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Features of the volume change and a new constitutive equation of hydrogels under uniaxial compression

Y.R. Zhang[a,d], K.J. Xu[a], Y.L. Bai[a,c], L.Q. Tang[a,b,*], Z.Y. Jiang[a], Y.P. Liu[a], Z.J. Liu[a], L.C. Zhou[a], X.F. Zhou[d]

[a] School of Civil Engineering and Transportation, South China University of Technology, No.381, Wushan Road, Guangzhou, Guangdong, China
[b] State Key Laboratory of Subtropical Building Science, South China University of Technology, No.381, Wushan Road, Guangzhou, Guangdong, China
[c] LNM, Institute of Mechanics, Chinese Academy of Sciences, Beijing, China
[d] Guangdong Institute of Intelligent Manufacturing, Guangzhou, China

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ABSTRACT

For high-water content hydrogels in compression, the water inside of hydrogels contributes to the response of hydrogels to external loads directly, but part of the water is expelled from hydrogels in the meantime to change the volume of the hydrogel and reduce the contribution. In order to consider the contribution of the water in the constitution equation, PVA (polyvinyl alcohol) hydrogels with high-water content were used as examples, and compressive experiments were carried out to measure both the stress-strain relation and the change of the volume in the meantime. By considering the effect of the difference of the contribution of water in different directions of the hydrogel, we deduced a new constitutive equation, which can pretty well depict the stress-strain of hydrogels with different water contents. The results showed that the contribution of water to the total stress increases with the compression strain and even exceed that of the polymer, although the expelled water reduces the contribution at the early loading stage, which well explains the difference of elastic moduli of hydrogels in compression and tension.

1. Introduction

Polymeric hydrogels are promising soft materials in tissue engineering and medicine; that consist of continuous polymerized network structures that can absorb and retain a large amount of water (Baker et al., 2012; Hodge et al., 2015; Kobayashi and Oka, 2004; Oyen, 2013). For tissue engineering applications, the mechanical properties of hydrogels, especially their compressive performance are critical (Curley et al., 2014; Gofman and Buyanov, 2017; Hayes et al., 2016; Kanca et al., 2018; Tingting et al., 2017). The water content of hydrogels can be higher than 90% and even up to 99.7% (Appel et al., 2012; Si et al., 2017), and water is one of the significant factors that causes the hydrogel to respond differently in tension and compression. Polyvinyl alcohol (PVA) hydrogels with about 80% water content are shown in Fig. 1, and the tensile curve is more nonlinear than the compression curve. This is mainly due to the greater change in fiber alignment during the stretching (Dong et al., 2017). Even under small deformation ($< 5\%$), the tension elastic modulus (about 0.15 MPa) of the hydrogel is smaller than the compression modulus (about 0.25 MPa). Within such a small deformation, the tensile and the compressive responses of the polymer network should be similar. Thus, what making the difference between tension and compression in the hydrogel only be the water inside the hydrogel. The water may resist compression but not tension.

The high-water content of hydrogels is one of the key factors that contributes to their excellent biocompatibility and resemblance of living tissues (Ovsianikov et al., 2011; Van Vlierberghe et al., 2011). Free water in hydrogels with high-water content can be expelled out of the specimen under compression, which means that the volume will change even in air (Frensemeier et al., 2010; Milimouk et al., 2001; Nakamura et al., 2001; Urayama et al., 2008; Urayama and Takigawa, 2012; Vervoort et al., 2005; Zhang et al., 2017); therefore, it is necessary to measure the change of volume induced by the expelled water in compression. Most compressive constitutions of hydrogels were summarized phenomenologically from experiment (Kaufman et al., 2008; Korchagin et al., 2007; Sasson et al., 2012; Święszkowski et al., 2006) without considering the effect of expelled water. Professor Suo and his team considered the change of Helmholtz free energy generated by the polymer network stretching and the surrounding environment, and proposed a set of equations of state in which the changes of hydrogel volume were included (Cai and Suo, 2012; Faghihi et al., 2014; Hong

* Corresponding author at: School of Civil Engineering and Transportation, South China University of Technology, 581 Wushan Road, Guangzhou, Guangdong, China.
E-mail address: lqtang@scut.edu.cn (L.Q. Tang).

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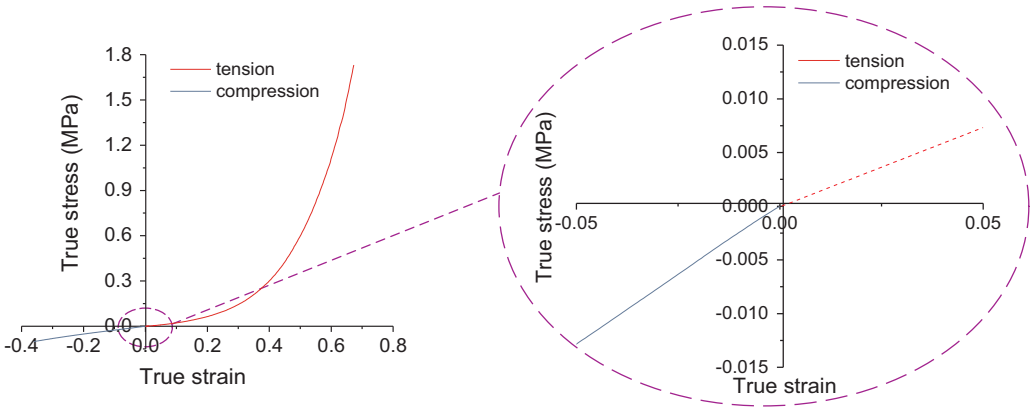

Fig. 1. The difference of the tensile and compressive properties of the PVA hydrogel with about 80% water content.

et al., 2008; Hong et al., 2009; Hong et al., 2010; Li et al., 2014; Marcombe et al., 2010). In these models, the contributions of water are directly related to the change of volume of water, which means that the water's contributions to hydrogel stresses are the same in all directions. However, such an assumption is questionable when the deformation of the hydrogel is large.

