Mechanical Properties of Double Network Poly (Acrylic Acid) Based Hydrogels for Potential Use as a Biomaterial*

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Abstract— **Load-bearing applications of hydrogels include soft robots, tissue engineering, and stretchable electronics. This paper presents an extensive study of double network poly (acrylic acid) based hydrogel on stress relaxation, compression fatigue, shear stress, and shock absorption properties as a potential load-bearing soft tissue replacement biomaterial. Double network poly (acrylic acid) hydrogel was selected due to simple processing and availability. The optimized formulation of poly (acrylic acid) hydrogel was used for samples preparation. The compression modulus varied with hydrogel formulation, crosshead speed and swelled amount of the hydrogel. Stress relaxation and shock absorption properties of hydrogel were compared with polyurethane gel used in soft insoles (Shore 5A). Developed hydrogel displayed good fatigue properties up to 10,000 loading cycle at maximum stress of 390±30 kPa and at 84±4% strain. Further, maximum average shear stress and shear modulus of 80 kPa and 140 kPa respectively were observed at 84% strain before fracture.**

I. Introduction

Hydrogels have distinct three-dimensional network structure with water-swelling capability [1, 2]. During the last decade, hydrogel applications have been developed intensively in the fields of tissue engineering [3, 4], drug delivery [5], and soft robotics [6, 7]. Hydrogels tend to be soft and brittle, but many applications require hydrogels to withstand different levels of static and cyclic loads, and deformations especially in load-bearing soft tissues such as cartilage and intervertebral discs. Solutions have been proposed for drawbacks of hydrogels. Tough hydrogels with the double network [8] and dually crosslink single network [9, 10] are developed to overcome brittle properties.

There was a limited study on fatigue and shear properties of hydrogels. Recently more attention has given on [11, 12] studying the fatigue fracture of hydrogel under cyclic tensile load. Most of these reported hydrogels are polyacrylamide based. Compression fatigue testing has been conducted for the application of nucleus pulposus replacement [13, 14]. Maximum strain in these compression tests has been reported in the range of 15% -25%.

Shear strength is another important parameter to be considered in biomedical applications. Direct shear testing [15] and mechanical lap testing [16] are the two main methods used for shear testing of hydrogels.

Even though few researchers have tested hydrogel for rebound resilience [17, 18], no studies were reported to the best of our knowledge for double network (DN) poly (acrylic acid) (PAA) hydrogels for rebound resilience and had done a comparison with polymer materials with similar hardness.

This study hopes to investigate the DN PAA hydrogel as a potential load-bearing soft tissue replacement biomaterial and compare viscoelastic properties with polyurethane gel used in soft gel insoles (Shore 5A). The biocompatibility of PAA hydrogel has been assessed by several researchers [19, 20]. This study only focuses on the mechanical properties and the toxicity studies will be the subject of a future publication.

II. Experimental Methods

A. Materials

The three main chemicals used for hydrogel formation were acrylic acid (AA) - 99.5% (Daejung, 1017-4105), N, N′-methylene-bisacrylamide (MBA) 99 % (Sigma, 146072) and potassium persulfate (KPS) 95 % (Duksan). All the chemicals were used as received unless otherwise noted.

B. Sample preparation

The first network of 1M 10 ml AA solution was prepared by mixing 0.7 ml of acrylic acid in 9.3 ml of deionized water. Next 4 mol% of MBA was added as crosslinker (CL) and 0.2 mol% of KPS was added as the initiator (I). The mixture was stirred with a magnetic stirrer for 15 min. The mixture was transferred into cylindrical plastic containers of 35 mm internal diameter and heated in an oven at 70°C for one hour. After drying the samples, the second crosslinking solution with 2M AA, 0.1 mol% MBA and 0.2 mol% KPS were prepared and the samples were swelled for 24 h in the solution.

The swelled samples were placed in the oven at 70°C for 1h to synthesis second network. The DN PAA hydrogel samples were swelled for 48 h in deionized water to remove any unreacted monomer molecules. The samples were fully dried and swelled to the desired swelling percentage before testing. This composition with 4 mol% is referred to as 1M 4CL /2M 0.1CL hereafter.

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C. *Mechanical Characterizations*

Mainly compression, creep, stress relaxation, fatigue, shear and rebound resilience tests were conducted. All hydrogel samples were triplicated (Figure 1(a)) and average stress-strain behavior was considered for calculations.

The mechanical tests were conducted on a Testometric M350-10 AT universal material testing machine (Rochdale, England, +/-0.5% down to 1/1000th) at ambient temperature (30°C), with different crosshead speeds (1, 5, 10, 20 and 100 mm/min). The graphs of force vs displacement and force vs time at constant displacement (stress relaxation) were generated. Weight, diameter, and thickness of the samples were measured before and after the test. The stress (σ) was calculated by using the equation (1)

$$\sigma = F/\pi r^2 \quad (1)$$

Where F is the applied load and r is the original radius of the specimen. The strain (ε) was calculated from the ratio of change of the thickness (t) and the initial gauge thickness (t_0) of the measured sample (equation (2))

$$\varepsilon = t/t_0 \quad (2)$$

The modulus was calculated from the slope of the stress-strain curve. The compression strengths were measured (Figure 1(b)) at different crosslink percentages, swelling percentages, and crosshead speeds. The loading-unloading cycles were conducted at a constant crosshead speed of 200 mm/min, maximum 60% strain and 1Hz cycle frequency at ambient temperature. The sample was kept in a moisturized container to minimize dehydration during the test (Figure 1(c)).

