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A Methodology to Determine Spherical Hydrogel Swelling Kinetics and Stress-Strain Relationships

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Abstract

This study developed experimental methods to determine: a) the swelling characteristics of hydro-gel spheres; and b) their stress-strain characteristics, as a function of the induced swelling, and to compare experimental results with theoretical-analytical formulations. Hydrogels absorb large volumes of water during swelling and have many applications, including pharmaceutical, agriculture and many household products. The characterization of swelling dependent stiffness is a critical first step in potential utilization of hydrogels for stabilization of loose saturated ground subject to earthquake vibrations. The rate of hydrogel swelling and change in the stiffness will have direct impact on interlocking forces necessary to stabilize against liquefaction. Experimental methodology described in this paper is developed and carried out on generic swelling water beads used for plant hydration. The observed swelling is well captured by the spherical diffusion model through collective diffusion coefficient, and a linear relationship is established for swelling dependent stiffness in a log-log scale.

Keywords: Hydrogel, Liquefaction, Stability, Swelling

1. Introduction:

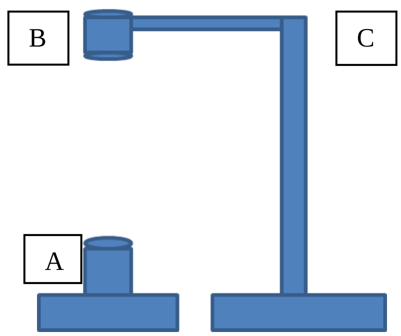
Soil liquefaction is the collapse of a saturated loose soil subject to vibration due to earthquake. As a result of the vibration the fluid in the voids gets pressurized and pushes the soil apart, reducing particle contact and friction forces and resulting in a loss of stability. This type of response causes the ground to act like a quicksand momentarily and can lead to extensive damage and structural failure of buildings residing on the surface. The use of hydrogel particles within soil and their expansion may result in increased contact forces and enhanced friction between particles.

Hydrogels are formed from various levels of networked polymer chains. The hydrogels have been utilized from drug delivery to sensing[1] and actuation. The swelling dynamics of spherical[2,3] disks and cylindrical gels[4,5,6] are subject to various formulations. The purpose of this project was to develop and evaluate a methodology that can be used to characterize potential candidate hydrogels. The two properties of interest, for this project, are the Swelling Kinetics and the swelling dependent Stress-Strain characteristics of hydrogel spheres. Swelling Kinetics describes the time dependent enlargement due to water sorption by diffusion. Swelled Stress-Strain characteristics describe the load-deformation response which depends on the amount of water the gel has absorbed in relationship to its mass. This paper will describe the methods developed to ascertain these properties.

2. Methodology:

2.1 Free Swelling Data Collection:

A volumetric measurement approach through Time Lapsed Photography of the spherical hydrogel free swelling in water was used to obtain the swelling kinetics response of the hydrogel. The experimental setup consisted of a Plexiglas® cylindrical container, of 2.5 inch diameter and 3 inch height, with a camera filter lens fitted at the bottom to reduce distortions as an interface for imaging. The sample container was placed at a fixed distance above a camera. The hydrogel diameter and weight were measured and recorded at the dry state. A calibration target consisting of known dimensions at various heights was used to adjust for change in perspective with distance in the water filled container. The obtained perspective calibration is required to calculate the correct dimension of swelling hydrogel as the distance between particle diameter and camera lens increases during the hydrogel swelling. A single hydrogel was placed in the center of the container. The camera was focused to target on the hydrogel in the center of the camera's view and set to take a picture every 30 seconds for the entire period of swelling. Concurrent with the camera being started the container was filled with water.



A: The Camera
B: The Plexiglas® container
C: The raised clamp, to hold the container

Figure 1: Free swelling test apparatus

The apparent hydrogel dimensions were obtained from images and corrected to obtain actual dimensions. The calibration/correction process addressed issues such as acquiring images through an interface, within a fluid, and on a particle that changes size and focal distance during the entire process. The first of these issues was the change in perspective caused by distance going through the air, filter lens and water. This was corrected by using a calibration target of known height and lateral dimensions at several elevations. The calibration target and hydrogel will obey identical perspective distortion in fluid allowing to conversion of measured pixels to actual length while accounting for change in perspective. The lens distortion can cause the objects in the center of the camera's field of vision to appear to have a different size than similar sized objects on the edge. This was accounted for by taking a picture, at 90 degrees, of a square gridded graph paper. The heights and widths of the squares in the central area, where the hydrogel and calibration target would be, were measured. They were all found to be within 1/32 of an inch of each other, and within the expected accuracy of the image acquisition.

Image analysis was handled in ImageJ version 1.47d, with the FIJI distribution[7]. The calibration for perspective distortion was used to create the size scale. The isotropic swelling of "spherical" gel provides a known relationship between the measured apparent diameter and the perspective change due to increase in distance between hydrogel diameter and the lens. This change in distance and the apparent measured diameter are related geometrically through similar triangles, and provide the scale correction needed for conversion. A macro was created in ImageJ and applied to the image sequence of the test. The application of the macro automated the measurement of hydrogel size from sequence of images. The macro converted the images to gray scale, the spheroid particle area was obtained and the average diameter for hydrogel was determined for each image. Furthermore a color thresholding approach was used to identify the water front diffusing into the hydrogel. These measurements were then entered into a spreadsheet, scaled and corrected for height distortion. A graph of measured change in radius with time due to swelling was obtained.