To study the contribution of water, the volume change should be measured first. Although the measurement of expelled water from hydrogels is very difficult, several researchers have reported experiments. Urayama et al. (2008), Urayama and Takigawa (2012) and Vervoort et al. (2005) measured the volume loss by digital image processing and obtained the correlation between the loss amount and some experimental conditions such as loading rate, water content of specimens and boundary friction. These experiments with digital image methods have great reference value, but there are still some technical difficulties for measuring the volume changes of hydrogels: hydrogels are so soft that the samples may not maintain their revolving shape, and the semi-transparency may blur the specimen boundaries.

In this paper, we used high-water content PVA hydrogels as examples to study the volume change behaviour under compression. We used experiments to measure the uniaxial stress-strain relations and the change of volume. The volume measurements used a digital image-based system in which two cameras ensured the volumes of the specimens under axisymmetrical deformations. Furthermore, to distinguish the contributions of the polymer network and the water of hydrogels in compression, we deduced a constitutive equation considering the different contributions of water to hydrogel stresses under different directions. The model not only explains the contributions of the polymer network and water in compression, but it also explains the differences in elastic moduli of hydrogels in compression and tension.

2. Method

2.1. Experiment

2.1.1. Sample preparation

The mixture of PVA powder (SIGMA-ALDRICH, Mw 89000–98000) and deionized water was maintained at 110 °C in an autoclave for approximately 5 h. The mass of water was decided according to the desired water content of the mixture. The viscous aqueous PVA solution was poured into moulds and subjected to 6 cycles between −25 °C and 25 °C, and each period was 12 h. The height of samples was 30 mm, and the diameter was also 30 mm. Fig. 2(a) is a photo of three samples with different water contents, and Fig. 2(b) is their remaining polymer after drying. The exact initial water content c_w of each specimen was determined by a drying test after the compressive experiment,

$$c_w = \frac{m_{whole} - m_{dry}}{m_{whole}} \quad (1)$$

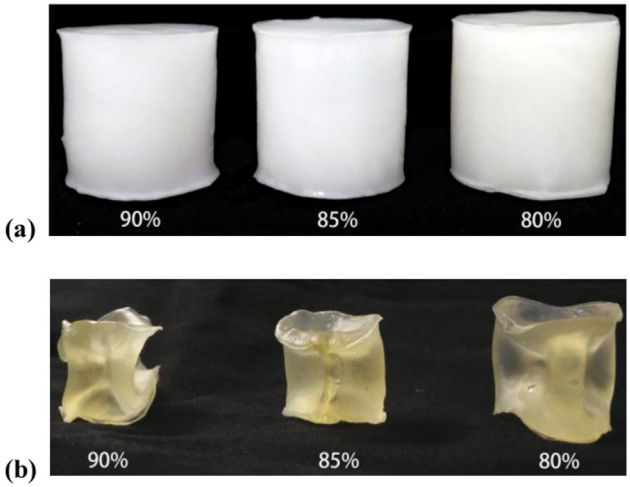

Fig. 2. Photos of the sample: (a) three PVA hydrogel samples with different water content: 90%, 85% and 80%. (b) The remaining polymer after drying the samples.

where m_{whole} is the mass of the sample, and m_{dry} is the remaining mass after drying.

2.1.2. Volume measurement

Digital image processing can evaluate the volume variation (or Poisson's ratio) during loading without contact (Baghereih et al., 2008; Chen et al., 2013; Pritchard et al., 2013; Urayama et al., 1993). We also used this technique to measure the volume change of the hydrogels. As mentioned above, soft specimens may deform unexpectedly during loading. Thus, calculation methods using a revolving column become inapplicable. Therefore, the deformations need to be monitored and such specimens should be removed. Besides, the sharpness of the specimen contour is crucial to the reliability of the experimental results, but the translucence of PVA hydrogels decreases photo clarity. To solve these two problems, we used two cameras to record deformation from different directions concurrently. We used fluorescent powder to cover the specimen surface so that the self-luminous specimens contrast strongly with a dark background (Fig. 3). Imaging data are sufficient to calculate the volume of a revolving body, and the second camera can monitor whether the specimen has shear or other unexpected deformation. The dark environment can be achieved with a large carton. More details of the experimental method are introduced in Appendix I.

2.1.3. Testing system

The two SLR (single lens reflex) cameras were Canon 80D (EF-S 18–200 mm f/3.5–5.6 IS) and Sony α55 (DT 3.5–5.6/18–55 SAM). The