

Compression Fatigue and Stress Relaxation Properties of Single Network Polyacrylamide Hydrogels

Ruwan Udayanandana
Department of Electronic and
Telecommunication Engineering
University of Moratuwa
Moratuwa, Sri Lanka
email: 178039f@uom.lk

Pujitha Silva
Department of Electronic and
Telecommunication Engineering
University of Moratuwa
Moratuwa, Sri Lanka
email: psilva@uom.lk

Thilini Gunasekera
Department of Polymer Science
University of Sri Jayewardenepura
Nugegoda, Sri Lanka.
email: thilimidg@sjp.ac.lk

Abstract—Double-network hydrogels of different chemical compositions have been developed in recent years for specific load-bearing applications such as tissue engineering, soft robots, and stretchable electronics. The broader commercial applications of these hydrogels have been limited by high manufacturing cost and complex synthesis processes. Single network hydrogels have a potential advantage when compared to the complexity and cost of synthesis processes, although their performance and limitations under different loading conditions have not been investigated thoroughly. This paper presents the limitations of single network polyacrylamide based hydrogel on compression fatigue, stress relaxation and creep properties. Single network polyacrylamide hydrogel was selected as model material due to simple processing and availability. The optimized formulation of hydrogel was used for sample preparation. Better pressure relieving property of hydrogel was observed by stress relaxation and creep properties of the hydrogel. Developed hydrogel displayed good fatigue properties up to 13,000 loading cycle at maximum stress of 520 ± 50 kPa and 200 mm/min crosshead speed.

Keywords—single network polyacrylamide hydrogels, compression fatigue, stress relaxation, creep

I. INTRODUCTION

Synthetic hydrogels are composed of hydrophilic polymer chains crosslinked in a 3D network [1]. Hydrogels can hold a large amount of water due to its porous structure. The combination of liquid and solid properties in hydrogels cause specific relaxation behaviors that are not found in either a pure solid or pure liquids.

The stress-relaxation behavior of hydrogels is strongly affected by the crosslinking method. The stress relaxation method of hydrogels with ionic crosslinks is mainly through breaking and subsequent reforming of the ionic crosslinks. By contrast, in hydrogels with covalent crosslinks, stress relaxes mainly through the migration of water. The time scale of the relaxation increases with the size of the sample for the gels with covalent crosslinks [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 withstand deformations especially in load-bearing soft tissues

such as cartilage and intervertebral discs. Solutions have been proposed for the drawbacks of hydrogels. Tough hydrogels with the double network [8] and dually crosslink single network [9, 10] are developed to overcome brittle properties but broader commercial applications of these hydrogels have been limited by high manufacturing cost and complex synthesis processes.

Polyacrylamide (PAAm) is a hydrophilic polymer for the preparation of hydrogels [11]. The common method to the synthesis of PAAm hydrogels is the covalently crosslinked free radical polymerization. PAAm is a key component in several recently developed tough hydrogels. Ronken et al [12] showed PAMPS (poly (2-acrylamido-2-methylpropane sulphonic acid))/PAAm compositions with lower water content result in stiffness parameters closer to cartilage and Sun et al [13] synthesized extremely stretchable and tough hydrogels by mixing two types of crosslinked polymers: ironically crosslinked alginate and covalently crosslinked polyacrylamide. Many aspects of the mechanical behavior of polyacrylamide hydrogels have been characterized by elasticity, viscoelasticity, and fracture [14].

There was a limited study on fatigue properties of hydrogels. Recently more attention has been given on studying the fatigue fracture of hydrogel under cyclic tensile load [15-17]. Most of these reported hydrogels are polyacrylamide based. Compression fatigue testing has been conducted for the application of nucleus pulposus replacement [18, 19]. The maximum strain in these compression tests has been reported in the range of 15%-25%.

This study hopes to fill the gap of compression fatigue fracture and stress relaxation properties of single network PAAm hydrogels at high-stress levels (maximum stress 520 ± 50 kPa at strain $60 \pm 4\%$).

II. EXPERIMENTAL METHODS

A. Materials

The three main chemicals used for hydrogel formation were Acrylamide (AAm) - 98% (Sigma, 01700), N, N'-methylene-bisacrylamide (MBA) 99 % (Sigma, 146072) and potassium persulfate (KPS) 95 % (Duksan). All the chemicals were used as received unless otherwise noted.

