Effect of geometrical imperfections on swelling-induced buckling patterns in gel films with a square lattice of holes

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Dai Okumura [a,b,*], Tsuyoshi Kuwayama [b], Nobutada Ohno [a,b]

[a] *Department of Mechanical Science and Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*
[b] *Department of Computational Science and Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

ARTICLE INFO

ABSTRACT

In this study, we investigate the effect of geometrical imperfections on swelling-induced buckling patterns in gel films with a square lattice of holes. Finite element analysis is performed using the inhomogeneous field theory of polymeric gels in equilibrium proposed by Hong et al. (2009). Periodic units consisting of 2×2 and 10×10 unit cells are analyzed under a generalized plane strain assumption. Geometrical imperfections are introduced using randomly oriented elliptical holes. The 2×2 unit cells show that the resulting buckling patterns are sensitive to imperfections; three different buckling patterns are obtained, and the most dominant one is the diamond plate pattern observed in experiments, which cannot be described using the model without imperfections. The 10×10 unit cells reveal that random imperfections are responsible for inducing homogeneous transformation into the diamond plate pattern. Furthermore, domain wall formation is simulated using a 10×10 unit cell model containing two elliptic holes.

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1. Introduction

Swelling-induced instability creates a variety of complex and periodic wrinkle patterns in thin polymeric films (e.g., Tanaka et al., 1987; Guvendiren et al., 2009; Cai et al., 2011), and also causes more complicated pattern transformation in thin polymeric films with periodic arrangements of holes (Zhang et al., 2008; Singamaneni et al., 2009; Zhu et al., 2012). This instability and the resulting pattern transformation are spontaneously induced by in-plane compressive stress caused by solvent swelling of thin polymeric films constrained on a substrate. The resulting complicated periodic patterns have wavelengths in the order of 0.1–10 μm, and can form over large regions depending on the size of a film. This property has allowed researchers to create complex patterns on nano- and microscales, switch photonic and phononic properties, tune surface adhesion and wetting, and develop nano-printing methods (Zhang et al., 2008; Jang et al., 2009; Yang et al., 2010; Zhu et al., 2012).

When thin polymeric films containing circular holes in a square array are exposed to a solvent, a diamond plate pattern is typically observed (Zhang et al., 2008; Singamaneni et al., 2009; Zhu et al., 2012). The square array of circular holes buckles and transforms

into the diamond plate pattern, in which circular holes are deformed into elliptical slits, and neighboring slits are arranged mutually perpendicular to each other. Experiments using poly(dimethylsiloxane) (PDMS) films (Zhang et al., 2008) revealed that this pattern transformation can occur under a wide range of conditions, including hole diameter d = 0.35–2 μm, pitch l = 0.8–5 μm, and depth h = 4–9 μm. The slits formed in the case of d = 1 μm, l = 2 μm and h = 9 μm are 78 nm wide and 2.3 μm long. It should be noted that although these characteristic dimensions are very small, pattern transformation occurs homogeneously over the entire sample with an area of up to 1 cm² with no random defects.

This homogeneous transformation may be interpreted as a result of microscopic bifurcation of perfectly periodic microstructures (Geymonat et al., 1993; Ohno et al., 2002; Bertoldi et al., 2008). However, scanning electron microscope (SEM) images show that the initial configurations of individual holes are not perfect circles and include obvious irregular imperfections (Zhang et al., 2008). This implies that geometrical imperfections do not strongly affect microscopic bifurcation and the resulting pattern transformation. On the contrary, this observation suggests the possibility that geometrical imperfections play an important role in causing the homogeneous transformation. It is therefore interesting and worthwhile to investigate the effect of geometrical imperfections, and to elucidate the mechanism underlying the homogeneous transformation into the diamond plate pattern.

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* Corresponding author at: Department of Mechanical Science and Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan. Tel.: +81 52 789 2671; fax: +81 52 789 4477.

E-mail address: okumura@mech.nagoya-u.ac.jp (D. Okumura).

Zhang et al. (2008) and Matsumoto and Kamien (2009) used the linear elasticity theory to demonstrate that the diamond plate pattern minimizes the strain energy. They assumed that each hole collapses to a slit with an arbitrary orientation, and used the theory of cracks to model the slits as a double climb pileup of edge dislocations; i.e., a dislocation dipole (Hirth and Lothe, 1982). They calculated the set of individual orientations of slits that minimizes the strain energy, correctly predicting the orientational order in the diamond plate pattern. However, as stated by Matsumoto and Kamien (2009), their method did not intend to capture the entire deformation process of the collapse of the holes. The presence of imperfections could not be considered in their analysis, so their method cannot access the effect of geometrical imperfections on the homogeneous transformation of gel films.

Hong et al. (2009) developed an inhomogeneous field theory of polymeric gels in equilibrium, and performed a finite element analysis of the diamond plate pattern to demonstrate the wide applicability of their theory. In their theory, the free energy function of Flory and Rehner (1943) was applied to polymeric gels, and was implemented into the finite element package Abaqus using a user-defined subroutine UHYPER. Hong et al. (2009) successfully reproduced the diamond plate pattern using a particular unit cell containing quarters of four neighboring holes. The initial and deformed configurations of the unit cell were depicted in their paper. The present authors however found by measuring the initial dimensions in the figure that they introduced an imperfection into one of holes. The imperfect hole is elliptical, with its major diameter in the horizontal direction, and promotes the transformation into the diamond plate pattern. Ding et al. (2013) might have used the same unit cell to reproduce the diamond plate pattern, but imperfections were not mentioned in their paper. Therefore, more general analyses including random imperfections, as well as using larger periodic units have not been performed yet.

