinked Agar helix could happen throughout the entire tensile strain region of pre-necking, necking and hardening. An important point to note is the absence of chain scission in the first network due to the physical nature of the network contrary to the case of chemically
crosslinked network. This is also the case for many physical-chemically crosslinked DN gels although significant variation in the internal fracture mechanism is present depending on the type of physical polymer and its interaction with the chemical network. In the case of alginate PAAM physical-chemical hydrogel, the internal fracture mechanism is based on the unzipping of the alginate networks while the PAAM network bridges the crack [135]. A large hysteresis is obtained predominantly due to the unzipping of the alginate network chains. The toughening effect is a consequence of the unzipping and crack bridging of the two individual networks.

2.10 Summary
The review summarizes the structural design, mechanical properties and toughening mechanism of mechanically robust hydrogels. The key criterions for achieving mechanically strong hydrogels are the selection of polymers, network design and synthesis routes. There are two types of network design approaches that can be carried out, i.e. covalent bonded approach or physically bonded approach. The major types of physical bonding that can be inferred from the review are ionic bonding, hydrogen bonding and crystallites. The review clearly shows that the combination of different network types has a positive/synergistic effect on the mechanical properties.

The toughening mechanism in hydrogels has been systematically reviewed. The key factors such as first network brittleness, inhomogeneity, strong entanglement between the networks have been shown important for achieving robust hydrogels. The review illustrates dissimilarities in the toughening mechanism between purely chemically crosslinked and physical-chemically crosslinked hydrogels. A small section on hydrogen-bonded hydrogels has been presented to address its significance on enhancing mechanical properties.

2.11 Questions arising from the literature review
The preparation of mechanically strong hydrogels is increasingly becoming an area of considerable research interests in engineering and biomedical applications. The use of two polymers and varying network topology seem to play a vital role in
achieving mechanically strong and tough hydrogels. A majority of the work have been conducted on acrylamide-based polymers. Although they have shown very good mechanical properties, their broader applications have been hindered by higher cost, toxicity, complicated synthesis route/lengthy processing time and non-availability as commercial materials. Moreover, chemical crosslinkers are used mostly for achieving enhanced mechanical properties but are undesirable due to their toxicity. Consequently, it is of utmost importance to look for cost effective, commercially available and biocompatible materials with easier synthesis routes for achieving similar results.

Poly (vinyl alcohol) and epoxy-based materials are commercially available and widely used for load bearing applications. Both poly (vinyl alcohol) and polyethylene glycol diglycidyl ether type epoxy are biocompatible materials and hence are of interest in their application as hydrogels. Moreover, the reactive hydroxyl group of the PVA and the oxirane groups are well suited for various network interactions. The toughening mechanism in hydrogels vary based on the network structure, molecular interaction and association. The structure and morphology of the hydrogels play an important role in determining the mechanical properties of the hydrogels. Thus a systematic study which addresses the structure, morphology, toughening mechanism and compositional effects of a novel hydrogel system based on PVA and polyethylene glycol diglycidyl ether type epoxy would be particularly beneficial to the research of mechanically robust hydrogels.
2.11 References


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CHAPTER THREE

SYNTHESIS AND CHARACTERIZATION OF PVA/EPOXY DOUBLE NETWORK HYDROGELS

3.1 Introduction

Hydrogels can be chemically cross-linked such as double network hydrogels and macromolecular microsphere gels. They can also be physically cross-linked through heat treatment [1], phase separation using theta-solutions [2], freeze-thaw cycling [3] and by using cationic salts [4]. The polymerization of hydrophilic monomers in the presence of exfoliated clay leads to the development of nanocomposite hydrogels. Slide ring hydrogels have a linear polymer chain end-capped with bulky groups while cyclic molecules are threaded on linear polymer chain. Chemically cross-linked hydrogels such as double network gels have high mechanical strength but are weak under fatigue loading. Physically cross-linked gels have inherent low 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 [3, 5-10]. Three different phases exist in such hydrogels, namely “free water”, crystallized PVA aggregates and swollen amorphous PVA [11]. 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 method have shown enhanced mechanical properties [3]. Anisotropic PVA hydrogels have been prepared using directional freezing method, by applying oriented stress to the hydrogels during freeze thaw drying [12] or by the application of magnetic field [13]. 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 [14]. Chemically cross-linked PVA hydrogels have
been synthesized and characterized using glutaraldehyde [15, 16] and borates [17], however they are limitations in mechanical strength.

Freeze thaw hydrogels have been prepared by 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 [18-20]. Tong et al used carbon nanotubes with PVA to prepare freeze thaw PVA/carbon nanotube hydrogels [21]. Higher swelling ratio and 94% increase in tensile strength were achieved for these hydrogels. PVA was blended with biopolymers such as chitosan, starch and gelatin to study the structure, mechanical and swelling properties [22]. Chitin/PVA hydrogels were also prepared by freeze thaw drying which exhibited compressive strength as high as ~2.1MPa [23]. The improvements were purely due to the reinforcing effect of PVA on chitin as a result of the formation of PVA and chitin crystallites. The improvement in mechanical properties was primarily due to the presence of two physical networks in the case of PVA/biopolymer hydrogels. While in the case of PVA/nanomaterial hydrogels, the improvements were caused by the reinforcing effect of the nanomaterials. Nevertheless, 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 [24-26]. Epoxy hydrogels have been studied for their use in load bearing applications [27, 28]. Ionic-covalent entanglement was used to prepare sufficiently strong hydrogels. Carrageenan and gellan gum biopolymers were used to build ionic links using calcium ions and poly (ethylene glycol) diglycidyl ether (PEGDGE) with amine terminated polaxamer, served as covalent bonding in forming ICE hydrogels[27]. 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 cystamin acted as the branching [29].

In this chapter, 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 hours at -18°C and a thawing time of 20 hours at 25°C.
5 hours at room temperature. PEGDGE forms covalent and physical bonding with PVA macromolecules while PVA forms crystallite networks. These hydrogels exhibited enhanced mechanical properties and toughness.

3.2 Experimental

3.2.1 Materials and 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°C for 1 hour 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°C for 20 hours and then thawed for 5 hours 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.

3.2.2 Water content of the epoxy/PVA hydrogels
The water content of the hydrogels was measured by drying the hydrogels to a constant weight using a vacuum oven, i.e. Wd. 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.

3.2.3 Swelling ratio
The dried hydrogels (Wd) were placed in deionized water and the swollen weight (Ws) was recorded every 24 hours by removing the hydrogels and by gently blotting the excess water using a filter paper. The swelling ratio is expressed as:

\[
\text{Swelling ratio (\%)} = \frac{(W_s-W_d)}{W_d} \times 100
\]
3.2.4 Fourier transform infrared spectroscopy (FTIR)
Infrared spectrum was recorded using a Bruker FTIR spectrometer at a resolution of 4 cm\(^{-1}\). Data was collected over a wavelength of 400 – 4000 cm\(^{-1}\) with 64 scans. The hydrogels were dried in an air circulating oven at 40°C for 48 hours and later using a vacuum oven at 40°C for 48 hours before testing.

3.2.5 Differential scanning calorimetry (DSC)
The hydrogels were dried at 40°C for 48 hours in oven and then in vacuum oven at 40°C for 48 hours. DSC was performed using TA Instruments DSC Q200. The samples were heated from room temperature to 250°C at a heating rate of 10°C/min.

3.2.6 Mechanical characterization
Tensile, hysteresis and fracture energy characterizations were performed on a 30KN Instron mechanical tester (Instron 5567, USA) with a load cell of 100N on as-prepared hydrogels. The as-prepared hydrogels were subjected to mechanical characterization within 24 hours of preparation. They were kept sealed in a plastic bag to prevent loss of water. Dumbbell shaped gel specimens with width of 4 mm, gauge length of 20 mm and thickness of 3 mm were used for tensile tests. Tensile tests were performed at a cross-head speed of 40 mm·min\(^{-1}\).

Tensile hysteresis measurements were conducted using a crosshead speed of 40 mm·min\(^{-1}\). Two different hysteresis measurements were carried out. The first type of hysteresis measurements involved subjecting the samples to a fixed strain (100%) and then unloading to zero strain within 5 min. Five loading-unloading cycles were carried out and their hysteresis \(U_{\text{hist}}\) was calculated using the following equation

\[
U_{\text{hist}} = \int \sigma \, d\varepsilon \text{ (loading)} - \int \sigma \, d\varepsilon \text{ (unloading)} \tag{3.1}
\]

where \(\sigma\) and \(\varepsilon\) are the tensile stress and strain respectively.

The second type of hysteresis measurements involved subjecting the samples to certain strain and then unloading to zero strain within 30 seconds. The fracture energy was calculated using trouser tear specimens with the length of 50 mm, the
width of 14 mm, the thickness of 5 mm and the tear length of 20 mm. Measurements were conducted at a constant crosshead speed of 40 mm·min\(^{-1}\). The fracture energy \(G\), defined as the energy required for creating a unit area of fracture surface in a sample, was calculated by the following equation [30, 31]

\[
G = \frac{2F_{\text{ave}}}{w}
\]  \hspace{1cm} \text{(3.2)}

where \(F_{\text{ave}}\) is the average force required for crack propagation and \(w\) is the width of the specimen.

Compressive testing was carried out on as-prepared hydrogels at 25°C using a 30 kN Instron with a load cell of 1 kN. Hydrogel samples with diameter of 15 mm and height of 14 mm were used for testing. Compression tests were conducted at a strain rate of 3 mm·min\(^{-1}\) till a strain of 80%.

### 3.3 Results and Discussion

Scheme 3.1 shows the freeze thaw methodology for the preparation of PVA/epoxy hydrogels. PEGDGE was added to 15 wt% PVA solution under agitation at 95°C for 1 hour. This initiates the ring opening reaction between diepoxides and hydroxyl groups. The homogenous viscous solution was poured into suitable moulds and underwent three freezing and drying cycles for 20 hours and 5 hours respectively. The freezing cycle involves the phase separation of PVA from water due to the freezing of water. The phase-separated PVA forms regions of high concentration and gather together creating crystallites and hydrogen bonding to create physical cross-links in the hydrogels. During the thawing cycles, post curing of the epoxy network takes place resulting in the increase in brittle chemical network in the hydrogels. These hydrogels can be knotted, stretched under knotting and can be easily formed into intricate and complex shapes as shown in Scheme 3.1.

The prepared hydrogels are different from the double network and ionic/covalent network since crystallites and covalent networks are used to form the hydrogels. The networks grow simultaneously with every freezing and thawing cycle and
hence are different from conventional double network hydrogels where the networks are prepared sequentially.

Scheme 3.1 Schematic illustration of the synthesis and crosslinking mechanism in PVA/epoxy hydrogels. (A) Structure of chemicals used. (B) Schematic illustration of interaction between PVA and PEGDGE on solution mixing at 95°C. (C) Chemical reaction of epoxy with PVA (R represent (CH-CH₂) repeat units). (D) Schematic illustration of covalent crystallite networks.
3.3.1. Chemical cross-linking mechanism

It is well known that the freeze thaw method induces physical crystallite networks in PVA. Therefore, to understand the chemical crosslinking reaction, ATR-FTIR was performed on the hydrogels as shown in Figure 3.1. Dried hydrogels were used in order to effectively characterize the chemical groups which would be difficult in as-prepared hydrogels due to large water content. Three peaks were observed at 914, 847 and 754 cm\(^{-1}\) in the virgin PEGDGE corresponding to the oxirane groups (Figure 3.1a). In hydrogels with 4wt% epoxy, the peaks at 914 and 754 cm\(^{-1}\) disappear while the peak at 847 cm\(^{-1}\) appears weaker and broader due to the rupture of the epoxide (oxirane) ring indicating crosslinking between hydroxyl groups and the epoxy. Similarly, in hydrogels with 10 wt% epoxy, the peak at 914 cm\(^{-1}\) disappears while a weak peak is present at 754 cm\(^{-1}\) indicating ring opening of the epoxide groups and crosslinking. It is clear that no prominent absorbance peak is present for the PEGDGE in the region between 3000-3700 cm\(^{-1}\) (Figure 3.1b). The crosslinking reaction is further confirmed by the broad absorbance band between 3000 and 3700 cm\(^{-1}\) indicating the presence of OH groups due to the crosslinking reaction. PVA shows a broad absorbance peak at 3287 cm\(^{-1}\) due to strong intra- and intermolecular hydrogen bonding. The PVA/epoxy hydrogels show peak shifts towards higher frequency due to crosslinking and hydrogen bonding interactions. The strong absorption band at 2866 cm\(^{-1}\) is attributed to the stretching vibrations of CH\(_2\) groups of PEGDGE.

Apparent viscosity measurements were conducted immediately after 1-hour reaction time (Figure 3.1c). The PVA solution exhibited typical non-Newtonian shear thinning behavior while PVA/epoxy mixtures showed shear thickening followed by nearly constant viscosity profile. PVA crosslinked by hydrogen bonding exhibits a shear thinning regime [32] while the PVA/epoxy solution showed shear thickening indicating chemical crosslinking. Further increase in the apparent viscosity of the PVA/epoxy solution compared to the PVA solution suggests crosslinking. PEGDGE solutions cannot be measured using parallel plates due to extremely low viscosity even at high concentration of 10 wt%.
The tensile strength was measured after each freeze-thaw cycle as shown in Figure 3.2 to understand the post cure of epoxy. The tensile stress for PVA hydrogels after the first freeze-thaw cycle could not be measured due to the brittle nature of the samples. However, PVA/epoxy hydrogels showed higher tensile strength than PVA hydrogels during all cycles. PVA/epoxy hydrogels with 10 wt% epoxy showed higher mechanical strength than hydrogels with 4 wt% epoxy for the first cycle. The second freeze-thaw cycle showed a higher increase in tensile strength for PVA/epoxy hydrogels, however PVA/epoxy hydrogels with 4 wt% showed higher tensile strength than hydrogels containing 10 wt% epoxy. This indicates that higher crosslinking of epoxy enhances tensile strength in the first cycle, however further increase in freeze-thaw cycles induces brittleness leading to lower tensile strength in hydrogels containing 10 wt% epoxy. Combining FTIR, rheological and mechanical measurements, it is clear that crosslinking between epoxy and PVA took place. Therefore, the hydrogels are formed by a combination of physical crystallite networks, chemical covalent networks and hydrogen bonding interactions.
Figure 3.1 (a) and (b) are FTIR spectra of PVA/epoxy hydrogels and PEGDGE. (c) shows the apparent viscosity for PVA and PVA/epoxy hydrogels.
3.3.2 Water content and swelling ratio

The water content and swelling ratio of PVA and PVA/epoxy hydrogels are shown in Figure 3.3. The water content decreases as expected due to the increase in the epoxy content. The swelling ratio increases with the increase in the epoxy content. It is expected that epoxy is crosslinked by hydroxyl groups of PVA, resulting in a decrease in crystallite formation. A decrease in crystallite formation however enhances the free volume for water uptake. The swelling ratio increases sharply till 4 wt% addition of epoxy and then stabilizes. This is probably caused by the growing and then stabilized crosslinked network as a result of the increase in crosslink density by the formation of covalent bonds between the epoxy and hydroxyl groups of PVA and the physical interaction such as hydrogen bonding.

