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Effective formation of hierarchical wavy shapes using weak photopolymerization and gradual thermal curing process

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ABSTRACT

We propose a simple method to generate hierarchical wrinkles on a single-layered substrate by using a weak photopolymerization and a thermal curing process. Rough and relatively large-scale wrinkles having 300–500 μm width sizes are fabricated by a repetitive volume dividing (RVD) method, which is known as one of the effective processes to generate wrinkle patterns in a large area. After generation of the primary wrinkles that are weakly polymerized, microscale wrinkles with width of 10–20 μm on the large-scale ridges are formed spontaneously by room-temperature-based thermal curing. We rationalize the mechanism for the generation of hierarchical abnormal shaped structures and quantify the experimental findings by a parametric study. Through this work, we show the relevance of these structures for use in diverse applications such as surface modification for wettability control and antifouling.

1. Introduction

Surface wrinkles, which are commonly found in the natural world with a huge variety in sizes and shapes, have been a broad area of interest for the development of diverse functional engineering devices. The generation of wrinkles holds significance for research in material science, physics, and chemistry.

There are several meaningful reports on the application of surface periodic shapes. Efimenko et al. used a hierarchical nest having wrinkles in microfluidics [1]. Fu et al. utilized metallic periodic nanostructures for fluorescence sensing to increase the sensitivity for DNA and protein microarrays [2]. Another application of cell alignment using guided wavy patterns was reported in the field of biology research [3,4]. Stafford et al. used wrinkling features in measuring the elastic modulus of polymer films [5]. Chen et al. showed anisotropic formation of wrinkles on memory polymer [6]. Dan et al. suggested a method for controlling surface wrinkles to be used in flexible electronic devices [7]. Harrison et al. utilized the wrinkles as phase gratings [8]. The outstanding features of wavy surfaces also have potential to be used in heat transfer enhancement [9], surface modification [10–12], anisotropic wettability [13–15], and antifouling [16].

With the increasing interest in the various applications of periodic surface patterns, a great deal of research has been devoted to the development of fabrication technologies for wrinkles [17–26]. Ding et al. produced partial wrinkle patterns on the surface of a copper grid using the O_2-plasma process [17], and Lin et al. succeeded in generating wrinkle patterns based on distortion rate disparity caused by surface tension [12]. Guvendiren et al. proposed a process of producing wrinkles through the expansion and contraction of a polymer film by moisture absorption [18]. The thermal mismatch of bi-layered heterostructures causes buckling that generates surface wrinkles [19,20]. Park et al. proposed a simple method to form wrinkles by a repetitive volume dividing (RVD) process [21]. Some works reported on the fabrication of a directional wavy surface using directional pre-stretching of a compliant substrate to overcome the drawback of randomness [22–24]. Others have also been conducted on the formation of surface wrinkles by metal heating, ion beam, and so on [25,26].

The methods for wrinkle generation thus far have centered on the mechanical instability caused by applying physical force or heat on a thin film or substrate. Despite their usefulness and convenience, such methods have the following limitations: (1) the generation of surface wrinkles on a large area cannot be realized easily due to the difficulty in inducing deformation by applying tensile force or compression on a large-area substrate or film and (2) the generation of hierarchically structured wrinkles is limited since the wrinkles produced by the existing methods mostly have single-shaped patterns. The hierarchical wrinkles have a few merits such as the formation of much larger

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surface area and the improvement of surface characteristics like a high contact angle, which can lead to more diverse engineering outcomes.

We propose the facile generation of hierarchical wrinkles using a two-step method, where the RVD process with weak polymerization is conducted to produce relatively large-scale (width of several 100 μm) primary wrinkles using an ultraviolet (UV) photo-curable resin, and secondary fine wrinkles (width of tens of μm) are formed around the ridge of the primary wrinkles by gradual thermal curing at room temperature. In this work, we focused on the simple fabrication process of hierarchical wrinkles and showed their formation mechanism. Then, the morphological characteristics of wrinkles were described. Finally, we discussed the functional features and applicability of the hierarchical wavy shapes by measuring a contact angle on the diverse shapes of surface wrinkles.

2. Methodology

Before proceeding further, it is important to understand the fundamental mechanism of hierarchical wavy surface formation. As described in Fig. 1a, the primary wrinkles having line widths of several 100 μm are realized by the RVD process. By several iterations of contact and detachment of two glass plates, the inner thin layer of resin is divided into a number of small parts, creating many viscous micro-pillars between the plates by the action of infiltration of air inside [21]. Then, UV-light is exposed for a short period of about 30 s or longer to weakly polymerize the surface of the divided resin layer, resulting in sol–gel state wrinkles having a gradient of photo-polymerization according to the direction of thickness. The degree of polymerization differs between the surface where the UV-light is directly exposed and the inner part of wrinkles. That is, weaker polymerization takes place inside the zone, forming much softer state. In the lower part of Fig. 1a, the experimental setup for the RVD process is depicted. When the lower plate moves down after compressing a droplet of resin between plates, a capillary adhesion force (F_c) is generated, as follows:

$$F_c = \pi R^2 (2\gamma \cos \theta / H), \tag{1}$$

where R, γ, θ, and H are the radius of a compressed liquid drop, surface tension, contact angle, and the gap between plates, respectively [27]. The F_c is relative large in the initial state of separation due to the small value of H, so a large force is required for pulling down the lower plate in the initial separation stage. However, the internal capillary forces in the whole plate become unbalanced locally due to a few reasons such as a slight difference in the local thickness of resin layer, imperfect homogeneity of the resin, and other uncertainties. For these reasons, non-uniform wrinkles can be generated on the plate.

