

비등방성 좌굴현상에 의한 물리적 자기배열 미세구조

유필진, 서갑양, 박세영, 이홍희
 서울대학교 대학원 응용화학부

Physical Self-Assembly of Microstructures by Anisotropic Buckling

Pil Jin Yoo, Kahp Y. Suh, S. Young Park and Hong H. Lee
 School of Chemical Engineering, Seoul National University

Introduction

Self-assembly involving monolayers has become the cornerstone for fabricating micro- and nano-structures. This self-assembly exploits chemical interactions between a self-assembled monolayer (SAM) and a substrate surface and as such may be termed “chemical” self-assembly. On the other hand, physical forces can be the driving force for self-assembly. The self-assembly realized by physical forces can then be termed “physical” self-assembly to differentiate it from the chemical self-assembly.

Presented in this letter is a physical assembly driven by a mechanical force of stress. When a bilayer of metal and polymer on a substrate is heated above the glass transition temperature of the polymer, buckling takes place to relieve the stress generated by the difference in the thermal expansion coefficients of the two layers.^[1] This buckling is isotropic and the wrinkles generated lack directional order although they have a certain wavelength associated with them. Spontaneous pattern formation has been reported that results due to buckling when a heated thin metal layer on a pre-patterned polymer is cooled.^[2] However, an ordered structure forms only in the vicinity of the pre-patterned underlying polymer surface such that only local, but not global, ordering takes place. In contrast, the physical assembly reported here is global and can be realized without defects over a large area up to several cm². Furthermore, this physical self-assembly has controllability over the direction of ordered pattern whereas previous work does not have.

Theory

We investigate the buckling phenomenon first for the buckling wavelength. For the system being considered, the film thickness of the underlying polymer is finite and of the same order of magnitude as the metal layer. To take into account the effects of the thin underlying layer, we adopt an approach based on a scaling theory for polymer layer.^[3]

For a buckled bilayer of thin film, the total free energy is given by the sum of the bending energy of the metal layer and the deformation energy of the underlying polymer layer. For a sinusoidal deformation in one direction, the low amplitude ($t_m k \ll 1$) wave profile $w(x)$ can be written as

$$w(x) = \varepsilon \sin(kx) \quad (1)$$

where t_m is the metal film thickness, ε is the amplitude of the buckling wave, and the wavelength λ is given $2\pi/k$, k being the wave number. Referring to Figure 1a, the free energy per unit area to bend a

metal film of thickness t_m , Young's modulus E_m and Poisson ratio ν_m is given by^[4]

$$F_{Bending} = \frac{E_m t_m^3}{48(1-\nu_m^2)} \varepsilon^2 k^4 \quad (2)$$

For the free energy of deformation of an isotropic elastic film, we use the free energy expression approximated by the sum of the energy in the long-wavelength limit ($t_p k \ll 1$) and that in the short wavelength limit ($t_p k \gg 1$):

$$F_{Deformation} = \frac{E_p \varepsilon^2}{4k^2 t_p^3} + \frac{1}{6} E_p \varepsilon^2 k \quad (3)$$

where the subscript p is for the polymer layer. For the small amplitude ($\varepsilon \ll \lambda$) being considered, the external strain U can be approximated^[4] by $(\varepsilon k / 2)^2$. Then, the total energy F_t can be written as

$$F_t = \left(\frac{E_m k^2 t_m^3}{12(1-\nu_m^2)} + \frac{E_p}{k^4 t_p^3} + \frac{2E_p}{3k} \right) U \quad (4)$$

The intrinsic buckling wavelength can be obtained by minimizing the free energy with respect to the wave number and in dimensionless form, it is

$$L = \left(\frac{Y}{1 + \sqrt{1 + 12YH^3}} \right)^{\frac{1}{3}} \quad \text{where } L = \frac{\lambda}{2\pi m}, \quad Y = \frac{1}{2(1-\nu_m^2)} \times \frac{E_m}{E_p} \quad \text{and} \quad H = \frac{t_m}{t_p} \quad (5)$$

To test the adequacy of equation 5 in predicting the wavelength, experiments were carried out in which the thicknesses of the metal and the polymer layer were varied with aluminum as the metal and polystyrene (PS) as the polymer on silicon substrate. For the system being considered, $T_0 = 373\text{K}$, $\nu_m = 0.33$, $E_m = 70\text{Gpa}$, $E_{p,0} = 3.2\text{Gpa}$. Shown in Figure 1b by the solid line is the plot of equation 5 with $H (= t_m / t_p)$ as the abscissa, along with the experimental data. It is seen that the agreement between theory and experiment is excellent.