Figure 3.2 Variation of tensile stress as a function of freeze thaw cycles.
3.3.3 Mechanical properties

The mechanical properties of PVA and PVA/epoxy hydrogels are shown in Figures 3.4 and 3.5. The PVA hydrogels showed ~ 0.3 MPa of stress and 310 % of strain at breaking point. The epoxy/PVA hydrogels with 4 wt% epoxy showed the highest elongation strength (~1.1 MPa) and elongation strain (600%). The reported tensile
strength is comparable to that of double network hydrogels [33], however DN gels possess a much higher elongation at break characterized by a large necking region. The addition of epoxy improved the tensile strength and elongation at break in comparison with PVA. However, the maximum increase was attained with 4 wt% epoxy addition while further addition of epoxy decreased both the strength and elongation at break. All the PVA/epoxy hydrogels showed higher tensile strength and elongation at break in comparison to pure PVA.

The tensile loading curves display “J” shaped stress-strain curves which are analogous to those reported for biomaterials (Figure 2a). Such curves represent two linear regions, a slow rate of increase in stress with strain linearly in the first region (zone I) followed by a much faster rate to a second linear range (strain hardening) until fracture (zone II). The work of extension, a measure of the toughness of the hydrogel and the elastic moduli (E) of the hydrogels are shown in Figure 2c. The reported E values have been taken from the second linear region. The hydrogels with 4 wt% epoxy content illustrated the maximum toughness and modulus of ~2838 kJ/m$^3$ and 126 kPa respectively. The maximum toughness increased by 575% while the modulus increased by six times in comparison with PVA.

PVA hydrogels consist of both crystalline and amorphous regions which can be referred as hard and soft regions. The PVA hydrogels are comparable to that of thermoplastic polyurethanes, due to the simultaneous presence of hard and soft regions in both cases. The soft regions sustain the applied force by the movement of the flexible polymer chains during the initial strain. This causes a slow rate of increase in strain, while further increase in strain causes the soft regions to fully expand and hence the applied force is mainly sustained by the hard segment, i.e. the crystalline region, which is seen as a rapid increase in stress.

By comparison, PVA/epoxy hydrogels have three components consisting of crystalline, amorphous and crosslinked regions. The soft regions (amorphous) sustain the applied force and fully expand at low strain. While with further increase in strain, the applied force is sustained mainly by the crosslinked network. The crosslinked network ruptures with additional strain bringing the hard segments (crystallite) into work which causes a linear increase in stress with strain.
Figure 3.4 (a) Typical tensile stress strain curve for PVA and PVA/epoxy (4 wt%) hydrogels (b) Tensile strength and tensile strain of PVA/epoxy hydrogels and (c) Toughness and elastic modulus of PVA/epoxy hydrogels with different epoxy contents. The PVA content was fixed at 15 wt%.

The compressive strength of hydrogels is essential mechanical property in load-bearing applications. PVA/epoxy hydrogels cannot be broken and hence the samples were subjected to a compressive strain of 80% at a crosshead speed of 3 mm·min\(^{-1}\). Figure 3.5 shows the compressive strength of PVA/epoxy hydrogels with varying epoxy content. With the addition of epoxy, the compressive strength of the hydrogels was improved. It is worth noting that the hydrogels with 6 wt% epoxy displayed a maximum compressive strength of ~3.7 MPa that is much higher than PVA hydrogels as a result of the effective crosslinking reaction between epoxy and PVA. The compressive strength can be further increased by means of reducing the water content and increasing the freeze–thaw cycles.

![Compressive strength of PVA/epoxy hydrogels at a compressive strain of 80%](image)

Figure 3.5 Compressive strength of PVA/epoxy hydrogels at a compressive strain of 80%.
Since the degree of crystallinity and the interactions between the chains of PVA and epoxy are the major factors which affect the mechanical properties of the hydrogels, DSC and SAXS were used to study the influence of epoxy upon the crystallization of PVA and its internal structure respectively. The DSC scans were carried out on dried hydrogels over as-prepared hydrogels to avoid the influence of the water content. The first DSC heating scan of PVA and PVA/epoxy (4 wt %) hydrogels display significant changes in thermal transitions (Figure 3.6). Table 3.1 presents the thermal data for the studied hydrogels. Crystallinity was obtained using the following equation

$$\chi_c (%) = (\Delta H_m / 150) \times 100$$

(3)

where $\Delta H_m$ is the heat of melting (J/g) and 150 (J/g) represents the heat of melting of a 100% crystalline PVA sample [6].

A depression in crystallinity is clearly observed as expected, due to the increase in crosslinking with the increase in the epoxy content. This is also believed to be due to the fact that the crystallinity of poly (ethylene glycol) (PEG) is hindered by epoxy groups and it has been shown to have no crystallinity when PEGDGE is cured [34]. Hence we can assume that only PVA is responsible for the formation of physical network, i.e. crystallite formation. This is contrary to the case when PEG and PVA are blended together [35]. The melting temperature ($T_m$) of PVA/epoxy hydrogels is much lower in comparison with PVA hydrogels. The $T_m$ of pure PVA is 229°C while PVA/epoxy with an epoxy loading of 10 wt% has a $T_m$ of 220 °C. This is understood due to the thermosetting nature of the epoxy crosslinks.
Figure 3.6 First heating DSC curves for a pure PVA hydrogel and PVA/epoxy hydrogel (4 wt%).

Table 3.1 DSC data of PVA and PVA/epoxy hydrogels

<table>
<thead>
<tr>
<th>Epoxy content in PVA (wt %)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$\chi_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>228</td>
<td>86.05</td>
<td>57.36</td>
</tr>
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<td>224</td>
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</tr>
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</tr>
<tr>
<td>10</td>
<td>220</td>
<td>46.28</td>
<td>30.85</td>
</tr>
</tbody>
</table>

3.3.4 Fracture energy

The fracture energies (G) of the PVA/epoxy hydrogels were measured by trouser-tear tests (Figure 3.7). All the hydrogels showed similar behaviour, i.e. the notch could not propagate and the fracture occurred in one arm of the specimen. Such load-displacement curves (Figure 3.7a) are typical of PVA hydrogels with isotropic mechanical properties[36]. It is surprising to note that the specimens with epoxy loading of 2 wt% have the maximum fracture toughness and the toughness...
drops sharply with increasing epoxy content after 2 wt%. We believe that the fracture energy and crystallinity of the hydrogels are closely related. Brittle characteristics are attributed to the epoxy network and hence a higher content of epoxy leads to macroscopic crack propagation which causes failure at low fracture energies. While crystallites act as knots interconnected partly by amorphous swollen PVA chains[10] leading to higher resistance to crack propagation. Hydrogels with epoxy loading of 2 wt% have the highest crystallinity among PVA/epoxy hydrogels and this could be a possible reason for achieving the highest fracture energy. However, the fracture energy of the PVA/epoxy hydrogels (160 – 450 J/m²) are much higher than conventional synthetic hydrogels and similar to or less than double network gels[37].
Figure 3.7 (a) Force displacement curves of the PVA/epoxy hydrogel with 4 wt% epoxy. (b) Fracture toughness of PVA/epoxy hydrogels with different epoxy contents.

3.3.5 Hysteresis measurements

A cyclic loading–unloading tensile test is a simple way to understand structural transitions occurring in hydrogels. Figure 3.8 shows the typical loading-unloading curves for hydrogels subjected to 5 cycles with a maximum strain of 100%. PVA and PVA/epoxy with 4 wt% and 10 wt% loading of epoxy were subjected to hysteresis measurement and the results are shown in Figure 3.8a, 3.8b and 3.8c, respectively. A single sample was subjected to 5 cycles with a time of 5 minutes between loading and unloading cycle for each type of the hydrogels. The calculated hysteresis ($U_{hyst}$) for the hydrogels are shown in Figure 3.8d.

In Figure 3.8(a-c), all the hydrogels display hysteresis loop for all the cycles. All the hydrogels show significant hysteresis in the first loading–unloading cycle, and the hysteresis is almost negligible in the remaining cycles. The third loading cycle closely follows the path of the first unloading cycle and this can be observed for all the cycles. This phenomenon can be related to the Mullins effect seen in filled rubbers, pure crystallizing gums and double network hydrogels. We predict that the origin of Mullins effect in PVA hydrogels and PVA/epoxy hydrogels are contrasting in nature. Wang et al attributed the Mullins effect in PVA hydrogels to
the breakage of crystalline regions[36] while Creton et al ascribed the Mullins effect in double network hydrogels to the breakage of first covalent network[38].

We suggest that the amorphous regions in PVA hydrogels sustain the initial strain which can be approximated within a strain of 100%. This can be predicted by the change in the slope of tensile stress – strain curve (Figure 3.4a). Thus the first cycle hysteresis obtained in pure PVA hydrogels can be assumed to be mainly from the uncoiling of the amorphous chain. The amorphous chain becomes fully extended and does not return to its uncoiled state and hence the hydrogels do not recover in further cycles displaying stress softening. However, in the case of PVA/epoxy hydrogels, a hysteresis of the order of 10 times of that of PVA hydrogels are obtained (Figure 3.8d). This indicates a major structural transition leading to higher energy release, which could be explained by the breakage of covalent bonds during the first loading cycle that creates a permanent irrecoverable damage seen as stress softening in further cycles. The fact is corroborated by a larger hysteresis seen for 10 wt% epoxy loading in comparison with 4 wt% epoxy loading, suggesting that more covalent bonds are ruptured when the epoxy content is increased.
(a) 0 wt%

(b) 4 wt%
Figure 3.8 Cyclic tensile loading-unloading tests for PVA/epoxy with varying epoxy content to 100% strain subjected to 5 cycles. (a) Loading-unloading curves for PVA hydrogels for 1, 3 and 5 cycles; (b) loading-unloading curves for PVA/epoxy hydrogels with 4 wt% epoxy content for 1, 3 and 5 cycles; (c) loading-unloading curves for PVA/epoxy hydrogels with 10 wt% epoxy content for 1, 3 and 5 cycles and (d) the calculated hysteresis ($U_{hist}$) for the run cycles.

The hydrogels were also subjected to loading-unloading cycles with increasing strain as shown in Figure 3.9(a-c). The calculated hysteresis ($U_{hist}$) for the hydrogels are shown in Figure 3.9d. When a specimen is cyclically stretched to a higher maximum strain, Mullins softening and hysteresis become more
pronounced. It can be clearly seen that higher percentage of epoxy leads to higher hysteresis. The yielding behaviour of the PVA/epoxy hydrogels is also different from the PVA hydrogels. The first occurrence of yielding-like behaviour for PVA hydrogels starts at a strain ($\varepsilon_y$) of ~125% while PVA/epoxy hydrogels show similar behaviour at ~80% and 65% for 4 wt% and 10 wt% epoxy loading respectively. This suggests different structural transition occurring in the hydrogels. The hysteresis in the PVA hydrogels is mainly contributed from the amorphous regions before yielding while the crystalline regions contribute to the hysteresis after yielding. In the case of 4 wt% PVA/epoxy hydrogels, the amorphous regions sustain the initial load at very small strain due to low amounts of amorphous regions. The breaking of the brittle covalent epoxy network and crystallites contributes to the hysteresis occurring in these hydrogels. In the case of 10 wt% PVA/epoxy hydrogels, the breaking of the brittle covalent epoxy network contributes to the hysteresis at low strain since the PVA macromolecules are either available as crystallites or as cross-linked networks. The PVA crystallites occurring in low numbers fail at a lower stress and strain. However, based on the fact that significant decrease in crystallinity is observed in 10 wt% PVA/epoxy hydrogels, we propose that the increase in hysteresis could be predominantly due to the breakage of covalent bonds. A right balance between epoxy content and crystallite distribution is achieved at 4 wt% loading for efficient load transfer leading to high strength and toughness. Therefore, the epoxy networks can act as sacrificial bonds leading to higher strength and strain at break.

![Graph showing tensile stress vs strain for different PVA/epoxy hydrogel compositions](image-url)
Figure 3.9 Cyclic loading-unloading tests to increasing strain for PVA/epoxy hydrogels (unloading curves not shown). (a) Loading curves for PVA hydrogels with increasing strain; (b) loading curves for PVA/epoxy hydrogels with 4 wt% epoxy content with increasing strain; (c) loading curves for PVA/epoxy hydrogels with 10 wt% epoxy content with increasing strain and (d) the calculated hysteresis ($U_{hist}$) for varying strain ($\varepsilon_{max}$).

3.4 Conclusions

PVA/epoxy hydrogels were prepared using solution mixing and freeze thaw method. The PVA/epoxy hydrogels exhibit significant increase in tensile strength, strain at break and compressive strength compared to pure PVA hydrogel. A 266% increase in tensile strength and 36% increase in compressive strength were seen with incorporation of 4 wt% epoxy to PVA. The fractal dimension and radius of gyration of the hydrogels were calculated from SAXS profiles and the results showed a dramatic change in the morphology with addition of epoxy. The excellent mechanical properties and ease of processing PVA/epoxy hydrogels make them excellent candidates for load-bearing engineering applications.
3.5 References


CHAPTER FOUR
STRUCTURE AND MORPHOLOGY OF PVA/EPOXY HYDROGELS

4.1 Introduction
Swelling is one of the main characteristics of a hydrogel. It is the mainly caused by the polymer matrix’s limited solubility due to the occurrence of crosslinks, solvent type and the physical structure[1]. The major contributor is the crosslinker without which the polymer will dissolve in the solvent. The effective/overall crosslink density in a hydrogel takes into account both chemical and physical crosslinks including chain entanglements, loose chains and tie chains [2]. The nature of crosslinks and effective crosslink density play a major role in determining the physical and mechanical properties of the hydrogel. It is challenging to accurately determine the effective crosslinking density using conventional methods such as dynamic mechanical analysis due to the solvent evaporation during testing[3]. The most commonly used method is to use swelling ratio to determine the crosslink density[4, 5]. The well-known Flory Rehner theory predicts the crosslink density of three dimensional networks consisting of randomly coiled chains from equilibrium swelling ratios. Another method is to use dynamic rheology to determine the crosslink density based on rubber elasticity theory at small shear values[6, 7]. Mechanical testing can also provide information regarding the crosslink density using the Mooney Rivlin model[8].

