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Generation of various wrinkle shapes on single surface by controlling thickness of weakly polymerized layer

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ABSTRACT

A simple method for generating various wrinkle shapes was investigated by varying the layer thickness of a photocurable resin. Resin layers with thicknesses ranging from 0.1–1.0 mm were coated on a 20 × 20 mm^2 mold in order to observe the formation of micro-scale wrinkle shapes. Short exposure to ultraviolet (UV) light resulted in a partial gradient of mechanical properties along the thickness of the layer. Surface wrinkles were generated in the fully thermally cured layers. These wrinkles formed during curing as a result of the volume shrinkage that generated a compressive force on the weakly polymerized skin. We fabricated dot-, short line-, and irregular long-line-shaped wrinkles via the proposed method, which provides a simple and cost-effective means of generating large areas of wrinkles having various shapes and line width of 10–35 μm. These wrinkles can be applied in many research fields including surface modification, coating technology, microfluidics, and wearable devices.

1. Introduction

Surface wrinkles occur abundantly in nature and with the development of modern technologies, micro-scale wrinkles have been used in various applications including optical surfaces [1–3], microfluidics [4,5], enhanced adhesion [6,7], cell culture bio-interfaces [8], and surface modification [9]. Until today, many studies have focused on the fabrication methods and applications of micro-scale wrinkles. For example, Martin et al. and Huck et al. reported that wrinkles formed through bi-material coating on polydimethylsiloxane (PDMS) [10,12]. Bowden et al. proposed that metal evaporation onto the PDMS could be used for structuring purposes [11]. Analogous to the formation of wrinkles, Volynskii et al. and Chen et al. described the mechanical buckling instability that results in the fragmentation of thin coatings deposited on soft polymer substrates [13,14]. Kim et al. proposed a simple method for generating hierarchical wrinkles via weak photopolymerization followed by thermal curing [15]. In addition, Takahashi et al. described a scheme for fabricating microstructures on thin oxide films through a sol–gel procedure combined with a photopolymerization-induced chemical process [16]. Miquelard-Garnier et al. proposed another method for generating wrinkles, that according to the authors, "exploits the local deformation of a soft substrate as it stretches to form an adhesive interface with a thin polymer film" [17]. Other studies have attempted to create wrinkles or surface patterns by using the non-uniform stresses, which result from surface modification via rapid heating and ion beams [18–23].

Although the various methods for winkle generation have been investigated by using tension and compression or surface polymerization of a thin film and soft substrate, there are some limitations: (i) the fabrication of large-scale wrinkles cannot be easily realized owing to the difficulty of applying tension and compression on a large film and substrate in order to pre-strain the surface. (ii) Controlling the selective generation of diverse wrinkle shapes, from dotted to line-shaped, is very difficult. (iii) The fabrication cost of wrinkles is somewhat high owing to the use of expensive equipment and processes such as photolithography and metal sputtering. However, the diverse wrinkle shapes, such as dotted and line-shaped, have several potential functions.

We propose a facile and cost-effective method for generating dotted and line-shaped wrinkles by controlling initial resin layer thickness. Micro-scale wrinkles were generated by weak photopolymerization using an ultraviolet (UV) light followed by complete polymerization during the thermal curing process. The formation mechanism of wrinkles is determined by examining their morphological features and we discuss the critical thickness of the resin layer for changing the wrinkle shape from dotted to line-shaped. Finally, the possibility of varied applications of diversely shaped wrinkles is discussed.

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2. Experiments

2.1. Materials

In this work, the commercially available adhesive, NOA-68T (Norland Co.), was used to generate micro-scale wrinkles as a UV-curable resin. The resin, which has a viscosity of ~20,000–25,000 cps at temperatures ranging from 25 to 28 °C, was polymerized under UV exposure of ~4.5 J/cm^2. UV absorption occurs best at wavelengths of 350–380 nm. We determined theoretically that a UV lighter with a power of 400 mW/cm^2 could completely polymerize the resin in an exposure time of ~12 s.

2.2. Wrinkling mechanism

We propose a promising way to generate wrinkles over a large area without the use of complicated processes, equipment, and bi-material layers, which are conventionally used to fabricate wrinkles. A single UV-curable resin layer is covered using a roller or scrubber in a mold (20 × 20 mm^2), as shown in Fig. 1a; the layer thickness can be controlled by varying the space height from 0.1 to 1.0 mm. The layer is then irradiated with UV-light for less than 10 s to induce weak polymerization and a change of material state from the top surface to the bottom; i.e., a gradient of state is generated along the thickness of the material; compared to the inner-side of the resin layer that becomes monomer state or softly polymerized, the top surface, which is directly exposed to relatively strong UV-light, becomes relatively dense and significantly more polymerized. Therefore, short exposure to UV light can easily generate different material states along the thickness of the layer (see Fig. 1b). We believe that this approach is simpler and more cost effective than a conventional method, which uses bi-layered materials.

After short UV exposure, the resin layer was thermally cured in a chamber maintained at room temperature (setting temperature of 30 °C). During thermal curing, the volume of the resin layer is reduced by induced complete polymerization of the interior. Therefore, wrinkles form on the hard surface (see Fig. 1c) as a result of the compressive force (f_c in volume and f_s on surface) that is generated by the volume shrinkage. As Fig. 1c shows, the resin layer undergoes topological changes during thermal curing. For example, although the total area of the top surface (A_T) is similar to that (a_T) of the fully cured layer, the initial thickness (H) is significantly reduced to h. A multitude of wrinkles is generated through the shrinkage of the thin resin layer, which has a hard top surface.