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B. Sample preparation

The first network of 1M 10 ml AAm solution was prepared by mixing 0.725 g of AAm in 10 ml of deionized water. Next, 1 mol% of the MBA was added as crosslinker (CL) and 0.2 mol% of KPS was added as an 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.

The synthesized polyacrylamide (PAAm) hydrogel samples were swelled for 48 h in a deionized water container to remove any unreacted monomer molecules. The samples were fully dried to measure dry weight and swelled to the desired swelling percentage before testing. This composition with 1M AAm and 1 mol% CL is referred to as 1M AAm-1CL hereafter.

C. Mechanical Characterizations

Mainly compression, creep, stress relaxation and compression fatigue tests were conducted. All hydrogel samples were triplicated (Fig.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 at ambient temperature (30°C), with crosshead speeds 10 mm/ min for compression. The cylindrical hydrogel samples were having initial diameter and thickness of 20±0.4 mm and 5±0.3 mm respectively at 65±5% swelling. The samples were kept inside a humid container as shown in Fig.1(a) to prevent water evaporation from the sample during the test. The graphs of force vs displacement, force vs time at constant displacement (stress relaxation) and displacement vs time (creep) were generated from the testing machine. Weight, diameter, and thickness of the samples were measured before and after the test. The stress (σ) was calculated according to the equation (1)

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

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

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

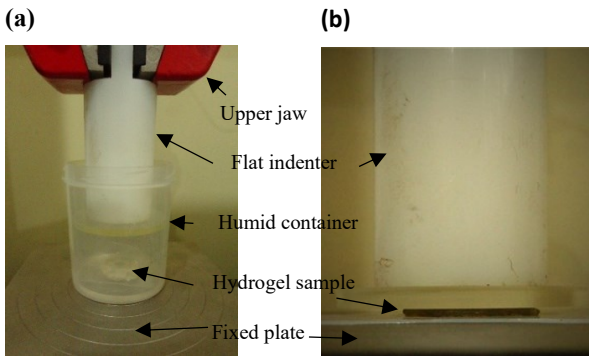


Fig. 1. (a) Hydrogel sample compression fatigue test arrangement to prevent water loss due to evaporation (b) During compression test.

The modulus was calculated as the slope of the stress-strain curve. The loading-unloading cycles were conducted at a constant crosshead speed of 200 mm/min, maximum load 180±10 N and 1Hz cycle frequency at ambient temperature

Typically, during a loading-unloading cycle, the hydrogel sample was compressed to a preset 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.

III. RESULTS AND DISCUSSIONS

Compression of a single network PAAm sample until the fracture is shown in Fig.2(a) and Fig.2(b) The maximum compression stress of 946 kPa was observed at 59% strain under the 10 mm/min crosshead speed and 65% swelling. A similar composition of PAAm hydrogel tested by Gong et al [20] at 93% swelling and 97% fracture stain showed 700 kPa fracture stress. The modulus of toughness or strain energy density of the single network PAAm hydrogel during initial compression was calculated to be 136.6 kJ/m³ based on the area under the stress-strain curve in Fig.2(b)

The Ogden hyperelastic material model coefficients were calculated in Abaqus finite element analysis software [21] based on experimental test data. The hyperelastic material model perfectly fit with the experimental stress-strain curve (Fig 2(a)) indicating hyperelastic behavior of the hydrogel sample.

The stiffness of the sample varied from 1 MPa to 3.7 MPa at 30% to 50% strain respectively. The maximum stiffness of 4.9 MPa was observed at 58% strain (Fig.2(c)). Based on the combined curves of stress relaxation and creep shown in Fig.2(d), 25% reduction in stress within 300 seconds and an increase in strain by 4% during 290 seconds could be observed indicating the pressure relieving properties of PAAm hydrogels. The viscoelastic material model with coefficients of g_i Prony = 0.6, k_i Prony = 0.4, and τ_i Prony = 60 from Abaqus software [21], curve fit with stress relaxation curve indicating the viscoelastic behavior of the sample.

When the load applied on the samples were kept at 180±10 N, variation in maximum strain 60±4% and stress 520±50 kPa could be observed (Fig.3(a)). Hysteresis in the first cycle of loading clearly showed the residual strain after unloading. When the sample was loaded, unloaded and then reloaded during consecutive cycles, the same stress produces an increased strain, indicating a softening of the hydrogel sample. Mullins effect has been considered as the major factor for the softening of the network of hydrogels over consecutive loading cycles [22]. This softening may stem from the breakage of covalent bonds [23].