The structure and morphology of the hydrogels can be predicted using scattering studies and electron microscopy. This chapter studies the structure and morphology of PVA/epoxy hydrogels using the crosslink density, fractal information obtained from SAXS and topography obtained from scanning electron microscopy.
4.2 Experimental

4.2.1 Materials and 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°C for 1 hour to initiate the ring opening reaction of the oxirane group. The solution was then transferred to a Teflon mould for the preparation of tensile samples. The mould was kept at -18°C for 20 hours and then thawed for 5 hours 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. These hydrogels are called as-prepared hydrogels while the hydrogels immersed in deionized water till constant weight are called fully swollen hydrogels.

4.2.2 Small angle X-ray scattering (SAXS)

SAXS experiments were conducted on the small angle X-ray scattering beamline utilizing an undulator source at the Australian Synchrotron. The intensity profiles were interpreted as a double logarithmic plot of scattering intensity (I) versus scattering vector, q = (4/λ) sin(θ/2) (θ = scattering angle, the wavelength λ was 0.062 nm). SAXS experiments were carried out on as-prepared hydrogels within 24 hours of sample preparation.

4.2.3 Scanning electron microscopy (SEM)

The hydrogel samples were frozen in liquid nitrogen and cut to obtain cross-sections. The frozen sections were dried using a Labconco freeze dryer. The lyophilised samples were gold coated with a Baltech sputter coater. A Zeiss supra scanning electron microscope operating at 5KV was used for imaging.

4.2.4 Rheological measurements

The PVA and PVA/epoxy hydrogels were characterized using a stress controlled rheometer (TA Instruments, HR -3). Initial amplitude sweeps were conducted to ascertain the linear viscoelastic region (LVR) and all further measurements were conducted well within the LVR. Frequency sweeps of the hydrogels were
conducted with a strain of 1%. The rheological measurements were conducted on both as-prepared and fully swollen hydrogels within 24 hours of sample preparation.

4.3 Results and Discussion

4.3.1. Structure parameters based on the Flory-Rehner theory

The Flory-Rehner equation is derived from three dimensional networks of randomly coiled chains, and is based on the equilibrium swelling of polymer in solvent [9-14]. The Flory-Rehner equation is given as:

\[- \ln \left(1 - v_p\right) + v_p + \chi v_p^2 \right] = NV_s \left[v_p^{\frac{1}{3}} - \frac{v_p}{2}\right] \tag{4.1}\]

where \(v_p\) represents the polymer volume fraction, \(\chi\) is the interaction parameter, \(V_s\) represents the molar volume of the solvent (1.8 x 10^{-5} m^3) and \(N\) represents the crosslinking density.

The interaction parameter can be found experimentally based on the following equation[15]

\[\chi = \frac{1}{2} + \frac{v_p}{3} \tag{4.2}\]

The mesh size and the molecular weight between crosslinks can be obtained using equations 4.3 and 4.4

\[\xi = v_p^{-\frac{1}{3}} \left[ C_n \left(\frac{2M_c}{M_r}\right) \right]^{\frac{1}{2}} l \tag{4.3}\]

where \(C_n\) is the characteristic flory ratio (8.3) for PVA[16], \(M_r\) represents the average molecular weight of the repeat units (PVA = 44, PEGDGE = 174), \(l\) is the carbon-carbon bond length (1.54Å) and \(M_c\) represents the average molecular weight between crosslinks. \(M_c\) has an inverse relationship with the crosslinking density \(N\) of the hydrogels as shown below:

\[N = \frac{1}{vM_c} \tag{4.4}\]
where \( \nu \) represents the specific volume of bulk polymer in the amorphous state (0.788 cm\(^3\)/g).

Figures 4.1 and 4.2 show the calculated crosslink density, molecular weight between crosslinks and the mesh size for both as-prepared and fully swollen PVA and PVA/epoxy hydrogels. Table 4.1 lists the parameters such as polymer density, polymer volume fraction and water content used in this study to calculate the above mentioned hydrogel internal structure parameters.

Table 4.1 Parameters used for calculating the crosslink density, molecular weight between crosslinks and mesh size for as-prepared and fully swollen hydrogels.

<table>
<thead>
<tr>
<th>Epoxy content (wt%)</th>
<th>Water content (wt%)\textsuperscript{a}</th>
<th>Water content (wt%)\textsuperscript{b}</th>
<th>Polymer volume fraction ((\nu_p)\textsuperscript{a})</th>
<th>Polymer volume fraction ((\nu_p)\textsuperscript{b})</th>
<th>(\chi)</th>
<th>Polymer density ((\rho_p)) (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>99.92</td>
<td>85.34</td>
<td>0.062</td>
<td>0.119</td>
<td>0.52</td>
<td>1.269</td>
</tr>
<tr>
<td>2</td>
<td>99.94</td>
<td>84.35</td>
<td>0.052</td>
<td>0.129</td>
<td>0.517</td>
<td>1.254</td>
</tr>
<tr>
<td>4</td>
<td>99.93</td>
<td>79.85</td>
<td>0.058</td>
<td>0.167</td>
<td>0.519</td>
<td>1.242</td>
</tr>
<tr>
<td>6</td>
<td>99.92</td>
<td>77.96</td>
<td>0.062</td>
<td>0.186</td>
<td>0.52</td>
<td>1.232</td>
</tr>
<tr>
<td>8</td>
<td>99.92</td>
<td>75.1</td>
<td>0.068</td>
<td>0.212</td>
<td>0.522</td>
<td>1.224</td>
</tr>
<tr>
<td>10</td>
<td>99.92</td>
<td>73.41</td>
<td>0.07</td>
<td>0.228</td>
<td>0.523</td>
<td>1.217</td>
</tr>
</tbody>
</table>

\textsuperscript{a} fully swollen hydrogel, \(\textsuperscript{b}\) as-prepared hydrogel. The volume fraction \((\nu_p)\) was calculated using the following equation: \(\nu_p = \frac{\rho_s}{\rho_s + \rho_p (q_w - 1)}\) where \(\rho_s\) is 0.998 g/cm\(^3\) and \(q_w\) is the weight fraction of polymer in the hydrogel.
Figures 4.1 and 4.2 show an increase in $N$ and a corresponding decrease in both the $M_c$ and $\xi$. Although this is more pronounced for as-prepared hydrogels than the fully swollen hydrogels. It is largely due to the huge difference in the swelling ratios. The increasing $N$ is predominantly due to the crosslinking reaction and hydrogen bonding interaction between PVA and epoxy. The obtained mesh size
decreases significantly with the increase in epoxy content corroborating the results from Chapter three which displayed lower crystallinity from DSC. Epoxy crosslinking produces a more homogenous structure indicated by the decrease in $\xi$. This also confirms the observation in Chapter three that the crosslink density increases with an increase in epoxy content leading to a brittle network. Thus it is concluded that an increase in crosslink density above ~ 150 mol/m$^3$ leads to a fall in the tensile stress (4 wt% epoxy addition showed a maximum tensile stress of 1.1 MPa and tensile strain of 600%).

4.3.2. Structure parameters based on the Mooney-Rivlin Theory

The large strain deformation in hydrogels is strongly dependent on the crosslinking properties and can be expressed by the Mooney-Rivlin equation[10, 17-21]. The Mooney-Rivlin equation was initially proposed for ideal rubber networks and can be extended to hydrogel due to their similarity. The Mooney-Rivlin equation has been used in the case of our hydrogel system since it works well for extension ratios below 10. The Mooney Rivlin equation based on volume fraction of polymer is shown in equation 4.5

$$\frac{\sigma_e v_p^\frac{1}{3}}{(\lambda - \frac{1}{\lambda^2})} = 2C_1 + 2C_2 \quad (4.5)$$

where $\sigma_e$ represents the measured tensile stress, $v_p$ represents the polymer volume fraction and $\lambda$ represents the extension ratio. The values of $C_1$ and $C_2$ can be obtained by fitting or plotting $\frac{\sigma_e v_p^\frac{1}{3}}{(\lambda - \frac{1}{\lambda^2})}$ against $\frac{1}{\lambda}$ which yields a straight line with the slope representing $C_2$ and the intercept $C_1$.

The molecular weight between crosslink and the crosslink density can be obtained using equation 4.6 and 4.7.

$$\frac{\rho RT}{M_c} = 2C_1 + 2C_2 \quad (4.6)$$
\[ N = \frac{2C_1}{kT} \]  

(4.7)

where \( \rho \) represents the density of the equilibrium swollen hydrogel, \( R \) is the gas constant (8.314 J/mol K\(^{-1}\)) and \( k \) is the Boltzmann constant (1.38 x 10\(^{-23}\) J/K),

It was not possible to perform tensile tests accurately on fully swollen hydrogels especially on PVA hydrogel due to its extremely fragile nature. This is also the case for many fully swollen hydrogel systems which have a fragile nature. Hence the interaction parameter (\( \chi \)) and the Flory Huggins theory were used to obtain the Mooney Rivlin parameters for fully swollen hydrogels. The interaction parameter, a unitless parameter provides information regarding the solubility of the polymer in a solvent. Thermodynamically, the Gibbs free energy of mixing can be induced by the volume fraction of the polymer and the interaction parameter by the Flory Huggins theory as follows:

\[ \Delta G = RT \left[ \ln(1 - v_p) + v_p + \chi v_p^2 \right] \]  

(4.8)

However, it is necessary to take into account the configurational entropy due to the water content for highly crosslinked systems such as hydrogels. The free energy in hydrogels contributes to the free energy of dilution of the uncrosslinked polymer and the free energy term from the elastic expansion of the Gaussian network

\[ (\Delta G_e = \frac{\rho RT}{M_c} V_S v_p^{\frac{1}{3}}) \]

Thereby, the overall free energy can be obtained by adding both the free energy based on the Flory-Huggins and the Gaussian configurational entropy,

\[ \Delta G = RT \left[ \ln(1 - v_p) + v_p + \chi v_p^2 + \frac{\rho V_S}{M_c} v_p^{\frac{1}{3}} \right] \]  

(4.9)

At equilibrium, \( \Delta G \to 0 \) so Equation 4.9 can be represented as

\[ \ln(1 - v_p) + v_p + \chi v_p^2 + \frac{\rho V_S}{M_c} v_p^{\frac{1}{3}} = 0 \]  

(4.10)
The following relationship is obtained for the interaction parameter as a function of \( C_1 \)

\[
\chi = -\frac{\ln(1-v_p)}{v_p^2} - \frac{1}{v_p} - \left( \frac{2C_1 V_S}{RT} \right) v_p^{\frac{5}{3}}
\]  

(4.11)

The values of \( C_1 \) can also be obtained by using the modified Flory Huggins equation as shown in Equation 4.12.

\[
\chi = -\frac{\ln(1-v_p)}{v_p^2} - \frac{1}{v_p} - \left( \frac{2C_1 V_S}{RT} \right) \left( v_p^{\frac{5}{3}} - \frac{1}{2v_p} \right)
\]  

(4.12)

The \( C_1 \) values obtained for PVA and PVA/epoxy hydrogels are shown in Table 4.2. Figure 4.3 and 4.4 show the obtained crosslink density, molecular weight between crosslinks and the mesh size for as-prepared and swollen hydrogels. The \( C_2 \) value was taken as zero since it has been shown that hydrogel systems with volume fraction close to or less than 0.2 have a \( C_2 \) value of zero. Although the obtained results are comparable to that obtained from swelling ratios, difference is found for the 2 wt% epoxy loading. The crosslink density decreases slightly when calculated based on \( C_1 \) values. This could be due to the decrease in crystallites and small amount of crosslinking with 2wt% addition. With further epoxy addition, a higher degree of interaction is realized between PVA and epoxy and hence leads to an increase in the crosslink density. Correspondingly, the \( M_c \) values are the highest for 2 wt% epoxy loading and drop sharply on further increment in the epoxy content. Similar results were found for small angle X-ray measurements (Figure 4.9) which showed a stark difference in the fractal values for 2 wt% epoxy loading, indicative of a sudden morphological change. Moreover, both versions of the Flory Huggins theory gave comparable results despite of the dissimilar \( C_1 \) values for the 8 wt% and 10 wt% epoxy content.
Figure 4.3 Crosslink density, molecular weight between crosslinks and mesh size for as-prepared PVA and PVA/epoxy hydrogels using calculated C1 values.

Figure 4.4 Crosslink density, molecular weight between crosslinks and mesh size for fully swollen PVA and PVA/epoxy hydrogels using calculated C1 values.

4.3.3. Structure parameters based on experimental tensile tests

The Mooney-Rivlin parameters for the as-prepared hydrogels were obtained from the experimental tensile stress-strain curves. Figure 4.5a shows the true strain of
the hydrogels under uniaxial tension. A linear relationship exists at small values of extension ($\lambda$) while strain hardening is seen for the hydrogels when the extension exceeds 1.5. The strain hardening values increases and falls after epoxy loading of 6 wt%. The strain hardening seen in PVA and PVA/epoxy hydrogels are caused by the breakage/orientation of the crystallites. Figure 4.5b illustrates the relationship between inverse of extension ratio and the reduced stress. The Mooney-Rivlin parameters were calculated from Figure 4.5b between $1/\lambda$ of 0.2 and 1. It is clear that the C1 values increased with an increase in the epoxy content. The tabulated results of the crosslinking density obtained using C1 are shown in Table 4.2. The crosslink density increases with an increase in the epoxy content and decreases after 6wt% of epoxy addition.
Figure 4.5 (a) True stress-strain curves for PVA and PVA/epoxy hydrogels. (b) Reduced stress based on volume fraction as a function of inverse extension ratio.

Table 4.2 Mooney-Rivlin parameter calculated using the Flory Huggins theory and from experimental tensile data.