2.1 Free Swelling Data Analysis:

The swelling kinetics of the hydrogel can be expressed through the diffusion equation in spherical coordinates, subject to no displacement at the center, and no surface stresses boundary conditions. The spherical geometry of the hydrogel leads to isotropic and symmetrical swelling. Tanaka and Fillmore[8] obtained a closed form solution for the spherical hydrogel subject to free swelling as shown below. Their equation models a simple two way diffusion problem. The expansion in radius (u) is expressed as:

$$u(t) = -6(R_f - R_i) \cdot \sum_{n=1}^{\infty} \frac{(-1)^n}{\lambda_n R_f} \left[\frac{\lambda_n R_f \cos(\lambda_n R_f) - \sin(\lambda_n R_f)}{(\lambda_n R_f)^2} \right] e^{-D\lambda_n^2 t} \quad (1)$$

$$\lambda_n = \frac{n\pi}{R_f}$$

Where R_f and R_i are the final and initial radius of the gel, t is the time, and D is the Collective Diffusion Coefficient.

2.2 Swollen Stiffness Data Collection:

The swollen stress-strain characteristics were ascertained through load-deformation tests. Hydrogels were allowed to reach equilibrium at various stages of swelling for load-deformation testing. The diameters and weights of each gel were measured and recorded prior and upon achieving equilibrium.

A deformation rate controlled micro-loading machine that was equipped with a force sensor, was used for testing (Figure 2). Each hydrogel was then individually tested at a rate of 1/1000 inch per second while recording the force readout. The deformation measurements were conducted by time elapsed photography with images acquired at every 10 seconds. The hydrogel was removed and weighed again at the end of the test.

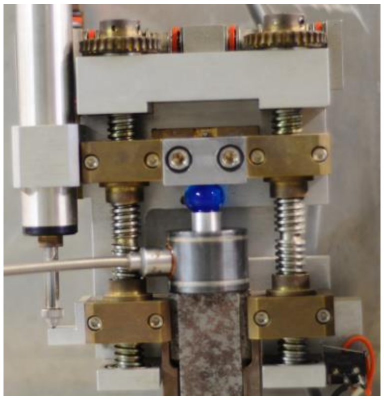


Figure 2: Experimental setup for load-deformation test

The hydrogel dimensions in pixels were converted to inches through known dimension of the pressure pad captured within each image. The pressure pad, being at the same distance from the lens as the center of the hydrogel, had the same perspective distortion as the hydrogel. The information gathered from each image through ImageJ includes, the height, the horizontal diameter of the gel, the width of the bottom contact area, and the width of the top contact area.

2.2 Swollen Stiffness Data Analysis:

A constant collective diffusion parameter, D as determined above for 100% equilibrium swelling is used for this study. Longer equilibrium swelling periods were observed for hydrogels subject to less than 100% fluid concentration suggesting the use of concentration dependent diffusion coefficient for partial swelling samples.

An unloading segment was carried out at the end of the load-deformation test. A full recovery to original dimensions was recorded. This led to the conclusion that the gel was fully elastic for the full range of applied deformation. The Hertzian contact stress model for a spherical particle[9] was used to analytically represent the load-deformation characteristic of the spherical hydrogel (Equation 2). The model response was calibrated with the experimental measurements through which the gel Shear Modulus, G, was obtained. A linear-elastic Hookean modulus and a Rubber Elasticity model based modulus (Equation 3) were also used for similar calculations[10,11,12]

$$\delta = \frac{1}{2R^{1/3}}\left[\frac{3(1-\nu)}{G}N\right]^{2/3} \qquad (2)$$

δ: Vertical deformation

N: Axial force

R: Initial radius

ν: Poisson ratio

G: Shear modulus

$$\sigma = G\left[\alpha - \frac{1}{\alpha^2}\right] \qquad (3)$$

σ: N/A_c

A_c: Contact area

α : Elongation ratio

3. Results and Discussion:

3.1 Free Swelling Results:

The analytical solution, for free swelling, was implemented in MATLAB®, (7.8, R2009a) and used to collocate with the experimental test data allowing the back calculation of the value of $6.7x10^{-5}\,\frac{in^2}{min}$ for the collective diffusion coefficient, D. The experimental and calibrated analytical model responses for the 100% swelling sample are shown below, in Figure 3.