Typically, during the loading-unloading cycle, the hydrogel samples were compressed to a pre-set maximum strain and then returned to the initial length. To examine the recovery of the hydrogel and swelling percentage, after the first 1000 cycle, the sample was measured for weight, diameter and thickness, relaxed for 10 min controlled times, and the cycle was conducted again. Shear properties of hydrogel were tested by bonding the hydrogel sample onto two metal plates as shown in Figure 1(d) and shear failure is shown in Figure 1(e).

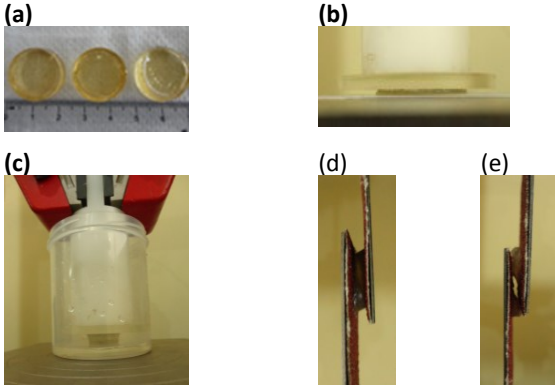

Figure 1. (a) Hydrogel samples before testing (b) During compression test. (c)Samples in a humid container during fatigue test (d) Shear testing arrangement (e) Shear failure of hydrogel sample.

III. RESULTS AND DISCUSSIONS

A. *Compression*

The stiffness of the sample increased with crosshead speed under constant swelling percentage (Figure 2(a)). The sample tested at 100 mm/min showed maximum stress and compression module of 800 kPa and 3 MPa respectively at 58% strain and 62% swelling. Comparison of stress relaxation of hydrogel with polyurethane (PU) gel is shown in Figure 2(b). The DN PAA hydrogel showed better pressure distribution properties than PU gel indicating good nonlinear and viscoelastic material behavior.

B. *Fatigue*

When the load applied on the samples were kept at 178±2 N, the maximum deformation and diameter were increased by 8% and 9% respectively. Softening of hydrogel were indicated by the increase in strain while the stress is almost constant at 395±2 kPa between 6000 and 10,000 cycles (Figure 3(a)). Sample outer edge deformation and crack propagation started at 5000 cycles and propagated circular crack at the outer edge could be observed at 10,000 cycles. After the completion of each 1000 loading cycle, there was only a 1% loss of total weight, indicating that water loss can be neglected.

C. *Shear*

The maximum average shear stress and maximum shear modulus were 82 kPa and 156 kPa respectively at 0.84 strain (Figure 3(b)). When the DN PAA hydrogel was compared with subcalcaneal soft tissue, shear modulus of the subcalcaneal soft tissue range from 18kPa to 124kPa [21] indicating shear modulus of DN PAA hydrogel was in an acceptable range.

D. *Rebound Resilience*

The rebound resilience of hydrogel was compared with EVA, and PU gel (Table 1). The lowest rebound height was given by the DN PAA hydrogel sample. It could be observed a 40% reduction in rebound resilience of hydrogel compared to PU gel which indicates the high shock absorption property of the DN PAA hydrogel. The increase in the thickness of PU gel by 100% and EVA sheet by 50% tend to increase rebound resilience by 57% and 19% respectively while DN PAA hydrogel thickness increase by 75% has increased the rebound resilience only by 10%.