Experimental Method

The procedure involved in the physical self-assembly by anisotropic buckling is illustrated schematically in Figure 2.^[5] As shown in step (a) of the figure, an elastomeric mold, which in this case is polydimethylsiloxane (PDMS) mold, with a certain periodic pattern (line-and-space pattern) is simply placed on the metal surface of the bilayer on a substrate. With the mold in place without any external force, the temperature is raised above the glass transition temperature of the polymer in step (b). After the buckling takes place (step (c)), the mold is simply removed (step (d)), finishing the self-assembly. For the physical self-assembly by anisotropic buckling, we used PDMS (Sylgard 184, Dow Corning) as the elastomer and for the polymer, we used commercial PS (molecular weight = 2.3×10^5) for the polymer and silicon wafer (100) as the substrate. Polymer films were spin-coated onto the substrate to various thicknesses ranging from 150nm to 800nm and the aluminum was deposited onto the polymer surface, ranging in thickness from 30nm to 100nm, by thermal evaporation. A patterned PDMS mold was then placed on the metal surface. The bilayer was then heated to a temperature above the glass transition (T_g) of the polymer for hours, typically two hours. The annealing temperature was varied between 110°C and 130°C . With the PDMS mold making conformal contact with the metal, anisotropic buckling resulted, unlike the isotropic buckling shown in Figure 3, because of the strong wetting of the PDMS pattern with the

metal surface by the strong interactions between the two hydrophobic surfaces. As such, the buckling wave has its peak points in the void regions of the mold that are not in contact with the metal surface. Therefore, sinusoidal buckling patterns form that are a negative replica of the PDMS pattern. After cooling to ambient temperature, the mold was removed and the resulting structures were examined by atomic force microscopy.

Results and Discussion

Figure 4 shows several bilayer structures obtained at 120°C by the anisotropic buckling. It is seen that the random wrinkles such as those in Figure 3 have self-assembled themselves into ordered structures. PDMS molds with protruding lines and spaces between them were used for the results in Figure 4a and b; the molds with a protruding cylinder-shaped dot pattern were used for the results in Figure 4c and d. In the case of the line-and-space pattern (Fig. 4a and b), a sinusoidal line structure forms that is the negative replica of the PDMS mold pattern. In Figure 4a, the period of the line-and-space pattern on the mold is 2μm and the intrinsic buckling wavelength is 2.6μm; in Figure 4b, the period is 4μm and the intrinsic buckling wavelength is 4.2μm. Although the intrinsic buckling wavelength is larger than the period of the mold pattern in both cases, the wrinkles conform to the period dictated by the mold, the period of the self-assembled bilayer being 2μm and 4μm in Figure 4a and b, respectively. As long as the difference is not too large between the intrinsic buckling wavelength and the period of the mold pattern, a sinusoidal surface structure results. The compliance with the mold pattern period is also apparent in Figure 4c and d that were obtained with cylinder-shaped dot patterns. A chessboard-like self-assembly is seen to have resulted in Figure 4c in which the intrinsic wavelength is 2.6μm and the pattern period is 2.4μm. In both micrographs, the cross-sectional profiles were obtained in the direction diagonal to the period.

The sample for Figure 4d was prepared for two purposes, first to check whether the self-assembled peaks are located in the voids of the mold and also to examine the pattern that results when there is a large difference between the intrinsic wavelength and the mold pattern period, which are 3.4μm and 6.3μm, respectively. The self-assembled pattern in Figure 4d shows that the peaks are indeed located in the mold voids. It also shows that instead of the sinusoidal wave observed so far, there results a non-sinusoidal periodic structure and yet the self-assembly still complies with the mold pattern period. With the intrinsic buckling wavelength of 3.4μm, making a one wavelength buckling wave of 6.3μm is energetically too costly. Therefore, instead of making a large bending of metal layer and a deformation of polymer layer with one wave, several small waves are generated in the part of the bilayer corresponding to the void region of the mold. This fact can be verified by the FFT image in Figure 4d.

References

- [1] H. G. Allen, *Analysis and Design of Structural Sandwich Panels*, Pergamon, New York (1969)
- [2] N. Bowden, S. Brittain, J. W. Hutchinson, G. M. Whitesides, *Nature* **393**, 146 (1998)
- [3] G. H. Fredrickson, A. Ajdari, L. Leibler, J. Carton, *Macromolecules* **25**, 2882 (1992)
- [4] J. Groenwold, *Physica A* **298**, 32 (2001)
- [5] P. J. Yoo, K. Y. Suh, S. Y. Park, H. H. Lee, *Adv. Mater.* **18**, in press (2002)

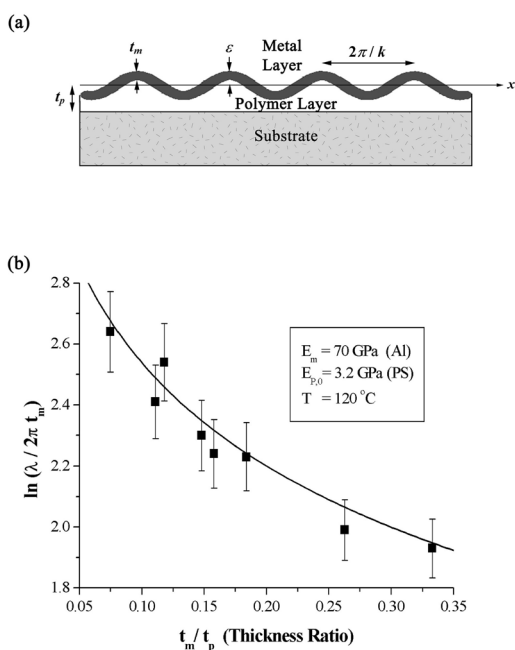


Fig. 1. Comparison between theory and experiment.

