

Chapter 2

Experimental Tools for Responsive Hydrogel Characterization

C.C. Benjamin, J.C. Springmann, S.A. Chindhy, and W.C. Crone

Abstract Responsive hydrogels are a class of shape memory materials that undergo a large elastic volumetric change when interacting with a stimulus and can return to their original shape. With the advent of microfluidics and subsequent ‘lab on a chip’ devices, the use of these responsive hydrogels has become more prevalent because of the ability to easily fabricate them into many various complicated geometries on the micro-scale. The mechanics of the interaction of a responsive hydrogel to its surroundings is of utmost importance in the fields of microfluidics and microelectromechanical-based devices (MEMS). This work will explore the issue of characterizing the adhesion energy of responsive hydrogels. With the use of fracture mechanics concepts, the strength of the attachment of a responsive hydrogel to various substrates can be studied.

Keywords Fracture mechanics • Microfluidics • Hydrogel • Crack propagation • Swelling

2.1 Introduction

The science of microfluidics emerged in the 1990s and has exhibited great potential for higher levels of functional integration, increased performance, lower cost advantages, decreased size, and increased reliability, in a wide range of potential applications. Responsive hydrogels are very attractive to microfluidic ‘lab on a chip’ systems for when reduced to this micro-scale certain aspects of the hydrogels begin to dominate. On this scale flow is typically laminar, diffusion times are short and the surface to volume ratio is large [1–4].

Hydrogels are cross-linked polymeric structures that are bound together through the process of polymerization. They can also result from the association of bonds such as hydrogen bonds and strong van der Waals interactions between chains [5]. A network of covalently cross-linked, long, and flexible polymer chains can group with water and form a hydrogel that has properties that resemble natural rubber. These are known as elastomeric ‘responsive’ hydrogels. Depending on the functional groups that reside along the polymer chain, various stimuli can cause a response within the hydrogel, dictating how much solvent the hydrogel absorbs or releases [6, 7]. These stimuli range from temperature [8] and pH [7], to electrical stimuli [9]. These materials have been successfully fabricated in microfluidic and biomedical devices [10, 11] and regenerative medicine [12]. They operate in a hydrated environment and respond with a significant volumetric reversible transformation through absorption or release of water within the polymeric network.

Research in the field of microfluidics has resulted in the ability to fabricate complicated geometries on the micro-scale. This has opened up micro-fluidics to much cross disciplinary research involving such fields as genomics [13], cell biology as well as many others. In this experiment pH-responsive hydrogels are being used and the interfacial energy between the

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hydrogel and the substrate it is polymerized on is being studied. The work done by Beebe et al. [14], Agarwal et al. [15], and Dong and Jiang [16, 17] in the field of microfluidics has motivated the experimental work being reported in this paper.

2.2 Experimental Methods

2.2.1 Hydrogel Prepolymer Solution

The hydrogel prepolymer solution contains 2-(dimethylamino) ethyl methacrylate (DMAEMA) 17.4 %, 2-hydroxyethyl methacrylate (HEMA) 78.2 %, ethylene glycol dimethacrylate (EGDMA) 1.4 % and 2,2-dimethoxy-2-phenylacetophenone (DMPA) 3.0 %. All reagents were purchased from Sigma-Aldrich. Prior to polymerization this hydrogel-liquid solution is stored at -8°C .

2.2.2 Responsive Hydrogel Fabrication

Using the in situ photo-polymerization techniques developed for the creation of hydrogel actuators in microfluidic devices as a starting point [18], we were able to modify the procedure to create the test samples for the experiments described below. The process starts by mounting a substrate in a standard petri dish and then placing a steel spacer on the substrate to create a well as shown in Fig. 2.1a. The hydrogel-liquid solution described above is placed in the well via pipette. A colorless DuPont Tenjin Film is placed over top of the steel space and hydrogel-liquid solution to provide an easily removable seal to the top of the well. A mask printed with the desired features, as shown in Fig. 2.1b, is then placed over top of the film and polymerization is achieved by exposing the hydrogel-liquid solution to UV light at an intensity of 20 mW/cm^2 for a total time of 49.0 s.

The UV-polymerization is done with an EFOS Acticure A4000 UV Spot Curing System. When the polymerization is complete, the mask is removed, followed by the colorless film. An ethanol rinse is used on the resultant polymer to remove any excess solution. For this experiment, these hydrogels were fabricated in the form of cylindrical posts. The diameters of these posts are $600\text{ }\mu\text{m}$ and the heights of the posts are $300\text{ }\mu\text{m}$.