The breaking of most sacrificial bonds in the network of the hydrogel is irreversible. Such bond breaking progresses cycle by cycle, and the stress-stretch curve keeps changing until it reaches a steady state. This progressive damage over many cycles is called shakedown [16]. Since the network is significantly damaged in the steady state after many cycles,

the stress-strain hysteresis is relatively small (Fig.3(a)), and the hydrogel can be assumed as elastic. The energy release rate is well defined in the steady state, $G = HW$, where W is the area of the stress-stretch curve in the steady state and H is the distance between the two jaws when the sample is undeformed [16]. During the 13,000th cycle, the difference between the energy release rates calculated from the loading and the unloading curves is 12%, while it is 33% during the initial cycle. The area within a hysteresis loop is energy dissipated during a cycle (usually in the form of heating or breaking of covalent bonds). This energy represents the plastic work from the cycle. The hysteresis loss of the first compressive cycle, rather different from the elastic behavior of the subsequent cycles, resulted in sacrificing the covalent bonds of the PAAm network.

The hydrogel sample variation during fatigue cycles could be observed in Fig.3(b). After the completion of each 1000 loading cycles, there was only a 1% loss of total weight, indicating that water loss can be neglected. This could be due to 65% swelling hydrogel used in the testing. The presence of both solid skeleton and fluid phase support carry loads in hydrogels. Due to the negligible water drain, the mechanical behavior of the tested hydrogel can be described by using the theory of rubber elasticity or single phase models of viscoelastic material.