<table>
<thead>
<tr>
<th>Epoxy content (wt%)</th>
<th>C1 swelling</th>
<th>C1 as-prepared</th>
<th>C1 swelling</th>
<th>C1 as-prepared</th>
<th>C1 from experimental results</th>
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<td>119</td>
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<td>29</td>
<td>602</td>
<td>31</td>
<td>740</td>
<td>174</td>
</tr>
</tbody>
</table>

a Flory Huggins theory  b modified Flory Huggins theory

4.3.4 Mesh size based on rheology
Rheology is a powerful tool to analyze the internal structure of the hydrogels. The hydrogels under study are composed of randomly coiled and crosslinked macromolecules enduring affine deformation [22]. The affine deformation model consists of a network of strands randomly connected to junction points. The model is based on the assumption that the relative deformation of individual network strand is equal to the macroscopic deformation of the hydrogel, i.e. classic networks. This assumption that the hydrogels are classic networks give us an opportunity to relate the shear modulus \((G')\) to the “average number of equivalent units in a network strand” \((N^*)\) by using the following relationship

\[
G' = \frac{RT}{N_{av}a^3N^*} \phi_0 \frac{2}{3} \phi^{\frac{1}{3}}
\]

where \(N_{av}\) represents the Avogadro’s number, \(\phi_0\) and \(\phi\) are the volume fractions of the relaxed and swollen hydrogel respectively, \(N_{av}a^3\) represents the molar volume of the solvent. The equation is valid for rheological experiments carried out at low strain and low frequency typically around 1Hz (6.28 rad/s). The volume fraction in the relaxed state is set equal to 1 assuming that the volume fraction is equivalent for both the relaxed and the dry state.

The network mesh size in as-prepared and swollen hydrogel can be calculated by using the following relationship based on the network strand [23]

\[
L_c = \phi^{-\frac{1}{3}} (C_{av}N)^{\frac{1}{2}} a
\]

Figure 4.6 shows the shear modulus as a function of the applied strain at 1 Hz for PVA and PVA epoxy hydrogels with epoxy content of 4 and 10 wt%. The linear viscoelastic region is defined as the region where the modulus is independent of the applied strain, a typical nature of viscoelastic solids. The end of linear viscoelastic region was determined as the point at which shear modulus deviates by more than 5%. The shear modulus deviates and decreases after this critical strain indicating transition to a liquid-like state. A critical strain of 1% was chosen for further rheological tests. Figure 4.7 shows the obtained shear modulus of fully swollen and as-prepared hydrogels as a function of epoxy content. A similar trend
was obtained for both the fully swollen and as-prepared hydrogels with the hydrogels showing an increase in the moduli with an increase in the epoxy content.

The calculated values for the mesh size are reported in Table 4.3. The mesh size of PVA hydrogel is of the order of hundred nanometers and is 10 times greater than the average correlation distance of PVA hydrogels reported by Ricciardi et al [24]. The occurrence of such a large mesh size indicates a high degree of heterogeneity of PVA hydrogels due to the freeze thaw process. This heterogeneity has been attributed to the existence of phase separation including variation in pore size from nanometers to micrometers [25-27]. However, the addition of epoxy reduces the mesh size thereby reducing the heterogeneity due to the occurrence of crosslinks. The epoxy addition reduces phase separation as a consequence of a reduction in the crystallite distribution across the hydrogel. The mesh size value decreases from 136 nm to 85 nm with the addition of epoxy following a similar decreasing trend as shown previously using the Flory Huggins theory.

![Figure 4.6 Oscillatory strain sweep of PVA and PVA/epoxy hydrogels measured at 1Hz.](image-url)
Figure 4.7 Shear modulus of PVA and PVA/epoxy hydrogels measured from plateau value of shear modulus vs angular frequency curves.

Table 4.3 Storage modulus and mesh size for as-prepared and fully swollen PVA and PVA/epoxy hydrogels

<table>
<thead>
<tr>
<th>Epoxy content (wt%)</th>
<th>Ge</th>
<th>Ge as-prepared (Pa)</th>
<th>Lc swollen (nm)</th>
<th>Lc as-prepared (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7003</td>
<td>11000</td>
<td>191</td>
<td>136</td>
</tr>
<tr>
<td>2</td>
<td>7717</td>
<td>13834</td>
<td>187</td>
<td>121</td>
</tr>
<tr>
<td>4</td>
<td>8764</td>
<td>15916</td>
<td>172</td>
<td>107</td>
</tr>
<tr>
<td>6</td>
<td>8985</td>
<td>17214</td>
<td>168</td>
<td>102</td>
</tr>
<tr>
<td>8</td>
<td>9309</td>
<td>19285</td>
<td>163</td>
<td>94</td>
</tr>
<tr>
<td>10</td>
<td>12798</td>
<td>22666</td>
<td>139</td>
<td>85</td>
</tr>
</tbody>
</table>

In order to understand the morphology of the hydrogels, scanning electron microscopy was performed. SEM images of the gel samples are presented in Figure 4.8 and the morphologies were found to be highly dependent on the epoxy content.
The morphology observed showed an apparent change of the pore size distribution to from large to smaller pores as the epoxy content increased from 0 wt% to 10 wt%. The occurrence of pores is a direct result of the swollen amorphous PVA formed during the freeze cycles. The reduction in the pore size corroborates the obtained decrease in the mesh size values which indicates a decrease in the heterogeneity of the hydrogel with an increase in the epoxy content. The drastic reduction in the size of pores implies efficient cross-linking of PVA with epoxy, as a consequence of limiting the occurrence of free amorphous PVA, in turn reducing the crystallite formation.

Figure 4.8 SEM micrographs of the PVA/epoxy hydrogels (a) PVA (b) 2 wt% epoxy (c) 4 wt% epoxy (d) 6 wt% epoxy (e) 8 wt% epoxy and (f) 10 wt% epoxy
The SAXS profiles of hydrogels with varying epoxy contents at room temperature are shown in Figure 4.9. Broad scattering peaks are observed in the q range between 0.04 and 0.06 Å⁻¹ for all the hydrogels. PVA hydrogels show a distinct peak (q_m=0.048 Å⁻¹) corresponding to a domain spacing of 131 Å⁻¹. This is ascribed to the semi-crystalline lamellar domains existing in the PVA hydrogels. A distinct shifting and broadening of the peaks can be observed with the increase in epoxy content, which also incurs changes in the morphology of the PVA/epoxy hydrogels. It is well known that hydroxide groups are well suited for physical or chemical bonding with various polymers aiding in the formation of nanostructures[28], complexes and miscible blends[29]. In our case, the ring opening reaction of epoxy with hydroxyl groups of PVA has altered PVA’s crystallinity and lamellae packing.

![Figure 4.9 Double logarithmic SAXS profiles of PVA/epoxy hydrogels with different composition.](image)

Power law was used to understand the fractal dimensions of the hydrogels within the q range of 0.05 to 0.11 Å⁻¹ [30, 31]:

\[ I(q) = I(0)q^{-p} \]

where \( p \) corresponds to the fractal dimension (D) and \( I(0) \) to the prefactor. The mass (\( D_m \)) or surface fractal dimension (\( D_s \)) is found from the value of \( p \) where
The mass fractal dimension indicates the presence of either loosely connected aggregates or dense aggregates. On the contrary, the surface fractal dimension indicates the occurrence of smooth or rough surfaces.

Power law plots can be obtained by displaying the SAXS profiles as natural log plots of the intensity and scattering angle. The power law exponent \( p \) can be obtained from the slope of the curves. Figure 4.10a shows the power law exponent \( p \) for the PVA/epoxy hydrogels calculated from the slope of the power law plots (Figure 4.10b). The \( p \) value of all the hydrogels display characteristics of surface fractal. The PVA hydrogel shows a \( p \) value of 3.87 indicating the presence of smooth and well defined interfaces in the hydrogel which is due to the crystalline lamellar structure. The addition of 2 wt% and 4 wt% epoxy shifts the \( p \) value to 3.22 and 3.44 respectively, and further addition of epoxy shifts the \( p \) value closer to that of the PVA hydrogels. The transition from smooth to a slightly rougher surface is seen for PVA/epoxy hydrogels with epoxy loading up to 4 wt%. This is due to the crosslinking of PVA with epoxy which introduces amorphous chains among ordered lamellar structure causing a slight change in the fractal dimensions. However, further addition of epoxy induces a higher content of amorphous chains as more and more PVA chains are involved in the cross-linking reaction which induces covalently cross-linked, well defined and smooth surfaces.
Figure 4.10 (a) Power law exponent $p$ and surface fractal dimension $D_s$ calculated from Equation 4.14 and 4.16 for PVA/epoxy hydrogels with varying epoxy content. (b) Power law plots of PVA/epoxy hydrogels with varying epoxy content. The curves are scaled vertically for clarity. The linear fits are represented by solid lines. The correlation coefficients of the fits are close to 0.99.
Cross-linking has pronounced effect on the radius of gyration ($R_g$). The $R_g$ can be obtained by applying the Guinier equation in the low-q region\cite{30, 32}:

$$I_g(q) = I_g(0)\exp(-q^2 R_g^2/3)$$

where $I_g(0)$ is the zero angle scattering intensity and $R_g$ is the measure of the polymer-rich solid-like realms in the hydrogel.
Figure 4.11 (a) Radius of gyration ($R_g$) of PVA/epoxy hydrogels as a function of the epoxy content. (b) Guinier plots of PVA/epoxy hydrogels with varying epoxy content. The curves are scaled vertically for clarity. The linear fits are represented by solid lines. The correlation coefficients of the fits are close to 0.99.

Figure 4.11a shows the $R_g$ values for PVA/epoxy hydrogels calculated from the slope of the Guinier plots $\ln [I(q)]$ vs $q^2$ (Figure 4.11b). A dramatic increase in the $R_g$ values can be seen from 14Å for PVA hydrogels to 71Å for PVA/epoxy hydrogels with 10 wt% epoxy loading. This is caused by the increase of crosslinking between PVA and epoxy which attributes to the increase in polymer-rich amorphous realms in the PVA/epoxy hydrogels.

The DSC and SAXS results indicate a decrease in the crystallinity which brings changes in the morphology and increase in polymer-rich amorphous crosslinked regions. Therefore, the high mechanical strength must be derived from the ring opening reaction of epoxide group with the PVA. The epoxy groups are well suited to form covalent bonds with the hydroxyl groups on the PVA macromolecules. These covalent bonds can act as sacrificial bonds that provide better load transfer between the PVA matrix and the epoxy, leading to enhancement of mechanical properties. However, when the epoxy content exceeds 4 wt%, the tensile strength decreases. This is probably caused by the increasing covalent network and decreasing crystallites that make the hydrogels more brittle. This is further corroborated by the changes in the $R_g$ and $p$ values. It is clear that the addition of up to 4 wt% epoxy causes a drastic change in the internal structure of the hydrogel and hence displays the maximum tensile strength and strain at break. Further addition of epoxy shifts $R_g$ and $p$ values towards that of tightly crosslinked chemical network and lightly crosslinked physical network, leading to a brittle network. Thus these PVA/epoxy hydrogels become promising candidates for load-bearing engineering applications due to their superior mechanical strength.

4.4 Conclusions
We have investigated the network parameters and fracture behavior of PVA/epoxy double network hydrogels in tension. The PVA epoxy hydrogels show an increase in the crosslink density while the molecular weight between crosslink and the mesh size decreases. This has been ascribed to the increase in chemical and physical interaction between epoxy and PVA.

4.5 References


5.1 Introduction

Hydrogels are carbon based soft materials displaying an ability to absorb large amount of water and can possess biomimetic properties, high stretchability and stimuli responsiveness [1]. Incorporation of these unique properties into hydrogels has led to commercial applications in waste treatment and agriculture as superabsorbent [2-4]. Moreover, they serve as model systems to develop fundamental research in medicine [5, 6], photochemistry [7] and tissue engineering [8, 9]. The first generation single network hydrogels possess poor mechanical properties due to their high water content and heterogeneous structure. Therefore, the origin of mechanical properties was rarely studied due to their fragile nature.

The past decade has witnessed humongous efforts towards synthesis of strong and tough hydrogels involving both homogenous and heterogeneous network structures. Double network hydrogels by Gong [10], nanocomposite hydrogels by Haraguchi [11], slide ring hydrogels [12], ionic – covalent hydrogels [13, 14], macromolecular microsphere hydrogels [15], to name a few, have been developed to address this issue. Double network hydrogels developed by Gong and co-workers still stand as a gold standard for high strength hydrogels and have shown to possess extremely high strength (tensile stress of 1–10 MPa and strain of 1000–2000%) and toughness (tearing fracture energy of 102–103 J/m²) [16]. These hydrogels have been prepared using sequential polymerization involving contrasting network structures with a brittle polyelectrolyte first network entangled with a loosely cross-linked neutral polymer. Another feature of these hydrogels is that the molar concentration of the second network is 20–50 times that of the first network. A wide range of double network hydrogels have been developed using these principles by changing the type of networks and the polymerization steps [17-22].
The fracture mechanism in chemically crosslinked networks have been extensively studied in the past decade [23-26] while very few studies have been conducted on hybrid hydrogels [27]. In general, it has been well established that the first tightly crosslinked network fractures into small clusters which act as sliding crosslinker for the loosely crosslinked network. These sliding crosslinkers provide the necessary resistance towards crack propagation by creating large damage zones at crack tips. It is the first network that is responsible for high fracture efficiency, which is about 85% higher than that reported for vulcanized rubbers. Recently Gong et al [24] have reported a continuous-discontinuous transition in double network hydrogels consisting of PAMPS/PAM networks.

The large strain behavior in hydrogels has become important to study due to the high extensibility of these tough hydrogels. Creton et al studied the large strain behavior in PDMA/silica nanocomposite hydrogels using biaxial compression and attributed the de-adsorption and re-adsorption of the PDMA chains to the large strain behavior. Wang et al studied the large strain behavior in nanocomposite hydrogels for as-prepared and swollen samples using the Mooney-Rivlin model and the Creton’s model which combines the Gent and Maxwell models [28]. They found that the addition of laponite increased the strain hardening while qualitative fitting was obtained for Mooney – Rivlin at small strain; the Creton’s model provided the same at high strains. It should be noted that the efforts to study the fracture and large strain behavior have been predominantly focused on chemically crosslinked DN gels and nanocomposite gels.

Recently fracture of hybrid hydrogel of agar helical physical network with PAM chemical network was explained using a chain-pullout mechanism [27]. This chapter reports on the fracture and large behavior of PVA/epoxy hydrogels.
5.2 Experimental

5.2.1 Hydrogel synthesis

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 and 4 wt% PEGDGE contents were mixed at 95°C for 1 hour to initiate the ring opening reaction of the oxirane group. Then the solution was transferred to a Teflon mould for the preparation of tensile and compressive samples. The mould was kept at -18°C for 20 hours and then thawed for 5 hours at room temperature. Three freeze thaw cycles were conducted for preparing samples. All measurements were conducted on as-prepared hydrogels.