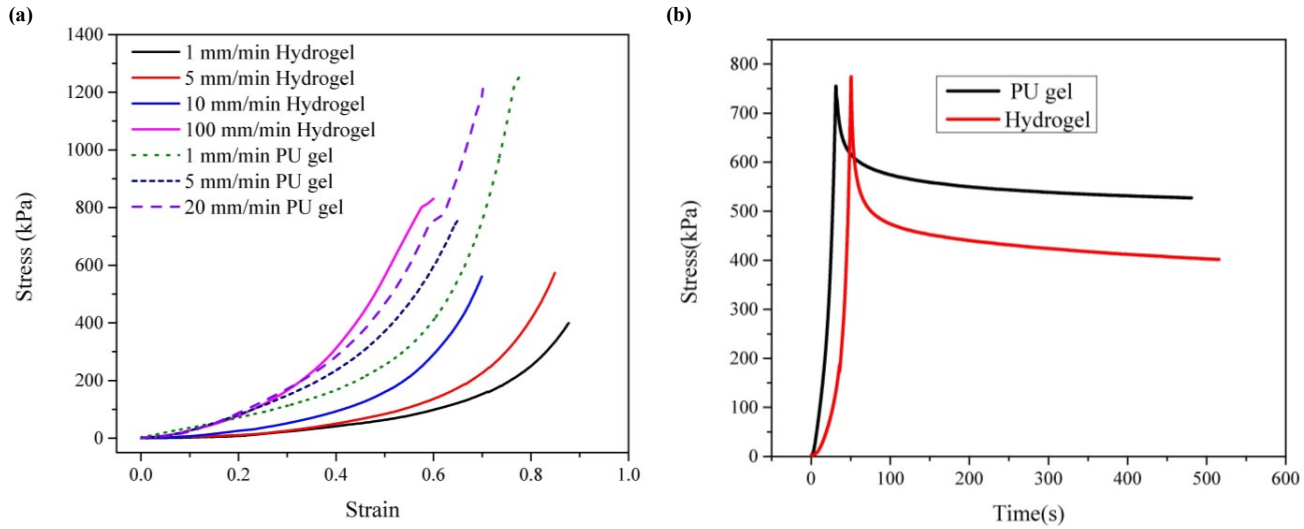

Figure 2. Compression of hydrogel and PU gel (a) Different crosshead speeds and constant swelling of 65±5% (b) Stress relaxation.

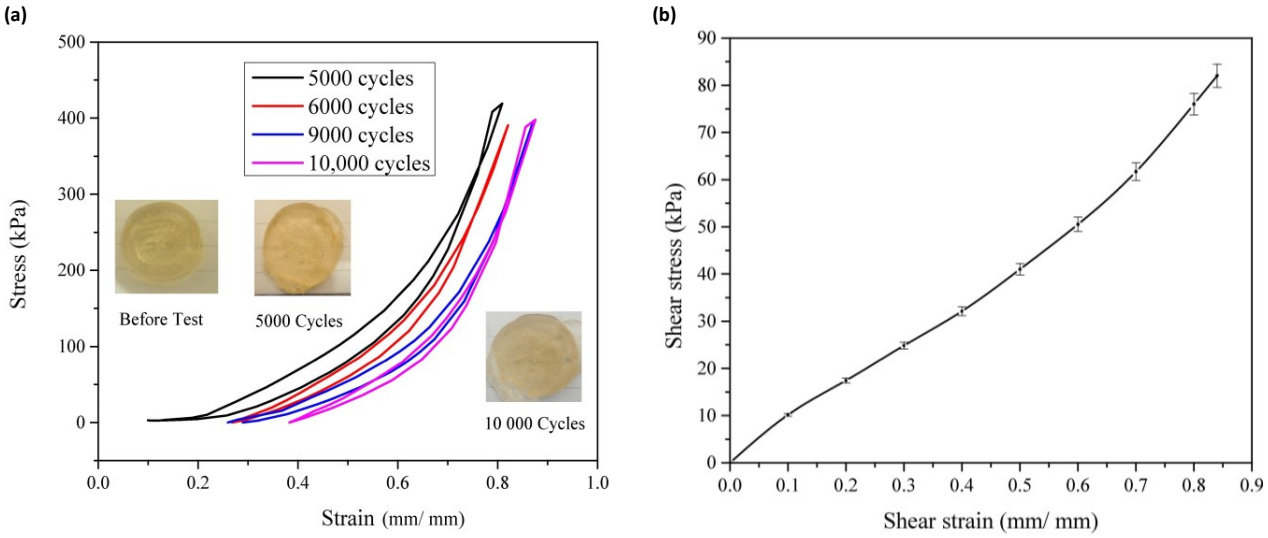

Figure 3. DN PAA hydrogel at 80±5% swelling (a) Fatigue test: variation of stress with strain between 5000 and 10,000 cycles at 200 mm/min crosshead speed (b) Shear stress variation with shear strain. The data represent the mean and deviation of three experimental results

TABLE I. REBOUND RESILIENCE TEST RESULTS

Material	Manufacturer	Thickness (mm)	Rebound resilience (%)	Hardness (Shore A)
EVA foam	DSI Samson Group, Colombo, Sri Lanka	4	32	20
EVA foam		6	38	
EVA foam		10	55	10
PU Gel	SIDAS , Voiron, France	4	35	5
PU Gel		8	55	
Hydrogel	-	4	21	5±1
Hydrogel	-	7	23	

IV. CONCLUSIONS

This study used a well-established, relatively simple synthesis and low-cost polyacrylic acid hydrogel as a model material for mechanical characterization and to compare with the similar hardness polymer material. The mechanical properties of the DN hydrogels were significantly influenced by the amount of cross-linker (MBA), compression cross-head speed and water content. The maximum stress of the hydrogel kept changing during fatigue cycles. Permanent deformation at outer edge and increase in diameter by 9% of hydrogel sample could be observed after 5000 loading cycles. Softening of hydrogel was visible after 8000 cycles and crack propagation started. Higher compression and shear strengths were shown by PU gel when compared to hydrogels but stress relaxation and shock absorption properties are better in hydrogels. Double network poly (acrylic acid) hydrogels are more suitable for maximum compression strength 700 kPa, maximum shear strength 80 kPa and fatigue cycles less than 10,000 applications. Improvement in fatigue strength of poly (acrylic acid) hydrogel with the usage of low-cost chemicals and simple synthesis processes are future aspects of this research.

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