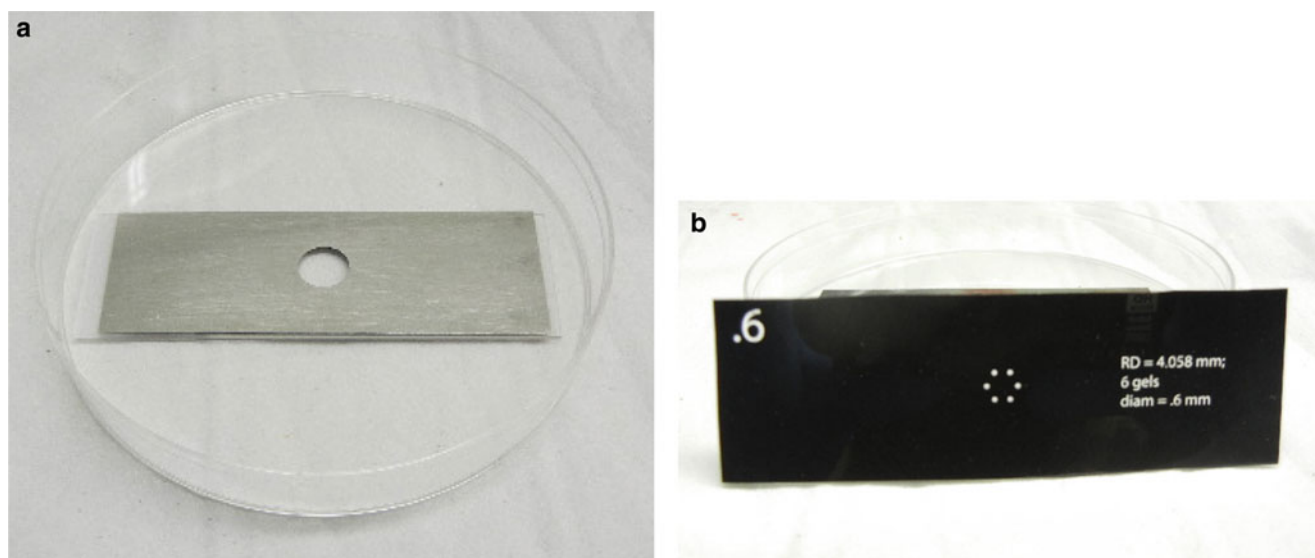


Fig. 2.1 Pictures of the substrate and spacer as well as the mask being used. (a) Substrate and spacer. (b) Mask

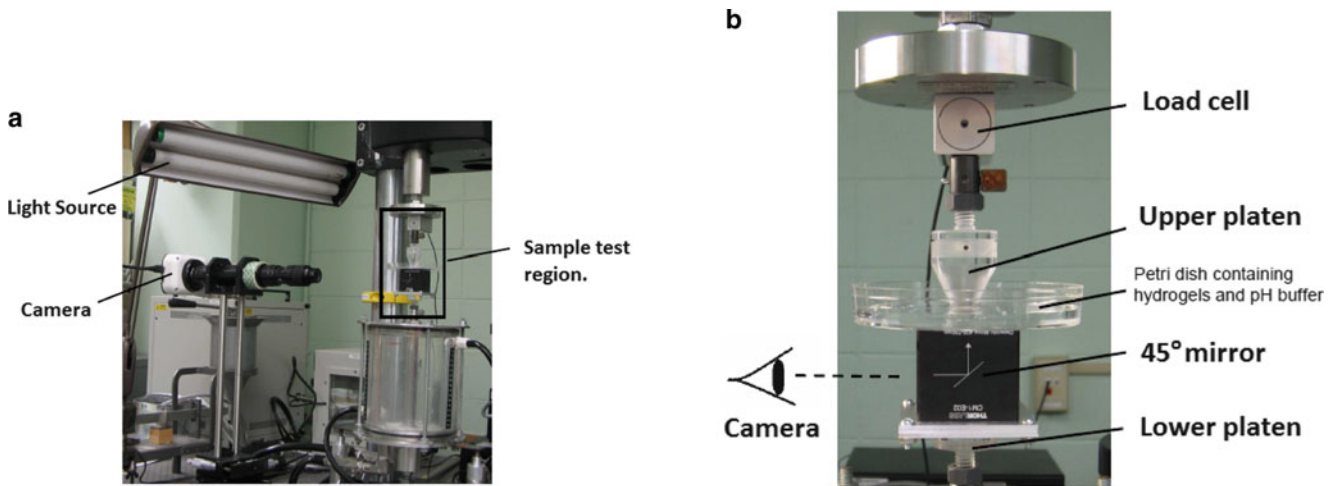


Fig. 2.2 Pictures of experimental setup and a closeup of the sample. (a) Experimental setup. (b) Close up of sample, mirror and compression platens

