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Surface wrinkles of swelling gels under arbitrary lateral confinements

Chen-Hsueh Yang, Yu-Yun Lin*

National Cheng Kung University, Department of Civil Engineering, Tainan, Taiwan

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ABSTRACT

Based on perturbation analysis, this study investigates surface wrinkling of a gel layer under arbitrary lateral confinements in the equilibrium state of swelling. Gels containing incompressible polymer networks and solvents may incur large deformations and increase the volume by several times after swelling. Owing to the restrictions on lateral expansions and surface imperfections, the instabilities may appear in the form of wrinkling. Wrinkling is strongly governed by the compressibility of swollen gel, confinements and gel thickness. Additionally, gel compressibility is attributed to the migration of solvent under stress at the confined-swelling state, and can be expressed in terms of a confined-swelling volume ratio. This work also discusses possible gel-solvent systems of wrinkling under different confinements. At equal biaxial confinements, the wrinkle pattern is a combination of plane waves with the same wavelength in all directions. Meanwhile, at non-equal biaxial confinements, the wrinkle pattern may be a sum of plane waves with dissimilar wavelengths and corresponding directions.

1. Introduction

Elastic instability generally occurs when a solid is subjected to large compressive forces. A similar instability phenomenon may also be observed on the surfaces of constrained swollen gels, as schematically shown in Fig. 1(a) (Southern and Thomas, 1965; Matsuo and Tanaka, 1992; Tanaka et al., 1992, 1987; Trujillo et al., 2008; Guvendiren et al., 2010a, 2010b; Yang et al., 2010). Gels, which consist of a solid polymer network and liquid solvents, swell when the solvents are absorbed into the polymer network, and shrink when the solvents flow out of the polymer network. Gel volume depends on the amount of liquid solvent imbibed, and may be significantly larger than that in dry state. For a situation in which a gel is bonded on a substrate and confined laterally, internal pressure is generated when it swells. Magnitude of the internal pressure depends on the geometrical configuration and the gel constraint, as well as the chemical composition of a solid network and solvents. When the pressure exceeds a certain level, the instability pattern is formed on the gel surface. As often observed in gel experiments, there are two distinct modes of swell-induced surface instability: wrinkles and creases (Hong et al., 2009b; Guvendiren et al., 2010a, 2010b; Yang et al., 2010). Wrinkles typically occur on gels after a brief swelling (Chan et al., 2008) or on a swollen gel with graded property (Guvendiren et al., 2010a, 2010b), subsequently forming patterns of small undulation that deviate from the flat state. Whereas creases form sharp folds and self-contacting surfaces on gels with extensive swelling (Trujillo et al., 2008). By adjusting the solvent quality, Guvendiren et al. (2010b) demonstrated the pattern transition from wrinkles to creases in thickness-gradient gels.

Biot's (1963) pioneering work on the calculation of elastomers introduced the analysis of surface instability. Biot (1963, 1965) and Nowinski (1969) both analyzed the linear instability of an incompressible hyperelastic half space subjected to lateral compression (Fig. 1(b)). The former considered the surface instability pattern as a plane wave, whereas the later extended the analysis to an arbitrary wavy pattern. Usmani and Beatty (1974) later analyzed the condition to form arbitrary surface patterns on a compressible hyperelastic half-space. For a half-space, linear instability analysis lacks a length scale, explaining the impossibility of determining the wavelength of a wavy pattern. The characteristic of an arbitrary wavy pattern is given by the wave ratio, n, the ratio of the wave numbers along two principal axes on the surface. The instability condition is given by a critical relative stretch ratio, which is defined by the ratio of the in-plane stretch to the out-of-plane stretch. This condition also depends on the compressibility of elastomer and the wave ratio. However, Gent and Cho (1999) found a sharp fold in an experiment involving bent rubber. Also, the condition for instability to occur is lower than the critical value, $\varepsilon_c \approx 0.46$, predicted by Biot's analysis.

Onuki (1989) studied the pattern formation of gels due to swelling, including wrinkling and creasing. In that study, a gel of finite thickness was confined equal-biaxially during swelling. Kang and Huang (2010) analyzed the wrinkling instabilities of swollen

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* Corresponding author. Tel.: +886 62757575.
E-mail address: cyylin@mail.ncku.edu.tw (Y.-Y. Lin).

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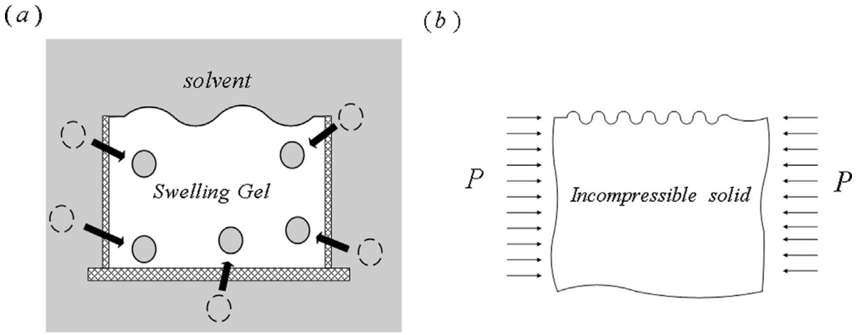