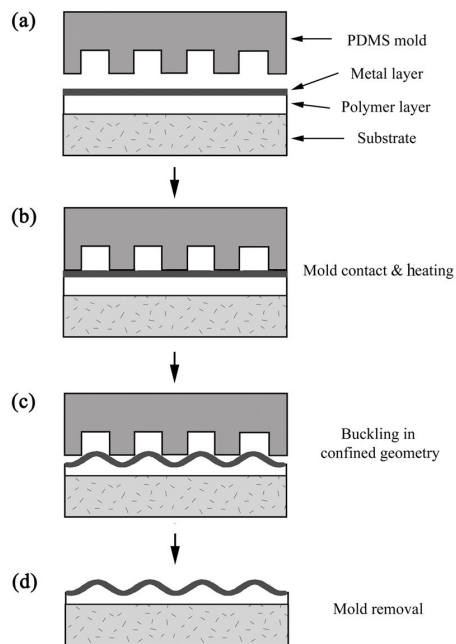


Fig. 2. Schematic illustration of the procedure

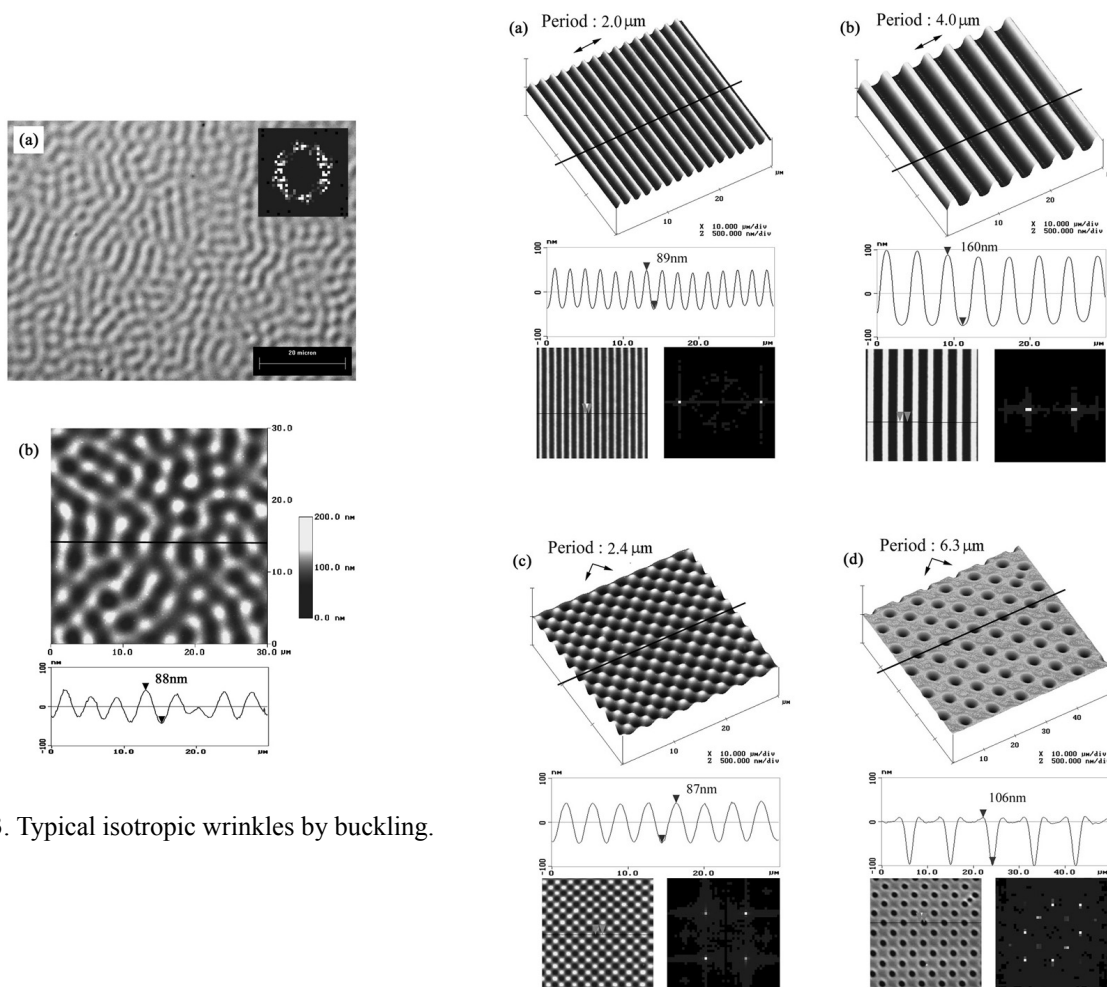


Fig. 3. Typical isotropic wrinkles by buckling.

Fig. 4. Several ordered structures resulting from self-assembly