Using an optical microscope (MIC-S39, Micro Scopes INC, USA), we observed the formation of wrinkles on the 1 mm-thick NOA68T resin layer during 108 h of thermal curing (see 50 times magnified images in Fig. 2a–h). As Fig. 2a and b shows, the surface of the resin layer remains non-wrinkled and perfectly smooth for up to 12 h of exposure to UV light but becomes rough and uneven after 24 h. We believe that these changes in the surface topography result from the volume shrinkage inside the resin layer during thermal curing. Micro-scale wrinkles started to form on the surface after 48–60 h, although the layer was not fully cured, we observed completely shaped wrinkles after 72 h. As Fig. 2g–h shows, delicate micro-scale wrinkles were generated on the surface of the fully cured (i.e., after 96 h of curing) layer. The wrinkles have random curved shapes, and average widths of up to ~15 μm. Furthermore, the thermal curing time can be reduced somewhat by increasing the ambient temperature. Therefore, we believe that these conjoined processes (weak polymerization and thermal curing) may be used to efficiently fabricate large areas of micro-scale surface wrinkles.

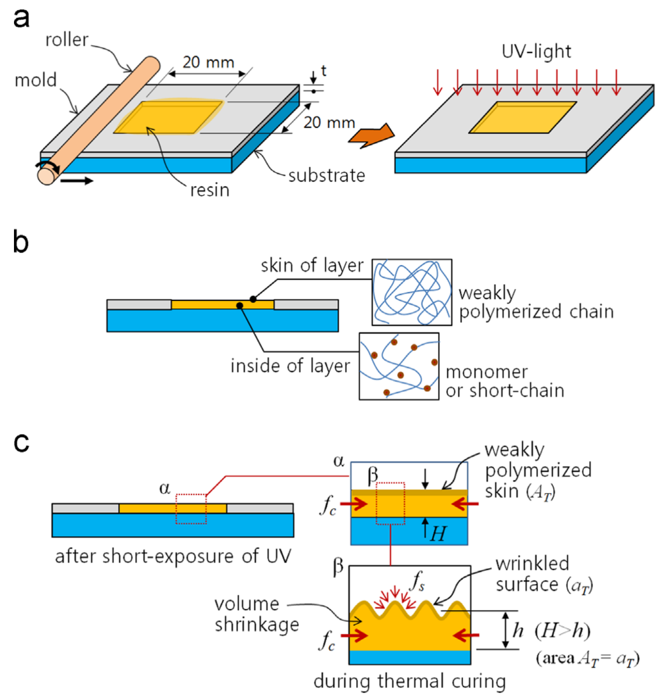

Fig. 1. Schematic diagram of fabrication process and wrinkling mechanism; (a) deposition of resin layer on a mold and UV-light exposure on the resin layer shortly. (b) Material gradient along the layer thickness due to the short exposure of UV-light. (c) The wrinkling mechanism on a single layer. Compressive force, f_c and f_s are generated in volume and on surface during thermal curing, respectively (dotted-window, α and β is magnified in (c)).

3. Fabrication of various shaped wrinkles and discussion

As mentioned in the previous section, wrinkles are generated by the volume shrinkage of the resin layer during the thermal curing process; hence the wrinkle shapes are determined in the thermal curing step. The amount of shrinkage varies with the thickness of the resin layer. Therefore, we can produce different wrinkle shapes by simply changing the thickness of the resin layer.

In order to verify the basic shaping mechanism, we generated wrinkles from resins with thicknesses of 0.1–1.0 mm. Fig. 3a–d illustrates the basic concept and method used for these experiments. A mold frame with varying local height was prepared using a 3M Scotch tape, and the NOA-68T resin was then poured into the mold. After 5 s of exposure to UV-light (400 mW/cm^2), the mold was placed in a chamber maintained at room temperature and thermally cured for 3 days. As Fig. 3b–c shows, dotted pattern shapes are generated at layer thicknesses of 0.1 and 0.2 mm. However, at a layer thickness of 0.3 mm, the patterns are composed of short-line-shaped wrinkles (see Fig. 3d). We think that the shape change of the patterns results from the different thicknesses of the layer. When the resin layer is <0.2 mm thick, the cohesion of monomers or short polymer chains occurs separately from the weakly polymerized surface, thereby resulting in the formation of ~10 μm-diameter dotted patterns. There are, however, sufficient monomers for layer thicknesses >0.2 mm, thereby resulting in the formation of line-shaped patterns. The boundary between the layer thickness of 0.1 and 0.2 mm shows the change of pattern shapes from dot to short line (see Fig. 3b). Irregular, unbroken line-shaped wrinkles with line widths of 20–35 μm are generated at layer thicknesses of 0.6–1.0 mm (see Fig. 4a–d). By changing the layer thickness continuously from 0.1 to 1.5 mm, we obtained diverse wrinkle shapes ranging from dotted to irregular unbroken lines in the same plane, as shown in Fig. 5a.