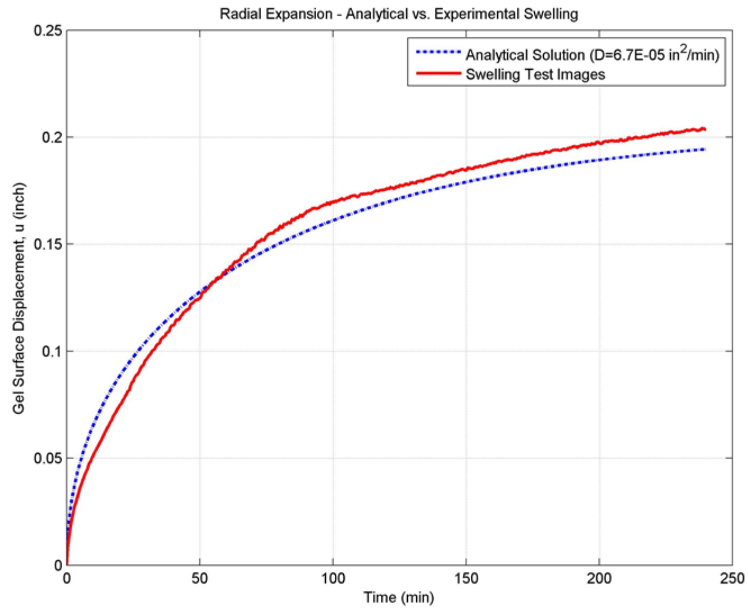


Figure 3: Experimental and analytical swelling response of hydrogel to full swelling

3.2 Swollen Stiffness Results:

The use of Hookean and Rubber Elasticity models lead to shear modulus values of 15,700 Pa and 14,000 Pa respectively for hydrogel samples at fully swollen stage. The experimental and calibrated analytical Hertzian model responses are illustrated in Figure 4. As observed below a calibrated Hookean linear-elastic model provides a good representation of the actual material response up to a deformation of 4mm. A better match over a larger deformation range was achieved through the Rubber Elasticity model; however the elastic response range, of the Hookean model, was accepted as sufficient for the expected deformation levels of this study.

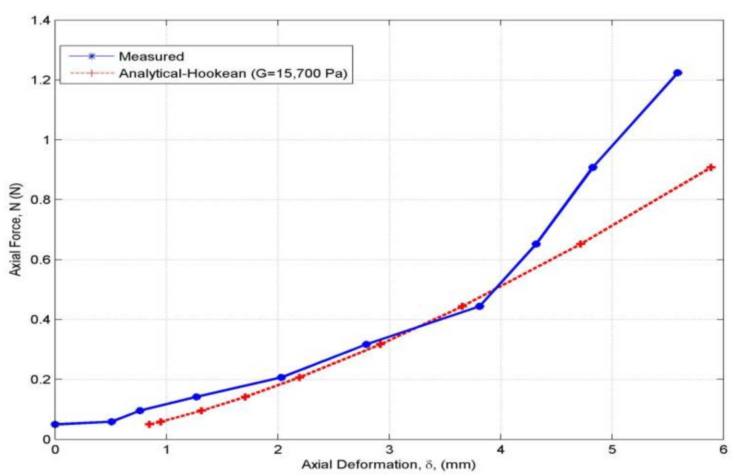


Figure 4: Experimental and analytical load-deformation response of fully swollen spherical hydrogel

Load-deformation tests were conducted for hydrogels swollen to equilibrium at less than 100% fluid concentration. Similar model calibration was conducted for all nine samples to determine the shear modulus. As is the case with most materials, the shear modulus was found to decrease as the swelling ratio increased. A linear relationship, as shown in Figure 5, was obtained between the shear modulus and swelling ratio when plotted in a log-log scale.

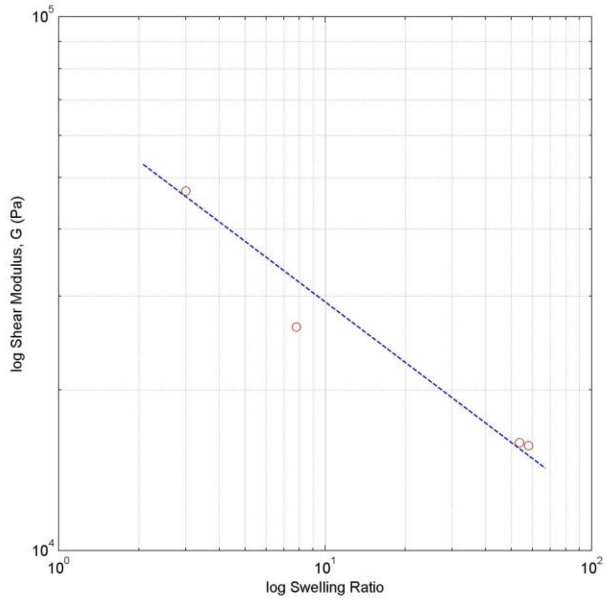


Figure 5: Swelling dependence of Shear Modulus

4. Conclusion:

A methodology was developed to determine spherical hydrogel swelling kinetics and stress-strain relationships. The characteristics, of a specific hydrogel, derived using this methodology compared well to theoretically expected results. The measurement methods utilized were calibrated and verified through existing analytical models. An investigation into concentration (swelling) dependent collective diffusion coefficient, D, is recommended for gels that are subject to swelling in less than 100% moisture.

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