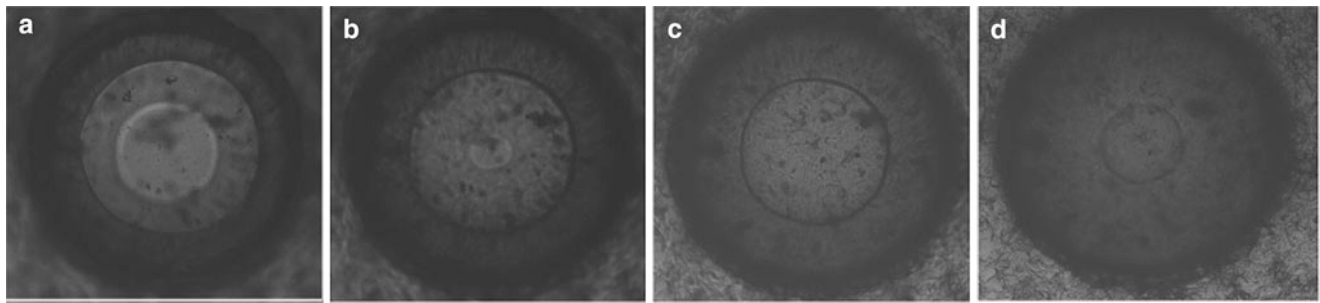


Fig. 2.3 Swelling of the responsive hydrogel on the frosted slides at (a) 5 min, (b) 10 min, (c) 15 min and (d) 30 min

2.2.3 Responsive Hydrogel Testing

The responsive hydrogels were polymerized on premium fully frosted microscope glass slides (cat. 12-544-5CY) purchased from Fisher Scientific. The responsive hydrogel is allowed to swell in 3.0 pH buffer solution for a period of 120 min. Images were taken every 30 sec using a 45° mirror below the substrate so that the bottom of the hydrogels could be viewed as they swelled. A Q-Imaging MicroPublisher 5.0 RTV camera with an Optem Zoom 200 lens was used to image samples during the test (Fig. 2.2). QCapture Pro software was used to record images.

2.3 Experimental Results

2.3.1 Delamination of Responsive Hydrogel Constrained in z -Direction

The height of the hydrogel posts are constrained such that no diffusion is allowed to take place at the top of the hydrogel. When the 3.0 pH buffer solution is added diffusion takes place only around the sides of the hydrogel posts.

As the gel swells, the outer ring of the gel delaminates from the substrate first. With further swelling, this ring of delamination propagates radially inward and creates a circular delamination front. Several images in Fig. 2.3 shows two fronts. The inner most front is associated with the top platen and completely delaminates between 10 and 20 min. Full delamination of the gel from the substrate occurs between 30 and 35 min of swelling. Between the times of 30 and 35 min the slow propagation of the delamination front becomes rapid and quickly completes the delamination process.

2.4 Discussion

During the polymerization process described above, the base of a hydrogel post becomes adhered to the substrate upon which it is polymerized. The un-adhered surfaces can be exposed to a stimulus, such as a pH solution, which causes swelling. When a responsive hydrogel sample is fabricated on a substrate in the manner described above and then exposed to a pH solution, the forces produced by volume expansion during swelling can be large enough to cause delamination at the interface between the hydrogel and the substrate. The delamination front and overall change in outer dimension of the gel post were observed optically. This experimental technique provides a system in which several parameters can be measured during the swelling and delamination process for a range of hydrogel/substrate material combinations.

The delamination front can be viewed at the edge of a propagating crack. From this view point fracture mechanics concepts can be employed. We define the *energy release rate* G as the energy present when external work is done to propagate a crack. We define R as the *crack resistance* and this corresponds to the elastic surface energy of the crack surfaces [19]. As work is done to propagate the crack, diffusion of the buffer solution into the hydrogel as well as osmotic pressure due to the chemical reaction of the hydrogel to the pH of the solution occurs and the interface is disrupted. The condition for stable crack growth is,

$$G \geq R \quad (2.1)$$

where the value for G can be determined experimentally and the value for R is determined by the geometry of the system. By finding values for G and R the interfacial energy can be obtained.

2.5 Conclusion

In this experiment cylindrical posts were fabricated from a (HEMA-DMAEMA) responsive polymer liquid solution, and subsequently caused to swell. A delamination front between the gel and the substrate was observed to propagate inwards as the gel expanded outwards. The propagation of the delamination front closely resembles that of a propagating crack front. Using this analogy, the interfacial adhesion energy can be calculated using fracture mechanics. In ongoing work an analytical model is being formulated by use of fracture mechanics.

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