5.2.2 Tensile test and mechanical hysteresis measurements

A 30kN Instron mechanical tester (Instron 5567, USA) with a load cell of 100N was used for mechanical characterization. Dumbbell shaped as-prepared hydrogel specimens with width of 4 mm, gauge length of 20 mm and thickness of 3 mm were used for tensile tests. The characterization was carried out within 24 hours of sample preparation. The hydrogels samples were kept sealed in a plastic bag to prevent evaporation of water prior to testing. Tensile tests were performed at cross-head speeds of 20, 40 and 100 mm.min\(^{-1}\). Hysteresis measurements involved loading the sample to a certain strain \(\varepsilon_1\) then unloading to zero strain in 30 seconds. The samples were stretched to increasing strain \(\varepsilon_2, \varepsilon_3, \varepsilon_4 \ldots \varepsilon_n\) till the specimen fractured. The tensile hysteresis \(U_{hys,n}\) was calculated using the following equation

\[
U_{hys,n} = \int \sigma d\varepsilon \text{(loading)}_n - \int \sigma d\varepsilon \text{(unloading)}_n \quad (5.1)
\]

The initial elastic modulus was calculated at a strain of 15% using the relationship \(E_{DN} = \sigma/\varepsilon\). The work required at a strain of \(\varepsilon_n\) was calculated using the following equation

\[
W_n = \int_0^{\varepsilon_n} \sigma_n d\varepsilon \quad (5.2)
\]
The fracture energy was calculated using trouser tear specimens with length of 50 mm, width of 14 mm, thickness of 5 mm and tear length of 20 mm in length. Measurements were conducted on as-prepared hydrogels at a constant crosshead speed of 40 mm.min⁻¹. The fracture energy $G$, defined as the energy required for creating a unit area of fracture surface in a sample, was calculated by the following equation [20]

$$G = \frac{2F_{\text{ave}}}{w}$$

(5.3)

where $F_{\text{ave}}$ is the average force required for fracture propagation and $w$ is the width of the specimen. Compression tests were carried out using cylindrical samples of 15 mm in diameter and 12 mm in height on as-prepared hydrogels.

5.3 Results and Discussion

5.3.1 Rate-dependent mechanical properties

The rate-dependent mechanical properties of the epoxy/PVA hydrogels are shown in Figure 5.1. Figure 5.1a shows the rate-dependent nominal stress-strain curves of the hydrogels. The nominal stress at break was 1.1 MPa and the strain at break was 620% at crosshead speed of 20 mm.min⁻¹; similarly, the break stress was 1.1 MPa and the break strain was 600% at crosshead speed of 40 mm.min⁻¹, and the break stress was 1.18 MPa and the break strain was 550% at crosshead speed of 100 mm min⁻¹. It is found that hydrogels stretched at a lower rate exhibit a higher strain at break while hydrogels stretched at higher rates show slightly higher nominal stress. The hydrogels show a rate independent yielding stress at a yielding strain of ~ 100%. The yielding-like phenomena in epoxy/PVA hydrogels is ascribed to the uncoiling of the amorphous PVA chains which can be shown as slow increase in stress as a function of strain. However, we observed that hydrogels stretched at 100 mm.min⁻¹ display much higher increase in stress with strain. Since higher stretching rate provides shorter relaxation times for the uncoiling of the amorphous PVA chains which directly correlates to much higher stress with increasing strain. Another interesting phenomenon is the presence of simultaneous necking instead of stable necking as seen in the PAM/PAMPS double network hydrogel. A “caterpillar” like simultaneous necking appeared in Agar/PAMPS...
[27] double network hydrogel is also observed in PVA/epoxy hydrogels. This could be due to the physical and biomaterial nature of the PVA networks. However, the necking regions did not disappear even at large strains. This phenomenon is similar to what happens in divalent crosslinked alginate/PAM hydrogels.

Figure 5.1b shows the rate-dependent fracture toughness of the hydrogels. The toughness can be expressed in terms of the dissipated energy (work of extension) or tearing energy. The tearing energy of the hydrogels was measured using the universally accepted “trouser tear tests” formulated by Gong et al. The hydrogels showed rate-dependent tearing energy similar to Agar/PAM double network hydrogels [27]. This is contrary to PAM/PAMPS double network hydrogels which display nearly rate independent mechanical properties.
Figure 5.1 (a) Typical stress-strain curves of PVA/epoxy hydrogels at different strain rates (b) fracture energy of PVA/epoxy hydrogel at varying strain rates

5.3.2 Fracture mechanism in PVA/epoxy hydrogels

Energy dissipation in hydrogels studied by cyclic loading-unloading tests provides significant insight into the structural transitions and fracture mechanism of the hydrogels. Figure 5.2a shows the cyclic loading-unloading tests under uniaxial tension. The hydrogels showed hysteresis before and after yielding suggesting that the internal fracture of the epoxy network occurs far below the yielding point. The first occurrence of hysteresis loops starts at a critical strain of 60% far below the yielding point, indicating the fracture of the epoxy network occurred well below yielding. Such phenomenon has been noted in both physical/covalent and purely chemical/chemical double network hydrogels. Figure 5.2b shows the cyclic loading-unloading tests under compression. A common feature in both tensile and compressive loading cycles is the slight recovery of the hydrogels which is completely absent in chemically crosslinked DN hydrogels.
Figure 5.2 Cyclic loading-unloading tests for PVA/epoxy hydrogels: (a) Tensile loading-unloading tests at a strain rate of 100 mm·min$^{-1}$. (b) Compressive loading-unloading tests at a strain rate of 3 mm·min$^{-1}$.

Figure 5.3a and 5.3b show the energy dissipation ($U_{hys}$) of the hydrogels at different stretching rates as a function of increasing strain. The hysteresis of the hydrogels is
very small at low values of strain but significantly increase after the strain reaches to 1.5. The hydrogels stretched at all strain rates exhibited hysteresis and the first occurrence of hysteresis was observed at a strain of 0.6. The hysteresis of gels was similar at small strains while the hydrogels stretched at 100 mm·min⁻¹ showed higher hysteresis at large strains. After reaching to a strain of 1.5, the Uhys increased rapidly but non-linearly with the increasing strain.

Figure 5.3b shows the efficiency of energy dissipation (Uhys/W) of the hydrogels at different stretching rates as a function of increasing strain. The hydrogels show energy dissipation of 70% which is higher than vulcanized rubbers and less than PAMPS/PAM double network hydrogels. This result implies that 70% of the work was used for the internal fracture of the epoxy network and crystallites. The Uhys/W has very low values at strains below 1.5 and significantly increases after 1.5 in contrast to PAMPS/PAM double network hydrogels which reaches to 85% at yielding and remains constant on further increase in strain [24]. This is also different from Agar/PAM double network hydrogels which show a gradual increase in Uhys/W [27]. This suggests different fracture mechanism in PVA/epoxy hydrogels.
Figure 5.3 Energy dissipation in PVA/epoxy hydrogels: (a) Stretched at varying strain rates. (b) Close up of energy dissipation at small values of $\varepsilon_{\text{max}}$. (c) Dependence of $U_{\text{hys}}/W$ at varying strain rates on $\varepsilon_{\text{max}}$. 
To further understand the fracture behaviour, we investigated the initial elastic modulus (E_DN) and Φ_b. Figure 5.4a shows the E_DN of the hydrogels for varying stretching rates as a function of increasing strain (ε_max). It has been established that the number density of “elastically effective” chains, i.e. the chains responsible for withstanding stress on deformation are proportional to the E_DN [23]. All the hydrogels stretched at varying strain rates show dissimilar phenomena. Three distinct regions are noted for the hydrogels at varying stretching rates: (I) ε_max of 0 and 1.5 (II) ε_max of 1.5 to 3 (III) ε_max >3. Noticeable differences are seen depending on the stretching rates. At 100 mm·min⁻¹, E_DN in region I is nearly constant while with decreasing stretching rates, the E_DN falls and the largest difference can be seen at lower stretching rate of 20 mm·min⁻¹. A similar phenomenon is noted in region II where a much higher drop in E_DN is observed for 20 mm·min⁻¹ stretching rate while a very small drop is observed for the hydrogels stretched at 40 mm·min⁻¹ and a nearly constant E_DN for hydrogels stretched at 100 mm·min⁻¹. The trend of increasing E_DN with increase in the stretching rate can be found in region III.

Φ_b represents the unstressed (broken/unloaded) epoxy chains out of all the nominally epoxy chains calculated using the following equation:

Φ_b = \frac{U_{hys}}{C_{c-c} - U_b} \tag{5.4}

where C_{c-c} (80 mol/m³) is the molar concentration of C-C bonds in the epoxy network and U_b (360 kJ/mol) is the fracture energy of a C-C bond. Fig. 5.4b shows the Φ_b of hydrogels stretched at varying strain rates to increasing ε_max. The Φ_b increases with increasing ε_max and reaches a value of ~4% at failure. A value of 4% is quite high but lower than that obtained for the PAMPS/PAM DN hydrogels.
Figure 5.4 (a) Dependence of initial elastic modulus ($E_{DN}$) at varying strain on $\varepsilon_{\text{max}}$. (b) Fraction of the fractured epoxy chains in PVA/epoxy hydrogels.
5.3.3 Sacrificial bond/crystallite orientation fracture mechanism

The PVA/epoxy hydrogels consist of mixture of PVA crystallites, amorphous PVA and cross-linked epoxy with PVA chains. Freeze thawed PVA hydrogels have been well studied by various groups [29-33]. These hydrogels are formed as a consequence of phase separation of PVA-rich and PVA-poor regions during the freezing cycle. The PVA-rich regions induce crystallization of PVA and are held together by hydrogen bonding and van der Waals’ forces. The crystallinity and mechanical properties are direct functions of the number of freeze thaw cycles. Generally speaking, crystallites in PVA undergo a phase transition due to molecular rearrangement of the lamellae into a fibrillar microstructure upon stretching. Unfolding of the lamellae and orientation of the crystallites occur at high strains [34, 35]. Various mechanism has been suggested for the above phase transition such as crystallographic slip, strain-induced melting and recrystallization. Recently, structural changes in PVA films were related to the rotation of the lamellae in the direction perpendicular to the tensile strain direction [36]. Elastic uncoiling of the amorphous regions, crystallite rupture, microfibrillation and strain-induced crystallization have been shown to occur with the increasing tensile strain [36].

We propose a sacrificial bond/crystallite orientation concept for the fracture in PVA/epoxy hydrogels as shown in Scheme 5.1. This can be explained by making parallels with semi-crystalline polymers and chemically crosslinked double network hydrogels. In our case, we found the $U_{hys}/W$ has three distinct regions. An initial decrease in region I between 0.3 and 0.6, an increase in $U_{hys}/W$ in region II between 0.6 to 3 and a small increase/smoothening of $U_{hys}/W$ in region III > 3. This is consistent for hydrogels stretched at varying strain rates. We propose that in region I, the amorphous PVA chains uncoil, stretch elastically and then break, transferring load to the epoxy network. This results in a drop in the $U_{hys}/W$ in these regions. The fracture of the epoxy network starts at a strain of 0.6 and continuously causes the chains to break preferentially till the strain reaches to 3. Region III illustrates the epoxy network cannot bear stronger stress anymore and the stress is then predominantly endured by the PVA crystallites. It can be concluded that the epoxy network is broken permanently.
in region II and III into small clusters. The epoxy network acts as sacrificial bonds with a phase transition from a continuous phase (Region II) to a discontinuous phase (region III), which is seen as a gradual smoothening of $U_{hyd}/W$. PVA crystallites are unfolded, reoriented and broken in region III. The crystallites are aligned perpendicularly to the stretching direction with the increase in strain and then break into microfibrils that occur near the macroscopic rupture.

Further insight into the fracture mechanism is obtained by closely reviewing the dependence of $E_{DN}$ on varying strain. It is clear that varying strain rate changes the $E_{DN}$ significantly especially in region III. We have predicted that PVA crystallites are responsible for load transfer in this region. It has been well established that PVA hydrogels physically crosslinked using freeze-thaw method have a strong strain rate dependence [37-39]. This is caused by the orientation of the PVA crystallites at large strain values. The value of $E_{DN}$ obtained in region III is close to the $E_{DN}$ of single network PVA hydrogel (11 kPa at 40 mm·min$^{-1}$). This indicates that further fracture of epoxy network into smaller sizes does not have significant influence on the overall stiffness of hydrogels in this region. These results demonstrate that the continuous epoxy network starts to break into discontinuous fragments in region II and III.

Finally, 3 times higher crosslink density for the 4 wt% PVA/epoxy hydrogel than PVA hydrogels results in a tightly crosslinked network as seen in Chapter four. This prevents crystallite orientation and rupture at low strains due to constraint of the tight network. As predicted, initial PVA/epoxy chemical and hydrogen bond breaks allow necessary movement for orientation and rupture of PVA crystallites at a later stage.
5.3.4 Large strain behaviour

The behaviour of hydrogels exhibiting large deformation is comparable to that of rubbers. The strain hardening behaviour can be differentiated easily using the Mooney stress or the reduced stress ($\sigma_{\text{red}}$) [40] calculated as

$$\sigma_{\text{red}} = \frac{\sigma_{\text{nominal}}}{(\lambda-1)/\lambda^2}$$  \hspace{1cm} (5.5)

where $\sigma_{\text{nominal}}$ is the nominal stress and $\lambda$ is the deformation ratio calculated as

$$\lambda = \frac{l}{l_0}$$  \hspace{1cm} (5.6)
where \( l \) is the height of the specimen and \( l_0 \) is its original height.

Figure 5.5 shows the true stress for PVA/epoxy hydrogels in uniaxial tension and compression. A linear stress strain relationship exists at low deformation \( \lambda < 1.5 \) for tension and \( \lambda > 0.9 \) for compression. As the deformation increases, a sigmoidal increase can be found in both tension and compression. During tension, this stress upturn starts at lower \( \lambda \) (small deformation) with an increase in epoxy content up to 6 wt\% and falls with further increase in epoxy content. The maximum true stress obtained for PVA/epoxy hydrogels (4 wt\%) is 7 times greater than that obtained for PVA hydrogels. During compression, the stress upturn starts at higher \( \lambda \) (small deformation) with an increase in epoxy content up to 8 wt\% and falls with further increase in epoxy content.
Figure 5.5 (a) Dependence of initial elastic modulus (EDN) at varying strain on $\varepsilon_{\text{max}}$. (b) Fraction of the fractured epoxy chains in PVA/epoxy hydrogels.