Fig. 1. (a) Instability pattern appearing on the surface of a confined swelling gel (b) Surface instability of an incompressible hyperelastic half-space subjected to compression.

hydrogel layer, which is laterally fixed from dry state. Above studies both assumed the wrinkling pattern of a plane wave. Owing to finite thickness of gels, the wavelengths of plane-wave pattern appear in the analysis, and affect the condition of wrinkling. While expressing this condition by the swelling ratio, Kang and Huang (2010) showed its dependence on gel parameters. Whereas Onuki (1989) used the relative stretch ratio as the wrinkling criteria, which is the same as in Usmani and Beatty (1974). Because Onuki considered the swollen gel as a compressible hyperelastic solid, the wrinkling criteria is expressed in terms of the effective compressibility of gels, which should be determined by gel parameters and deformation. However that study did not discuss this point further.

The feasibility of manipulating the swelling induced instability to create a desired surface pattern in wide applications has received considerable attention (Chan et al., 2008; Yang et al., 2010). More thoroughly understanding the critical condition of surface instability could facilitate the development of the controllable surface pattern, including wavelength and wave ratio. Therefore, this work develops an instability analysis for arbitrary wrinkling patterns by swelling on a gel layer under biaxial confinements. The proposed formulation is based on Biot's incremental deformation method (Biot, 1963, 1965). In this work, the solid network and solvent molecules in gels are assumed to be both incompressible. The entire swollen gel behaves like a compressible elastic solid, because solvents migrate into or out of a gel when subjected to stresses. The compressibility is generally coupled to the equilibrium configuration and the energy function of gel. As is expected, the normalized wave number, wave ratio and, most importantly the compressibility of the confined swelling gel should affect the instability solution. The compressibility for a wide range of gel parameters is studied in this paper, as well as how it affects the critical confinements of wrinkling.

2. Free-energy function of gel

While assuming that all molecules in a gel are incompressible, many studies have attempted to formulate a coupled deformation–diffusion theory for describing the nonlinear response of gels (Hong et al., 2008; Chester and Anand, 2010; Bouklas and Huang, 2012). However, considering many polymers are compressible, Chester and Anand (2011) took into account the compressibility of polymeric molecules and developed a thermo-mechanically coupled theory. Chester (2012) later extended that theory to include the viscoelastic property of polymeric molecules. In this work, we follow the assumption of molecular incompressibility (Hong et al., 2009a), i.e. both solid molecules and solvent molecules are incompressible.

The free energy of gel consists of strain energy W_e of a solid polymer network and mixing energy W_m between solvent molecules and the polymer network. The strain energy function W_e is related to the deformation of a polymer network, i.e. $W_e = W_e(I_1, I_2, I_3)$, where I_1, I_2, I_3 denote three invariants of Cauchy–Green strain tensor $\mathbf{B} = \mathbf{F}\mathbf{F}^T$, and $\mathbf{F}$ represents the deformation gradient. For instance, W_e can take the following form (Rivlin, 1948; Flory, 1950; Treloar, 1975; Hong et al., 2008, 2009a; Bouklas and Huang, 2012) of

$$W_e = \frac{1}{2}Nk_BT(I_1 - 3 - 2\ln J) \tag{1}$$

where $I_1 = F_{ij}F_{ij}$, $I_3 = \det(F_{ij})^2 = J^2$ and F_{ij} denote the components of deformation gradient $\mathbf{F}$; parameter k_B represents the Boltzmann constant; and N refers to the number of polymer chains per unit volume. The mixing energy W_m between solvent and polymer network can be expressed as

$$W_m = \frac{k_BT}{\nu}\left(\nu C\ln\frac{\nu C}{1+\nu C} + \frac{\chi\nu C}{1+\nu C}\right) \tag{2}$$

based on Flory–Huggins polymer solution theory (Huggins, 1941; Flory, 1950, 1953; Hong et al., 2008, 2009a; Kang and Huang, 2010; Bouklas and Huang, 2012), where concentration C denotes the number of solvent molecules per volume; χ represents the dimensionless interaction parameter between polymer network and solvent; and ν refers to the volume per solvent molecule. The gel volume consists of the volume of a polymer network and solvent molecules. According to the incompressibility of both solvent and network molecules, the total volume of a unit gel is

$$J = \det(\mathbf{F}) = 1 + \nu C \tag{3}$$

Since concentration C can be expressed as a function of F_{ij} and chemical potential μ, free energy function in the equilibrium state can be easily written in terms of the chemical potential μ using Legendre transformation (Hong et al., 2008, 2009a) as

$$W = W_e + W_m - \mu C \tag{4}$$

Based on (1)–(3), Eq. (4) can be written as

$$W = \frac{1}{2}Nk_BT(I_1 - 3 - 2\ln J) + \frac{k_BT}{\nu}\left[(J-1)\ln\frac{J-1}{J} + \frac{\chi(J-1)}{J}\right] - \frac{\mu}{\nu}(J-1) \tag{5}$$