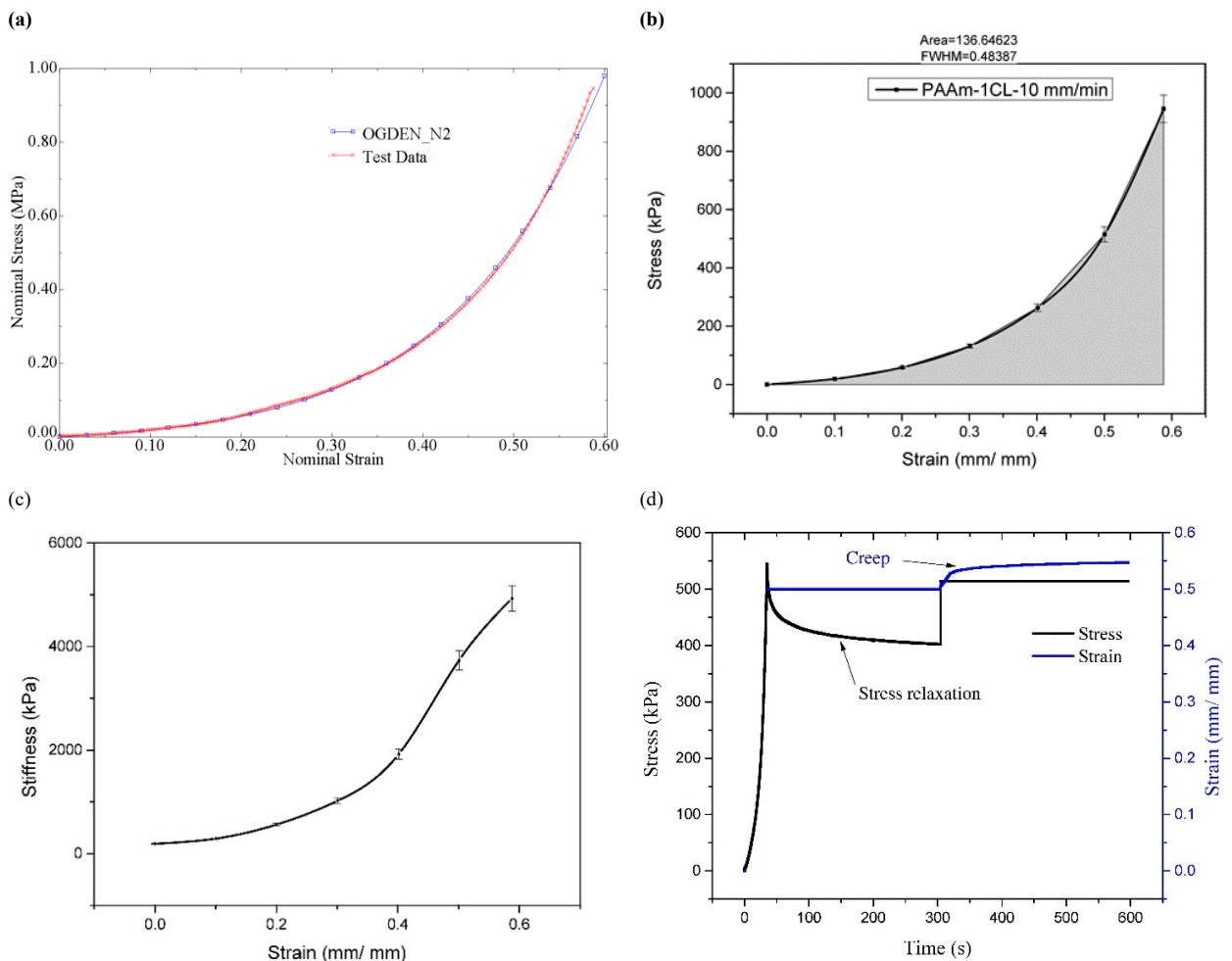


Fig. 2. Compression testing of single network PAAm hydrogel- swelling of $65\pm 5\%$ and a crosshead speed of 10 mm/min (a) Comparison of variation of stress with strain curves based on experimental data and Ogden hyperelastic material model. (b) The area under the experimental stress-strain curve. (c) Variation of stiffness with strain. (d) Stress relaxation and creep.

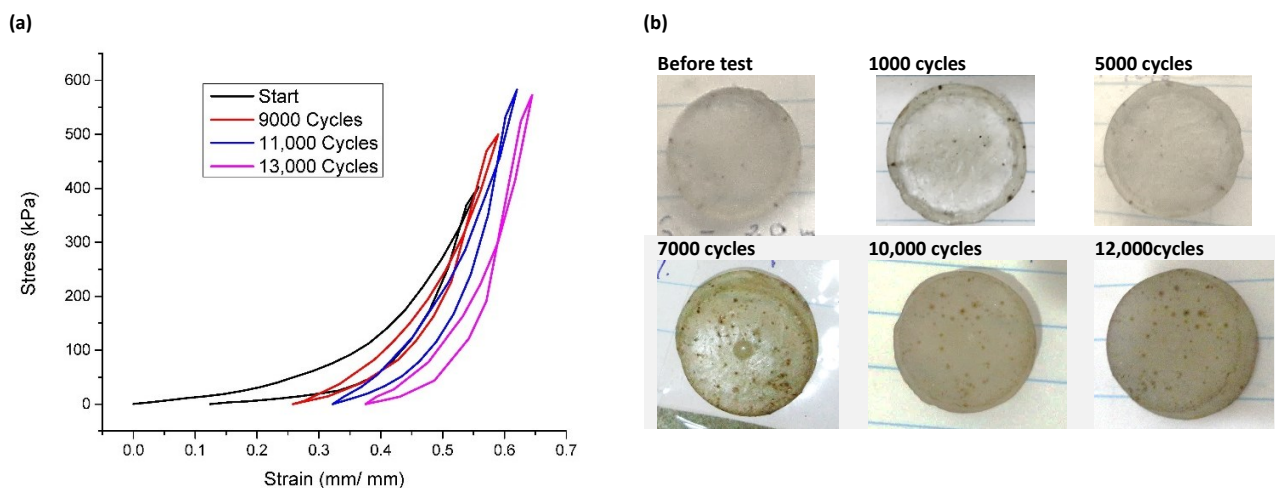


Fig. 3. Compressive fatigue test at 200 mm/min crosshead speed (a) Variation of stress with strain up to 13,000 cycles. (b) Hydrogel samples deformation with the number of cycles.

IV. CONCLUSIONS

This study used a well-established, relatively simple synthesis and low-cost single network polyacrylamide hydrogel as a model material for mechanical characterization. Even though the softening of hydrogel could be observed, negligible dimensional changes were visible during 13,000 loading cycles under maximum compression stress of 520 ± 50 kPa and 200 mm/min crosshead speed. Better stress relaxation and creep properties implied the pressure relieving property. The maximum compression strength of 946 kPa and stiffness of 6 MPa were observed at 58% strain. Improvements in fatigue strength, minimize dehydration of polyacrylamide hydrogel with the usage of low-cost chemicals and simple synthesis processes are future aspects of this research.

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