Figure 5.6 shows the reduced stress for PVA/epoxy hydrogels in uniaxial tension and compression. The large strain behavior is exhibited by all the hydrogels except for hydrogels with 10 wt% epoxy content under uniaxial tension (Figure 5.6a). The hydrogels experience strain hardening after a deformation of $\lambda > 2$. The large strain behavior clearly increases till 4 wt% epoxy addition and then gradually decreases with the increasing epoxy content, which is not exhibited by hydrogel with 10 wt% epoxy content. PVA hydrogels exhibit an increase in reduced stress from 80kPa to 100kPa while an increase from 110kPa to 140kPa for hydrogels with 2 wt% epoxy. While similar increase is seen in hydrogels with 4wt% and 6wt% of epoxy, a gradual flattening of the strain hardening is observed in hydrogel with 8 wt% epoxy; the hydrogel with 10 wt% epoxy does not show strain hardening. These hydrogels show a decrease in crystallinity with the increase in epoxy content. Thus it can be concluded that the presence of crystallites contributes to the large strain behavior rather than the covalent epoxy bonds. The orientation effect of the crystallites during tension could be
the predominant reason behind the strain hardening. Figure 5.6b shows the reduced stress for PVA/epoxy hydrogels in compression. Strain hardening is exhibited in all the hydrogels.
The large strain behavior is further discussed based on the Mooney-Rivlin model due to its simplicity and validity [41, 42]. The tension and compression results were fit with the following equation to arrive at the Mooney parameters 2C1 and 2C2.

\[ \sigma_{true} = (2C_1 + \frac{2C_2}{\lambda})(\lambda^2 - \frac{1}{\lambda}) \]  

(5.7)

Figure 5.7a shows the fitted compression curve for PVA/epoxy hydrogels with 4 wt% epoxy loading as an example. A very good fit is obtained even in the nonlinear regime and the parameters 2C1, 2C2 and regression parameter R2 were summarized in Table 5.1. The value of 2C2 is related to the viscous (relaxation) component of the viscoelastic modulus [43]. The value of 2C1, which is related to the elastic component of the viscoelastic modulus, can be viewed as the modulus of the hydrogels. The 2C1 of tensile and compression behavior increases with epoxy content up to 4 wt% and decreases with further increase in epoxy content. The 2C1 of tension and compression is 2 or 4 times higher than that for PVA when the epoxy content is 4 wt%.
**Figure 5.7** Mooney stress for PVA/epoxy hydrogels in (a) Tension and (b) Compression.

**Table 5.1** Fitting parameters of Mooney-Rivlin equation under compression.

<table>
<thead>
<tr>
<th>Deformation</th>
<th>Epoxy content (wt%)</th>
<th>2C1 (kPa)</th>
<th>2C2 (kPa)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>4.17</td>
<td>11.07</td>
<td>0.989</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10.04</td>
<td>10.94</td>
<td>0.991</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>18.86</td>
<td>14.81</td>
<td>0.992</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>16.51</td>
<td>17.12</td>
<td>0.986</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8.35</td>
<td>14.06</td>
<td>0.983</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>7.44</td>
<td>11.37</td>
<td>0.982</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2 Fitting parameters of Mooney-Rivlin equation under tension.

<table>
<thead>
<tr>
<th>Deformation</th>
<th>Epoxy content (wt%)</th>
<th>2C1 (kPa)</th>
<th>2C2 (kPa)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tension</td>
<td>0</td>
<td>52.21</td>
<td>-74.61</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>84.71</td>
<td>-58.56</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>102.17</td>
<td>-8.62</td>
<td>0.989</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>93.90</td>
<td>-5.90</td>
<td>0.989</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>76.60</td>
<td>-0.59</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>39.68</td>
<td>-2.57</td>
<td>0.992</td>
</tr>
</tbody>
</table>

5.4 Conclusions

The fracture and large strain behavior was investigated for PVA/epoxy double network hydrogels in tension and compression. The hydrogels showed a rate-dependent fracture behavior due to the PVA physical crystallite network. Notably, we found that higher strain rates achieve higher fracture stress and fracture energy. The $U_{hys}/W$ of PVA/epoxy double network hydrogels is about 70% with a phase transition from continuous to discontinuous regime similar to chemically crosslinked double network hydrogels. A sacrificial bond/crystallite reorientation mechanism was proposed towards predicting the fracture behaviour. The orientation/rupture of crystallites is reported to be the cause of strain hardening which has been well described quantitatively with the Mooney-Rivlin model.

5.5 References


CHAPTER SIX

COMPOSITIONAL EFFECTS ON THE MECHANICAL PROPERTIES OF PVA/EPOXY HYDROGELS

6.1 Introduction

Naturally occurring hydrogels such as cartilage and muscles possess water content ranging from 50 to 80% [1]. The mechanical properties differ significantly on dehydration or change in the water content. Rigidity and brittleness are typical manifestation of a dried natural hydrogel [2]. A classic example is cartilage which is a major load bearing hydrogel tissue in the body; however, it becomes ineffective towards its purpose when it is dry. The effect of water content of synthetic hydrogels were studied [3]. PAMPS, PAAM and DN hydrogels consisting of PAMPS and PAAM were studied to ascertain the role of water content on the mechanical properties. The DN hydrogel showed distinct mechanical properties based on the water content which was explained on the basis of the role of individual component [3]. The DN showed moderate stress and strain when the water content was between 80% and 90%, while showing brittle characteristics when the water content was lower (40% to 60%). The DN gels achieved excellent toughness as well as ductility in the water content range between 65% and 75%. The obtained mechanical properties were explained based on the fracture behavior of the first network and mobility of the DN hydrogel chains.

Similarly, variations in composition of the hydrogel has a significant effect on the mechanical properties of hydrogels. For example, the mechanical properties and swelling characteristics of NC hydrogels strongly depend on their composition [4, 5]. This is due to the difference in the network structure which induces a change in the crosslink density[4]. The increase in clay content increased the tensile stress with a slight decrease in the tensile strain in PNIPAM nanocomposite hydrogels [4]. Moreover, with the increment in clay content, the equilibrium swelling ratio and the deswelling ratio decreased below and above the lower critical solution temperature
(LCST) respectively [6]. Interestingly the optical clarity remained unaffected regardless of the clay content. It has been proven that clay acts as multifunctional crosslinkers and with the increase in clay content, an apparent increase in crosslink density is obtained which in turn is responsible for the changes in the mechanical and swelling characteristics in PNIPAM NC hydrogels [7-10]. Another study involved the study of polymer, clay and water content on the mechanical properties of DMAA NC hydrogels [5].

Other factors influencing the mechanical properties of the hydrogels is the application environment/medium, i.e. pH, salts etc. The change in mechanical properties with varying water content is also of research interest. This chapter studies the compositional effects on PVA/epoxy hydrogels in relation to water content, multivalent cationic salts, PVA composition and effect of time on the mechanical properties of the hydrogels.

6.2 Experimental

6.2.1 Materials and 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. Sodium chloride (NaCl), anhydrous calcium chloride (CaCl₂) and aluminium chloride (AlCl₃) was purchased from Sigma Aldrich. 15wt% PVA solution with 4wt% PEGDGE content were mixed at 95°C for 1 hour 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°C for 20 hours and then thawed for 5 hours 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.

6.2.2 Preparation of hydrogels with varying water content

The as-prepared hydrogels were swollen in water for five days with water change every 24 hours. These hydrogels are called as fully swollen hydrogels. The fully swollen
hydrogels were then dried at 40°C to a pre-determined weight to obtain hydrogels with varying water content with fully swollen hydrogels considered as having 100% water content. The hydrogels were further wrapped for another 5 days to uniformly distribute the water within the hydrogel. The characterization of the fully swollen hydrogels were carried out within 24 hours after the end of the 5 day period.

6.2.2 Preparation of hydrogels with varying salt and PVA compositions
The as-prepared hydrogels were immersed in varying molar concentration of NaCl, CaCl₂ and AlCl₃ for 3 days to achieve equilibrium swollen hydrogels with varying salt content. PVA solutions with initial concentration of 10, 15, 20 and 25 wt% were prepared. These solutions were mixed with 4wt% PEGDGE at 95°C for 1 hour 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°C for 20 hours and then thawed for 5 hours 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. The characterization of these hydrogels were carried out on as-prepared hydrogel within 24 hours of sample preparation. The hydrogel samples were kept in a sealed plastic bag to prevent evaporation.

6.2.3 Rheological characterization
The continuous step strain measurements in PVA and PVA/epoxy hydrogels were conducted by applying predetermined shear stress (expressed as shear strain) for varying time periods in order to study the recovery behavior. The following sequence was programmed for the step strain characterization: 1.0% (700 s) → 100% (700 s) → 1.0% (700 s) → 100% (700 s) → 1.0% (800 s); for PB-CNC 1, 10% (700 s) → 100% (700 s) → 10%(700 s) → 100% (700 s) → 10% (800 s) (strain% and duration in parentheses). The tests were carried out at an angular frequency of 1 rad/s and at the temperature of 25°C. The tests were carried out on as-prepared hydrogels within 24
hours of sample preparation. The hydrogel samples were kept in a sealed plastic bag to prevent evaporation.

6.3 Results and Discussion

6.3.1 Effect of water content

Figure 6.1 shows the tensile stress strain curves for PVA/epoxy hydrogels with epoxy content of 4 wt% with varying water content. The water content was varied from 50% to 100% where 100% represented the fully swollen hydrogel. The tensile stress strain curves show an increase in the tensile stress with a decrease in the water content as shown in Figure 6.2. However, the tensile strain shows inconsistent pattern with a decrease in the water content as shown in Figure 6.3. The elastic moduli exhibit a steep increase in the region between 60 – 80% and a drop when the water content becomes higher (Figure 6.4).

The tensile stress for PVA/epoxy hydrogels range from 0.6 MPa to 2.1 MPa when the water content was varied from 100% to 50%. The tensile strain changes from 460% to 410% as the water content decreases from 100% to 50%. The trend for tensile stress is very similar to that obtained for double network hydrogels although a higher tensile stress and strain were obtained [3]. This is due to the soft and ductile nature of PAAM which gives a higher tensile strain, a characteristic that has been exploited in many hydrogel systems to impart elasticity and extensibility [11-14]. However, in our case both PVA crystallites and epoxy behave as hard and brittle segments respectively which cause an increase in the tensile stress but not in the tensile strain values. The reduction in water content increases the overall concentration of PVA crystallite and epoxy content in the hydrogel causing hard zones in the hydrogel which is responsible for poor tensile strain. It should be noted that fully crosslinked epoxy thermosets show poor fracture and impact strength which shows it’s extremely brittle characteristics [15, 16]. Similar results are obtained for PVA nanocomposite films which show increase in tensile strength and decrease in strain as a result of hard and brittle segments [17, 18]. The elastic moduli display a concave shaped curve between the water content region of 50% to 80% and further increase in water content produces a plateau.
Figure 6.1 Tensile stress-strain curves of PVA/epoxy hydrogels (4 wt%) with varying water content.
Figure 6.2 Tensile stress of PVA/epoxy hydrogels (4 wt%) as a function of varying water content.

Figure 6.3 Tensile strain of PVA/epoxy hydrogels (4 wt%) as a function of varying water content.
Figure 6.4 Elastic modulus of PVA/epoxy hydrogels (4 wt%) as a function of varying water content.

The elastic modulus in a hydrogel can be correlated to the number of elastically effective load-bearing chains. The reduction in water content correlates to an increase in the elastically effective load-bearing chains. A normalized elastic modulus which is the elastic modulus of the hydrogel in dry state is postulated to remove the effect of variation in polymer density. The normalized elastic modulus $E_N$ is calculated as the ratio of modulus and the volume fraction. Figure 6.4 shows the calculated normalized elastic modulus $E_N$ as a function of water content. The volume fraction ($\phi$) used to calculate the normalized tensile properties are listed in Table 6.1. The shape of curve after normalization is concave in nature between 50 and 80% of water content; the curve flattens with further increase in water content. A good fit for Gaussian distribution was obtained with a much close fit in the region of 80 to 100% indicating that the chains are in a Gaussian state. The local maximum of normalized elastic modulus $E_N$ takes place at a water content of 60%.
Figure 6.5 Water content dependency on the normalized elastic modulus of PVA/epoxy hydrogels with 4 wt% epoxy content.

Figure 6.6 shows the normalized tensile stress of PVA/epoxy hydrogels with varying water content. The normalized tensile stress was obtained using the following relation $\sigma^N = \frac{\sigma}{\phi^3}$. The highest $\sigma^N$ was obtained for the water content of 60%. A decent Gaussian fit was obtained for the normalized tensile stress curve. Figure 6.7 shows the normalized tensile strain of PVA/epoxy hydrogels with varying water content. This is due to the change in length of the dumbbell shaped specimens with varying water content. Thus the parameter $\lambda^N$, i.e. extension at fracture can be calculated using the following equation, $\lambda^N = \varepsilon + 1$. The $\lambda^N$ curve shows a clear decrease in the tensile strain with a decrease in the water content, which is contrary to Figure 6.2 that does not show a clear trend. As expected, the decrease in tensile strain with decreasing water content is due to the increase in crosslink density of the hydrogel. An increase in crosslink density leads to brittle and hard junctions where stress concentration takes place and leads to lower tensile strain.
Figure 6.6 Water content dependency on the normalized tensile stress of PVA/epoxy hydrogels with 4 wt% epoxy content.