In the present study, the effect of geometrical imperfections on the swelling-induced buckling patterns in thin gel films with holes in a square array is investigated. Finite element analysis is performed using the inhomogeneous field theory developed by Hong et al. (2009), which is briefly described in Section 2. Section 3 is devoted to numerical modeling. Geometrical imperfections are introduced as randomly oriented elliptical holes. Periodic units consisting of 2×2 and 10×10 unit cells are analyzed under a generalized plane strain assumption. A measure of deviation from roundness is defined to quantify the progress of pattern formation. Section 4 presents and interprets numerical results. The buckling patterns predicted using 2×2 and 10×10 unit cells are shown, and the mechanism of homogeneous transformation into the diamond plate pattern and the role of geometrical imperfections are discussed. In addition, in Section 5, the domain wall formation observed by Zhang et al. (2008) is taken up for simulation using a 10×10 unit cell model containing two elliptic holes as basic geometrical imperfections. Finally, Section 6 summarizes the results of this study.

2. Inhomogeneous field theory

This section briefly describes the inhomogeneous field theory of polymeric gels in equilibrium, which was developed by Hong et al. (2009). This theory considers that a polymer network is in contact with a solvent and subjected to mechanical loads and geometric constraints at a constant temperature. If the stress-free, dry network is taken as the reference state, the deformation gradient of the network is defined as $F_{ij} = dx_i(\mathbf{X})/dX_j$, where X_j and $x_i(\mathbf{X})$ are the network coordinates of a gel system in reference and deformed states, respectively. When $C(\mathbf{X})$ is defined as the concentration of solvent molecules at a point in the gel system, the gel is in an equilibrium state characterized by the two fields $x_i(\mathbf{X})$ and $C(\mathbf{X})$. The free energy density of the gel, W, is assumed to be a function of the deformation gradient, $\mathbf{F}$, and the concentration of solvent in the gel, C; i.e., $W(\mathbf{F}, C)$. The inhomogeneous field theory may be applied to various free energy functions for swelling elastomers, but in this study, the specific free energy function of Flory and Rehner (1943) is used. This is because this form is well known to provide a basic for the interpretation of the swelling behavior of polymeric gels (Treloar, 1975).

The free energy function of Flory and Rehner (1943) for a polymeric gel consists of two terms associated with stretching and mixing of the free energies, and is written as

$$W = \frac{1}{2}NkT(I - 3 - 2\log J) - \frac{kT}{\upsilon}\left[\upsilon C \log\left(1 + \frac{1}{\upsilon C}\right) + \frac{\chi}{1 + \upsilon C}\right], \quad (1)$$

where $I = F_{ij}F_{ij}$ and $J = \det \mathbf{F}$ are invariants of the deformation gradient, N is the number of polymeric chains per reference volume, kT is the absolute temperature in the unit of energy, υ is the volume per solvent molecule, and χ is a dimensionless parameter that characterizes the enthalpy of mixing. As stated above, Eq. (1) takes an explicit form as a function of the deformation gradient, $\mathbf{F}$, and the solvent concentration, C.

Considering δx_i and δC to be arbitrary variations of x_i and C, respectively, from a state of equilibrium, the virtual work principle gives an equilibrium equation in which the change of the free energy of the gel equals the sum of the work caused by external mechanical force and external solvent. That is,

$$\int_V \delta W dV = \int_V B_i \delta x_i dV + \int_A T_i \delta x_i dA + \mu \int_V \delta C dV, \quad (2)$$

where V is the reference volume, and A is the reference surface. The first and second terms on the right hand side are the mechanical work done by body forces and surface forces, respectively, and the third term represents the work done by the external solvent. Here, μ is the chemical potential of the external solvent, and is equivalent to that in the gel; that is,

$$\mu = \frac{\partial W}{\partial C}. \quad (3)$$

A Legendre transformation allows the free energy function $W(\mathbf{F}, C)$ to be transformed into another form (Hong et al., 2009),

$$\hat{W} = W - \mu C, \quad (4)$$

which is defined as a function of $\mathbf{F}$ and μ; i.e., $\hat{W}(\mathbf{F}, \mu)$. Combination of Eqs. (2) and (4) leads to

$$\int_V \delta \hat{W} dV = \int_V B_i \delta x_i dV + \int_A T_i \delta x_i dA. \quad (5)$$

When the gel is in a state of equilibrium, the chemical potential of the solvent molecules in the gel is homogeneous and equals the chemical potential of the external solvent, μ. Consequently, μ is regarded as a state variable, and the equilibrium condition (5) takes the same form as that for a hyperelastic solid.

Assuming that the network of polymers and pure liquid solvent are incompressible, the volume of the gel can be expressed as the sum of the volume of the dry network and that of the swelling solvent. This assumption leads to (Hong et al., 2009)

$$1 + \upsilon C = J. \quad (6)$$

Using Eqs. (1), (4), and (6), the Flory–Rehner free energy function can be rewritten as

$$\hat{W} = \frac{1}{2}NkT(I - 3 - 2\log J) - \frac{kT}{\upsilon}\left[(J-1)\log\frac{J}{J-1} + \frac{\chi}{J}\right] - \frac{\mu}{\upsilon}(J-1). \quad (7)$$