After this, the gradual thermal curing is then conducted under the ambient temperature condition of about 30 °C in order to form secondary microscale wrinkles on the ridges of primary ones through the contraction of primary wrinkles (see Fig. 1b). Thermal curing is done with blocking UV-light to prevent any further progress of photo-induced polymerization. During the thermal curing, full polymerization takes place in the whole UV-cured part including the inner side, thereby reducing the total volume of primary wrinkles. In particular, the height of wrinkles decreases from H to h, as shown in Fig. 1b, consequently reducing the surface area. The width of the top part of the wrinkles is slightly changed due to geometrical constraints (the wrinkles fixed on a glass plate), that is, $T \fallingdotseq t$, but the side areas of wrinkles are significantly reduced ($L \rightarrow l$). Therefore, due to the large reduction of the surface area of wrinkles, secondary wrinkles, which are scores of micrometers in size, are formed on the side ridges.

3. Experiments

The resin used in this work is NOA-68T (Norland Co., Germany). Its viscosity is between 20,000 and 25,000 cps at a temperature of 25–28 °C, and its UV absorption is the best at a wavelength between 350 and 400 nm. As a result of fundamental experiments, it is found that full polymerization occurs by exposure of about 4.5 J/cm^2, and thermal curing condition occurs for about 14 h at a temperature of 50 °C.

As mentioned above, Fig. 1a schematically shows the experimental setup for the RVD process. The procedures of the RVD process are explained briefly as follows. NOA-68T is dropped on a glass plate. The glass plate is placed on the upper stage with a droplet of resin, and the lower stage is moved upward to the z-direction so that the two plates come into contact. When a conformal contact occurs between two plates with a pressing force reaching up to the pressure of 2000 gf/cm^2, the resin layer between them is compressed and formed as a thin circular-shaped layer. Then, as the stage is lowered slowly at a speed of 40–400 μm/s to allow the flow of air into the resin layer, the layer forms several columns in order to maintain its total volume. As this process is repeated several times, the layer is divided into many parts, and the surface becomes uneven, resulting in the formation of primary wrinkles. UV-lamp light is then applied to cure the wrinkles. The process parameters of the RVD are known to be contact pressure, amount of resin, and number of iterations of contact and detachment of two plates [21].

By controlling the process parameters of RVD, various wrinkling shapes having a range of line-widths (about 10–500 μm) can be realized. The upper image of Fig. 2a shows an AFM image of the smallest line-width case of 5–10 μm, which was obtained under the condition of a resin amount of 25 mg, contact pressure of 900 gf/cm^2, exposure time to UV light of 60 s, and 25 iterations of contact and detachment. Generally, irregular wrinkles having line-widths of 10–100 μm can be realized easily by controlling the process parameters of RVD. And Fig. 2b shows some wrinkling patterns generated using weak-polymerization by short exposure of UV light less than 10 s and a continuative thermal full curing process. Short-line shaped patterns (α and β in Fig. 2b) were realized by controlling resin layer thickness using the gap (G_c) between the glass plates near 0.4–0.5 mm when contacting and compressing two plates in the RVD (see Fig. 1a). These interesting odd shaped patterns were generated with a short exposure of UV-light for 10 s after only 1 or 2 times of contact and detachment in RVD and then thermal curing for 1 day at a temperature condition of 30 °C. With a large G_c of more than 0.5 mm, continuous line-shaped wrinkles were generated as shown in the third image (γ) in Fig. 2b. We cannot show the exact mechanism of shaping various wrinkles, but believe that those patterns were self-assembled by minimizing their surface energies through assistance from RVD and thermal curing. Further experiments will be done in order to clarify the reasons and conditions in the future work.

4. Results and discussions

A rough surface having several 100 μm of wrinkling width can be made by 3 or 4 iterations of contact and detachment of glass plates in the RVD process. As mentioned above, the resin layer is divided into a number of small volumes by iterations of contact and detachment of two plates. So, the iteration number of contact and detachment of plates is one of the main parameters to make coarse or fine wrinkle patterns in the RVD. In general, by less than 5 iterations of contact, we can easily make rough wrinkles nearly 500 μm in width. Also, if the UV-light is briefly introduced for less than 30 s in order to make the resin layer be weakly polymerized to have a gradient of polymerized