Table 6.1 Calculated volume fraction of PVA/epoxy hydrogels for varying water content

<table>
<thead>
<tr>
<th>Water Content (%)</th>
<th>Volume fraction ((\phi))</th>
</tr>
</thead>
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<tr>
<td>100</td>
<td>0.05804</td>
</tr>
<tr>
<td>90</td>
<td>0.06459</td>
</tr>
<tr>
<td>80</td>
<td>0.072806</td>
</tr>
<tr>
<td>70</td>
<td>0.083417</td>
</tr>
<tr>
<td>60</td>
<td>0.097649</td>
</tr>
<tr>
<td>50</td>
<td>0.117735</td>
</tr>
</tbody>
</table>

The volume fraction \((\nu_p)\) was calculated using the following relationship \(\nu_p = \frac{\rho_s}{\rho_s + [\rho_p(q_w-1)]}\) where \(\rho_s\) is 0.998 g/cm\(^3\) and \(q_w\) is the weight fraction of polymer in the hydrogel [19].
6.3.2 Effect of polymer content

Figure 6.8 shows the effect of PVA content on the uniaxial tensile properties of PVA and PVA/epoxy hydrogels. The PVA content was varied from 10 wt% to 25 wt% while the epoxy content was fixed at 4 wt%. The increase in PVA content leads to an increase in the tensile stress and strain; as expected, both PVA and PVA/epoxy hydrogels showed enhanced mechanical properties. The tensile stress in PVA hydrogels varies from ~0.16 MPa to ~1.2 MPa when the PVA content was varied from 10 wt% to 25 wt% respectively. PVA/epoxy hydrogels showed much higher tensile stress in comparison with PVA hydrogels and their tensile stress varied from ~0.28 MPa to ~1.87 MPa. Figure 6.9 shows the tensile strain results obtained for PVA and PVA/epoxy hydrogels with a variation in the PVA content. The tensile strain for PVA hydrogels varied from 138% to 503% with an increase in the PVA content. While the tensile strain for PVA/epoxy hydrogels varied from 300% to 690% with an increase in the PVA content.
PVA hydrogels prepared using freeze thaw method show an increase in mechanical properties with the increase in PVA content, degree of polymerization and freeze thaw cycles as a result of increase in crystallite distribution [20-23]. The increase in PVA content increases the phase separation of PVA during freezing to create zones of high PVA content that further forms crystallites on thawing, which is the general principle behind the freeze thaw method. The crystallites act as elastically hard segments and hence an increase in crystallite distribution provides a higher tensile strain at break. In the case of PVA/epoxy hydrogels, the epoxy covalent bonding and hydrogen bonding act as sacrificial bonds and provides enhanced mechanical properties. However, as the epoxy content was fixed at 4 wt%, we see a flattening of both tensile stress and strain as the PVA content increases due to the significantly lesser amount of interaction between PVA and epoxy. The higher PVA content in PVA/epoxy hydrogel (e.g., 25 wt%) tends to show a drop in the tensile stress and strain due to the presence of a higher crystallinity and lower covalent bonding.

![Figure 6.8](image)

**Figure 6.8** The PVA content dependency on tensile stress of PVA and PVA/epoxy hydrogels with 4 wt% epoxy content.
Figure 6.9 The PVA content dependency on tensile strain of PVA and PVA/epoxy hydrogels with 4 wt% epoxy content.

### 6.3.3 Effect of multivalent salts

Figures 6.10 and 6.11 show the influence of multivalent cationic salts on the tensile properties of PVA/epoxy hydrogels. A dramatic increase and a maximum in the tensile stress and strain is obtained when the concentration of the multivalent salts was 0.3 molar. Moreover, the highest increase in the tensile stress was obtained for sodium chloride. While the highest tensile strain was obtained for aluminum chloride, further increase in the molar concentration led to a drop in the tensile stress and strain for all the multivalent salts.

Various hydrogels show a change in the mechanical properties under the influence of cationic salts. The most notable of them are polysaccharides based hydrogel such as alginate/PAAM which show a marked increase in tensile properties with variation in the type and concentration of salts [24, 25] Chitosan based hydrogels also show
improved mechanical properties with anionic salts [26]. The improvement in the mechanical properties in the above cases is due to the formation of ionic bonds which lead to improved energy dissipation. PVA has been shown to be affected by the addition of salts due to the change in the crystallite structure [27, 28].

We propose that the PVA crystallites form micro-crystallites with the addition of salts. As a result, an increase in the micro-crystallite to amorphous network ratio corresponds to an increase in number of crosslinks. Komiya et al. also suggested that in PVA as-cast gels, a decrease in the rigidity of the crosslinks happens as a consequence of the increase in salt concentration. Thus when the molar concentration of the salts is 0.3, an increase in the elastic contribution takes place, as a result of the increase in the ratio of micro-crystallite to amorphous network. A significant increase in the tensile stress and strain values occurs consequently. The maximum value of tensile stress and strain was 1.54, 1.41 and 1.05 MPa for NaCl, CaCl₂ and AlCl₃ respectively. The maximum values for tensile strain was 562%, 673% and 543% for NaCl, CaCl₂ and AlCl₃ respectively. However further addition decreases the rigidity of the crosslinks which induces a slight reduction both in the tensile stress and strain of the hydrogels.
Figure 6.10 The effect of multivalent cationic salts on tensile stress of PVA/epoxy hydrogels with 4 wt% epoxy content. PVA/epoxy hydrogel with 0 mole salt concentration represents fully swollen hydrogels in water.

![Graph showing the effect of multivalent cationic salts on tensile stress of PVA/epoxy hydrogels.](image)

Figure 6.11 The effect of multivalent cationic salts on tensile strain of PVA/epoxy hydrogels with 4 wt% epoxy content. PVA/epoxy hydrogel with 0 mole salt concentration represents fully swollen hydrogels in water.

6.3.4 Effect of short – time shear strain

Figure 6.12 shows the response of short term strain loading on PVA and PVA/epoxy hydrogels. It is of interest to note that the PVA/epoxy hydrogels exhibit recovery of the storage modulus after a large amplitude oscillatory collapse which is true for a thixotropic material[29]. Figure 6.12a shows the effect of large amplitude oscillatory collapse on PVA hydrogels. The hydrogels show a storage modulus of ~ 11 kPa when the small amplitude shear strain of 1% was applied. The material represents solid-like characteristic (loss modulus < storage modulus) at small amplitude strain rate for a duration of 700 seconds. However, on application of a large amplitude strain rate of 100%,
the hydrogels show a quasi-liquid like state with a storage modulus of ~ 0.2 kPa, which is expected for hydrogels. On removal of the large amplitude strain after 700 seconds and we see a significant drop in the storage moduli indicative of network rupture i.e. break in the crystallites. The PVA hydrogels show further reduction in the storage modulus after one cycle of application of large amplitude strain. The storage modulus dropped from ~ 11kPa to 7 kPa from the first cycle to the third cycle, indicating damage of the crystallite network in the PVA hydrogels on application of large amplitude strain. We see contrasting phenomenon in the case of PVA/epoxy hydrogels as seen in Figure 6.12b. The PVA/epoxy hydrogels show a storage modulus of ~ 14kPa on application of small amplitude strain of 1%. The application of large amplitude strain of 100% for 700 seconds results in similar quasi-like behavior to PVA hydrogels. However, on removal of the large amplitude strain and application of small amplitude of 1%, the PVA/epoxy hydrogels showed excellent recovery of strain and showed a similar storage modulus of around ~ 14kPa. Further application of large amplitude strain leads to similar recovery behavior and the storage modulus remained the same. This indicates excellent recovery behavior of PVA/epoxy hydrogels for short-term strain application. The recovery behavior is due to the covalent epoxy network and hydrogen bonds which act as sacrificial bonds leading to recovery of the applied strain. PVA/epoxy hydrogels can be suited to be used in load-bearing application requiring repeated short term stress loading.
Figure 6.12 The storage modulus as a function of time during continuous step strain measurements (a) PVA and (b) PVA/epoxy hydrogel (4 wt%).

6.4 Conclusions

The compositional effects of PVA/epoxy hydrogels with 4 wt% epoxy loading on the mechanical properties were evaluated. PVA/epoxy hydrogels showed an increase in mechanical properties with a decrease in the water content and increase in the PVA content. This was attributed to the increase in crystallinity of the hydrogels. Moreover, the PVA/epoxy hydrogels showed enhanced mechanical properties at a salt concentration of 0.3 mol and further increment in the concentration led to decrease in the mechanical properties. This was attributed to the restructuring of the crystallites to micro crystallites which in turn increases the elasticity of the network. In addition, PVA/epoxy hydrogels showed excellent short-term recovery to applied oscillatory shear while PVA hydrogels could not recover under the same condition, indicating enhanced elastic properties for PVA/epoxy hydrogels.
6.4 References


CHAPTER SEVEN

MECHANICAL PROPERTIES OF PVA/EPOXY HYDROGELS USING HYDROGEN BONDING CROSSLINKER

7.1 Introduction

The mechanical properties of PVA based materials can be improved significantly by the use of hydrogen bonding due to its high affinity towards formation of hydrogen bonds[1-4]. Reinforcing PVA with nanomaterials have been shown to improve its thermal and mechanical properties. However, the addition of nanomaterials induces brittleness thereby limiting its extensibility. It has been confirmed that hierarchical hydrogen bonding is present in biological protein materials [5]. Hydrogen bonds are extremely weak, however hydrogen bonding assemblies can function as the primary building blocks providing biological protein materials with extremely high mechanical strength and toughness [6]. A typical example is the spider silk which possesses tensile stress of 1-2 GPa and tensile strain of 50% [7, 8]. The origin of such high strength has been attributed to the presence of highly ordered, densely packed hydrogen bonding of β-sheet nanocrystals [9].

Hydrogen bonding has been employed in hydrogels to significantly improve the mechanical properties. Physically crosslinked hydrogels using hydrogen bonds between PVP and polyacrylamide provided a tensile strength of ~1.2MPa and exceptionally high tensile strain of ~ 3000%[10]. A multifunctional amine, 2-vinyl-4,6-diamino-1,3,5-triazine was used to create hydrogen bonds with polyacrylates to synthesize high strength hydrogels [11]. PVA hydrogels formed using the freeze thaw method intrinsically form intermolecular hydrogen bonding by the hydroxyl groups and has been shown to improve the mechanical strength and provide self-healing capabilities when the PVA content is greater than 25 wt% [1]. Melamine has been used to prepare PVA hydrogels with improved mechanical properties. These hydrogels displayed exceptional mechanical strength along with ultrasound sensitivity[4].
This chapter studies the synthesis and characterization of PVA/epoxy hydrogels prepared using a multifunctional amine. Internal structure parameters along with mechanical characterization reveal the influence of hydrogen bonding.

7.2 Experimental

7.2.1 Materials and hydrogel preparation
PVA with a molecular weight of 89,000 – 98,000, 99% hydrolyzed was obtained from Sigma Aldrich. 4,6-Diamino-2-hydroxy-1,3,5-triazine (multifunctional amine) and PEGDGE with a molecular weight of 500 was obtained from Sigma Aldrich. 10 wt% PVA solution with varying amine content were mixed at 95°C for 4 hours to create hydrogen bonding interaction between PVA and amine. The solution was then mixed with PEGDGE based on a weight ratio of 15:4 (PVA: PEGDGE) at 95°C for 1 hour to initiate the ring opening reaction. Later the solution was transferred to a Teflon mould for the preparation of tensile samples. The mould was kept at -18°C for 20 hours and then thawed for 5 hours at room temperature. Three freeze thaw cycles were conducted for preparing the samples. PVA, PVA/epoxy and PVA/epoxy/amine hydrogels were prepared according to the same procedure. These hydrogels are called as-prepared hydrogels while the hydrogels immersed in deionized water till constant weight are called fully swollen hydrogels.

7.2.2 Water content of the epoxy/PVA hydrogels
The water content of the hydrogels was measured by drying the hydrogels to a constant weight using a vacuum oven, i.e. Wd. 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 hydrogels respectively.
7.2.3 Swelling ratio

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

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

7.2.4 Mechanical characterization

Tensile, hysteresis and fracture energy characterizations were performed on a 30KN Instron mechanical tester (Instron 5567, USA) with a load cell of 100N. Dumbbell shaped as-prepared hydrogel specimens with width of 4 mm, gauge length of 20 mm and thickness of 3 mm were used for tensile tests. The as-prepared hydrogels were tested within 24 hours of sample preparation. The samples were kept sealed in a plastic bag prior to testing to prevent evaporation of water. Tensile tests were performed at a cross-head speed of 40 mm·min\(^{-1}\).

Tensile hysteresis measurements were conducted using a crosshead speed of 40 mm·min\(^{-1}\) on as-prepared hydrogels. The as-prepared hydrogels were tested within 24 hours of sample preparation. The samples were kept sealed in a plastic bag prior to testing to prevent evaporation of water. Hysteresis measurements involved subjecting the samples to a fixed strain (100%) and then unloading to zero strain within 30 seconds. Five loading-unloading cycles were carried out and their hysteresis was calculated using the following equation

\[ U_{hist} = \int \sigma \, d\varepsilon \text{ (loading)} - \int \sigma \, d\varepsilon \text{ (unloading)} \quad (7.1) \]

where $\sigma$ and $\varepsilon$ are the tensile stress and strain respectively.

Fracture energy was calculated using trouser tear specimens with the length of 50 mm, the width of 14 mm, the thickness of 5 mm and the tear length of 20 mm. The as-prepared hydrogels were tested within 24 hours of sample preparation. The samples were kept sealed in a plastic bag prior to testing to prevent evaporation of water. Measurements were conducted at a constant crosshead speed of 40 mm·min\(^{-1}\).
1. The fracture energy $G$, defined as the energy required for creating a unit area of fracture surface in a sample, was calculated by the following equation [30, 31]

$$G = 2F_{\text{ave}}/w$$

(7.2)

where $F_{\text{ave}}$ is the average force required for fracture propagation and $w$ is the width of the specimen.

### 7.3 Results and Discussion

#### 7.3.1 Water content and swelling ratio

The water content and swelling ratio of PVA, PVA/epoxy and PVA/epoxy/amine hydrogels are shown in Figure 7.1. The water content decreases as expected due to the increase in the epoxy and amine content for the as-prepared hydrogel. The swelling ratio increases with an increase in the amine content. It is expected that epoxy is crosslinked by hydroxyl groups of PVA and the amine groups, resulting in a decrease in crystallite formation. A decrease in the crystallite formation increases the free volume for water uptake. The swelling ratio increases further with addition of amines due to the hydrogen bonding interaction between PVA and amines.
Figure 7.1 (a) Water content of the PVA/epoxy hydrogels with varying amine content (b) Swelling ratio of PVA/epoxy hydrogels with varying amine content. The PVA content was fixed at 10 wt%.

The Flory-Rehner equation is derived from three dimensional networks of randomly coiled chains and is based on the equilibrium swelling of polymer in solvent [12-17]. The Flory-Rehner equation is given as:

\[- \ln(1 - v_p) + v_p + \chi v_p^2 = NV_s\left[v_p^3 - \frac{v_p^2}{2}\right]\]

(7.3)

where $v_p$ represents the polymer volume fraction, $\chi$ is the interaction parameter, $V_s$ represents the molar volume of the solvent ($1.8 \times 10^{-5} \text{ m}^3$) and $N$ represents the crosslinking density.

The interaction parameter can be found experimentally based on the following equation[18]

\[\chi = \frac{1}{2} + \frac{v_p}{3}\]

(7.4)
The mesh size and the molecular weight between crosslinks can be obtained using equations 7.5 and 7.6.

\[ \xi = \nu_p^{-\frac{1}{3}} \left[ C_n \left( \frac{2M_c}{M_r} \right) \right]^{\frac{1}{2}} l \]

(7.5)

where \( C_n \) represents the characteristic Flory ratio (8.3) for PVA[19], \( M_r \) represents the average molecular weight of the repeat units (PVA = 44, PEGDGE = 174), \( l \) represents the carbon-carbon bond length (1.54Å) and \( M_c \) represents the average molecular weight between crosslinks. \( M_c \) has an inverse relationship with the crosslinking density \( N \) of the hydrogels as shown below:

\[ N = \frac{1}{vM_c} \]

(7.6)

where \( v \) represents the specific volume of bulk polymer in the amorphous state (0.788 cm\(^3\)/g)

Figure 7.2 shows the calculated crosslink density, molecular weight between crosslinks and the mesh size for as-prepared PVA and PVA/epoxy hydrogels with varying amine content. Table 7.1 lists the parameters such as polymer density, polymer volume fraction, interaction parameter and water content used in this study to calculate the above mentioned hydrogel internal structure parameters.

Figure 7.2 shows an increase in \( N \) and a corresponding decrease in both the \( M_c \) and \( \xi \), similar to that seen for PVA/epoxy hydrogels in Chapter 4. However, the reason for the increase in crosslink density of PVA/epoxy/amine is due to the hydrogen bonding interaction between PVA and amine. The obtained mesh size decreases significantly with the increase in amine content. The decrease in the mesh size has been attributed to the increase in a homogenous structure as shown in Chapter 4. This indicates that the hydrogen bonding interactions between PVA and amine produces a more homogenous structure. The mesh size of PVA hydrogel is of the order of hundred nanometers and is 10 times greater than the average correlation distance of PVA hydrogels reported by Ricciardi et al [23]. The occurrence of such a large mesh size indicates a high degree of heterogeneity of PVA hydrogels due
to the freeze thaw process. The heterogeneity has been attributed to the existence of phase separation including variation in pore size from nanometers to micrometers [24-26]. However, the addition of epoxy reduces the mesh size thereby reducing the heterogeneity due the occurrence of crosslinks. In addition, the hydrogen bonding interaction between PVA and amine significantly reduces the mesh size indicating significant influence of hydrogen bonding on the network structure in PVA/epoxy/amine hydrogels. The mesh size value decreases from 155 nm to 43 nm with the addition of amine.

**Table 7.1** Parameters used for calculating the crosslink density, molecular weight between crosslinks and mesh size for as-prepared hydrogels.

<table>
<thead>
<tr>
<th>Amine content (wt%)</th>
<th>Water content (wt%)</th>
<th>Polymer volume fraction ($v_p$)</th>
<th>$\chi$</th>
<th>Polymer density ($\rho_p$) (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>88.9</td>
<td>0.089</td>
<td>0.529</td>
<td>1.269</td>
</tr>
<tr>
<td>0.5</td>
<td>87.88</td>
<td>0.099</td>
<td>0.533</td>
<td>1.242</td>
</tr>
<tr>
<td>1</td>
<td>85.45</td>
<td>0.117</td>
<td>0.539</td>
<td>1.279</td>
</tr>
<tr>
<td>2</td>
<td>83.53</td>
<td>0.121</td>
<td>0.540</td>
<td>1.313</td>
</tr>
<tr>
<td>3</td>
<td>80.68</td>
<td>0.158</td>
<td>0.552</td>
<td>1.429</td>
</tr>
</tbody>
</table>

*PVA/epoxy hydrogel with 0 wt% amine. The volume fraction ($v_p$) was calculated using the following relationship $v_p = \frac{\rho_s}{\rho_s + [\rho_p(q_w-1)]}$, where $\rho_s$ is 0.998 g/cm$^3$ and $q_w$ is the weight fraction of polymer in the hydrogel.
7.3.2 Mechanical properties

The mechanical properties of PVA and PVA/epoxy/amine hydrogels are shown in Figures 7.3 and 7.4. The PVA hydrogels showed ~ 300 kPa of stress and 140% of strain at the breaking point. The PVA/epoxy/amine hydrogels with 1 wt% epoxy showed the highest elongation stress (~ 590 kPa) and elongation strain (325%). The reported tensile stress is three times greater than the tensile strength obtained for neat PVA hydrogels, while the tensile strain doubled in comparison with the pure PVA. PVA/epoxy/amine hydrogels with varying amine content show higher tensile stress and strain in comparison with neat PVA hydrogels. However further addition of amine leads to very weak mechanical properties and could not be analyzed using the mechanical tester.

The tensile loading curves display a similar “J” shaped stress-strain curves as shown in Chapter 3, which are analogous to those reported for biomaterials. The hydrogels with 1 wt% amine content demonstrate the maximum toughness of ~ 1000 kJ/m^3. The maximum toughness increased by 480% in comparison with PVA.
The increase in mechanical properties is directly related to the formation of hydrogen bonds in PVA and PVA/epoxy/amine hydrogels. PVA hydrogels possess crystallites which are connected by hydrogen bonding and extensive intramolecular hydrogen bonding. The addition of 4,6-diamino-2-hydroxy-1,3,5-triazine causes an increase in intermolecular hydrogen bonding. Song et al confirmed the formation of strong physical network by FTIR studies and rheological studies when using melamine and other multifunctional amines with PVA[2, 3]. In our case, the addition of 4,6-diamino-2-hydroxy-1,3,5-triazine significantly increases intermolecular hydrogen bonding which is directly responsible for the increase in tensile stress and strain up to 1 wt% addition of amine. However, further addition brings plasticization effect primarily due to the extensive intramolecular hydrogen bonding between 4,6-diamino-2-hydroxy-1,3,5-triazine and direct reduction in the hydrogen bonding between PVA and 4,6-diamino-2-hydroxy-1,3,5-triazine. This brings reduction in the mechanical properties with an increase in the 4,6-diamino-2-hydroxy-1,3,5-triazine content. Similar results were obtained by Song et al. Zhang et al also showed that higher addition of multifunctional amine resulted in a decrease in the mechanical properties of hydrogel[11].

![Graph showing tensile stress vs. strain for PVA and PVA/epoxy/amine](image-url)
Figure 7.3 (a) Typical tensile stress strain curve for PVA and PVA/epoxy/amine hydrogels (1 wt%) (b) Tensile strength and tensile strain of PVA/epoxy/amine hydrogels.

7.3.3 Fracture energy

The fracture energies (G) of the PVA/epoxy/amine hydrogels were measured by trouser-tear tests. All the hydrogels showed similar behavior, i.e. the notch could not propagate and the fracture occurred in one arm of the specimen, which is typical for PVA hydrogels with isotropic mechanical properties[20]. The
PVA/epoxy/amine hydrogel with 1 wt% amine showed the highest fracture energy ~ 190 J/m². In Chapter 3, we showed that the fracture energy is highly dependent on the crystallinity. However in the case of PVA/epoxy/amine, the increase in fracture energy is directly dependent on hydrogen bonding. Hydrogen bonding network is strong enough to provide elastic resistance towards crack propagation. However, addition of melamine above 1 wt% leads to aggregation of melamine which can act as stress concentrating regions leading to lower fracture energy.

![Figure 7.4](image.png)

**Figure 7.4** Fracture energy of PVA, PVA/epoxy and PVA/epoxy/amine hydrogels.

### 7.3.4 Hysteresis measurement

The cyclic loading–unloading tensile tests are a simple way to understand structural transitions occurring in hydrogels. Figure 10 shows the typical loading-unloading curves for hydrogels subjected to 5 cycles with a maximum strain of 75%. PVA and PVA/epoxy/amine with 1 wt% amine was subjected to hysteresis measurement and the results are shown in Figure 7.5 (a and b) respectively. A single sample was subjected to 5 cycles with a time interval of 30 seconds between loading and unloading cycles for each type of the hydrogels. The calculated hysteresis ($U_{hist}$) for the hydrogels are shown in Figure 7.5c.
In Figure 7.5, all the hydrogels display hysteresis loops for all the cycles. The hydrogels display a significant hysteresis in the first loading–unloading cycle, and the hysteresis is almost negligible in the remaining cycles. The third loading cycle closely follows the path of the first unloading cycle and this can be observed for all the cycles. This phenomenon can be related to the Mullins effect seen in filled rubbers, pure crystallizing gums and double network hydrogels. We predict that the origin of the Mullins effect in PVA hydrogels and PVA/epoxy/amine hydrogels are contrasting in nature. Wang et al attributed the Mullins effect in PVA hydrogels to the breakage of crystalline regions[20] while Creton et al ascribed the Mullins effect in double network hydrogels to the breakage of the first covalent network.[21]

We suggest that the amorphous regions in PVA hydrogels sustain the initial strain, which can be predicted by the change in the slope of tensile stress – strain curve. Thus the first cycle hysteresis obtained in pure PVA hydrogels can be assumed to be mainly from the uncoiling of the amorphous chain and certain breakage of the crystallites. The amorphous chains become fully extended and do not return to its uncoiled state, while the breakage of crystallites is also not fully recovered, which is responsible for the stress softening. However, in the case of PVA/epoxy/amine hydrogels, a hysteresis of the order of 4 times of that of PVA hydrogels are obtained (Figure 7.5c). This indicates a major structural transition leading to a higher energy release, which could be explained by the breakage of covalent bonds and physical hydrogen bonds during the first loading cycle that creates a permanent irrecoverable damage seen as stress softening in further cycles.
Figure 7.5 Cyclic tensile loading-unloading tests for PVA and PVA/epoxy/amine (1wt%) subjected to 75% strain and 5 cycles. (a) Loading-unloading curves for PVA hydrogels for 5 cycles; (b) Loading-unloading curves for PVA/epoxy/amine hydrogels with 1 wt% amine content for cycles; and (c) The calculated hysteresis ($U_{hyst}$) for the run cycles.

### 7.4 Conclusions

The impact of the multifunctional amine 4,6-diamino-2-hydroxy-1,3,5-triazine as hydrogen bonding crosslinker for PVA/epoxy hydrogels on the mechanical properties have been investigated. The PVA/epoxy/amine hydrogels show enhanced mechanical properties with 1 wt% amine addition showing the highest tensile stress, strain and fracture toughness. The PVA/epoxy/amine hydrogels with 1wt% addition show a much higher energy in comparison with PVA hydrogels owing to the reversible hydrogen bonding network.
7.5 References


CHAPTER EIGHT

CONCLUSIONS AND FUTURE WORK

8.1 General Conclusions

This work has led to the development of a novel hydrogel based on PVA and epoxy. The hydrogels were prepared using a combination of epoxy covalent bonding, PVA physical crystallite network and hydrogen bonding for the purpose of preparing robust and mechanically strong hydrogels. The structure, morphology, fracture behaviour and compositional effects of the prepared hydrogels have been well investigated in this study. This work promotes the use of biocompatible PVA and epoxy-based materials for the preparation of tough hydrogels for use in engineering and biomedical applications. The synergistic effect of covalent bonding, hydrogen bonding and crystallites provide both elastic and ductile characteristics of the prepared hydrogels. The composition of PVA and epoxy have a notable effect on the structure, morphology and mechanical properties of the hydrogels. The general conclusions of the research are briefed as below:

i) It is found that the addition of 4 wt% epoxy in 15 wt% PVA provides the maximum tensile strength and work of extension. While the addition of 2 wt% epoxy displays the maximum fracture toughness (Chapter 3). The hydrogels were characterised for their crystallinity, morphology and macroscopic properties. The crystallites act as hard segment and provide necessary resistance towards crack propagation. The crystallinity drops significantly with the increase in epoxy content and hence 2 wt% of epoxy gives the highest crystallinity and highest fracture toughness. Most importantly, all the PVA/epoxy hydrogels display higher mechanical properties than PVA hydrogels.
ii) The crosslink density, molecular weight between crosslinks and the mesh size were analysed based on the Flory-Huggins theory, Mooney-Rivlin and affine network models. The PVA/epoxy hydrogels display an increase in crosslink density with an increase in the epoxy content. The crosslink density could be correlated to the obtained morphology through SAXS and SEM, both of which indicates a change in the crystallite structure and surface characteristics. The obtained decrease in mesh size corresponds with a well-defined and homogenous structure with the increase in epoxy content although PVA hydrogels are heterogeneous in nature. SAXS provides information regarding both the fractal type and the crosslinking reaction.

iii) In addition, the effect of water content, salt content and composition of PVA were investigated (Chapter 6). The decrease in water content significantly increases the tensile stress while showing brittle characteristics. Multivalent cationic salts increase the mechanical properties of the hydrogel due to the change in the crystallite structure.

iv) Finally, it has been found that moieties that are capable of hydrogen bonding would have an appreciable impact on the mechanical properties. In our case, the use of multifunctional amine 4,6-diamino-2-hydroxy-1,3,5-triazine at a concentration of 1wt% gives enhanced tensile stress, strain and fracture toughness due to the influence of hydrogen bonding. These hydrogels show a much higher energy dissipation during hysterisis measurements making them excellent candidates for load bearing applications.
8.2 Future Works

The possibility of preparing mechanically strong and robust hydrogels using PVA and epoxy was extensively investigated in this study. The structure and morphology is closely correlated to their mechanical and fracture properties. Further work can be carried out in the future as stated below:

i) The role of chemical crosslinker for the epoxy network on the structure, morphology and mechanical properties of hydrogels could be studied. This will possibly lead to improved mechanical properties as well as providing diverse toughening mechanism and in depth knowledge in the area of PVA/epoxy hydrogels.

ii) A wide range of epoxies are available and hence the interaction between PVA and other non-PEG type epoxies could be investigated. Since PVA and a range of epoxies are soluble in DMSO, the future work could be carried out and provide further insight into this class of hydrogels.

iii) The influence of PVA and epoxy molecular weight on the structure, morphology and macroscopic properties of the hydrogels could be investigated to identify the criteria of limiting molecular weight for preparing the hydrogels.

iv) Quadruple hydrogen bonding chemicals could be used as hydrogen bonding crosslinker to promote self-healing properties in PVA/epoxy hydrogels.