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ORIGINAL ARTICLE

Surface texturing of natural ‘urushi’ thermosetting polymer thin films

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Japanese lacquer, known as *urushi*, is a traditional natural resin used for numerous applications, including tableware, art and furniture. The main component of urushi is urushiol, which is a catechol derivative with a long unsaturated hydrocarbon side chain. Utilizing the characteristics of urushiol as a thermoset, we have demonstrated the surface texturing of an urushi thin film with a thermal imprinting technique. Thermal imprinting was conducted at 100 °C for 10 min by pressing a patterned mold onto the film, and an indented surface that replicated the surface of the mold was obtained. The static water contact angle was changed from 70 ± 0.5° to 112 ± 3° after the fabrication of pillared patterns on the surface. Moreover, the imprinted line and space patterns caused strong anisotropic wetting depending on the direction. Our results demonstrate that the texturing of urushi thin films is a useful technique for controlling the wettability of natural thermoset urushi thin films.
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INTRODUCTION

Japanese lacquer, known as *urushi*, is a traditional natural resin coating. The main component of urushi, called urushiol, is a catechol derivative with a long unsaturated hydrocarbon side chain.[1–6] Urushi has excellent physical and chemical properties arising from the catechol structure; it is very durable and resistant to oxidation. Urushi also shows good adhesion properties. This characteristic is also found in other catechol derivatives, such as 3,4-dihydroxyphenylalanine and norepinephrine, which are currently attracting attention as biomimetic natural adhesives.[7–10]

The main difference between urushiol and other catechol derivatives is the presence of a long C_{15}–C_{18} hydrocarbon side chain in the third position. The hydrocarbon chains in urushiol are approximately 65% trienes, 20% monoenes and 20% dienes (Figure 1). The curing of urushi involves two steps. The first step is the oxidative polymerization of catechol moieties, which produces oligomeric urushiol. The second step is the aerobic oxidation of the unsaturated hydrocarbon chains and the subsequent coupling reactions, which take more than one month to complete. A tough coating is formed by the double network structure arising from the oxidative polymerization of catechol moieties and the coupling reactions of the hydrocarbon side chains. Urushi can also be cured thermally because these double bonds undergo thermal Diels–Alder reactions and addition reactions.[2,5,11] The thermal curing of the unsaturated hydrocarbon side chain is complete in several minutes. Moreover, the long hydrocarbon side chain has an important role in controlling the physical characteristics of the cured materials. We have previously reported that the robustness of a thermally cured urushiol thin film is better than that of a poly(dopamine) film, which suggests that urushiol may be a promising natural catechol derivative for polymer processing.[12]

In this article, we report the surface texturing of urushi thin films as an example of polymer processing. Surface texturing was accomplished by imprinting, which is a powerful surface texturing technique achieved by simple embossing.[13–18] The surface topography of a patterned mold was transferred onto urushi thin films by thermal curing during pressing. Because surface properties are determined by the surface topography and its chemical composition, the texturing of a material’s surface is one of the promising techniques that can be used to modify the substrate surface for specific functionalities. For example, the lotus effect, which refers to very high water repellence, is produced by the complex microscopic architecture of the surface.[19–21] Our results demonstrate that the texturing of natural urushi thermosetting polymer films is a methodology that could be used for the fabrication of functional surfaces.

EXPERIMENTAL PROCEDURE

Materials

The raw urushi lacquer was purchased from Kanwa-do Urushi Club Co. Ltd., Shiga, Japan. Iron(II) acetate was obtained from Acros Organics (Geel, Belgium). Solvents were purchased from Kanto Chemicals (Tokyo, Japan) and used without further purification.

Measurements

Ultraviolet–visible transmittance and reflectance measurements were performed using a ultraviolet–visible spectrophotometer (UV-3500PC,

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Shimadzu, Co., Kyoto, Japan). For the reflectance measurements, the incident angle was 15° (nearly perpendicular to the sample). Scanning electron microscopy (SEM) was performed using a VE7800 microscope (Keyence, Co., Osaka, Japan). Atomic force microscopy (AFM; 5500, Agilent Technologies, Santa Clara, CA, USA) was performed in noncontact AC mode with a rectangular 160-μm cantilever (OMCL-AC160TS-W2, Olympus, Co., Tokyo, Japan). The spring constant of the cantilever was $42\,N\,m^{-1}$. Surface texturing was carried out with a nano-imprinter (NM-0501-T, Meisho Kiko, Hyogo, Japan). Static water contact angle (CA) measurements were performed using a DSA10 Krüss CA measurement system (A. Krüss Optronic GmbH, Hamburg, Germany) equipped with an automatic liquid dispenser and a monochromatic charge-coupled device camera. During CA measurements, the temperature and humidity were controlled at 23.5 °C and 60%, respectively.

Film preparation procedure

Raw urushi lacquer was dissolved in ethanol, and then iron(II) acetate was added. The iron(II) acetate concentration was 0.83 equiv with respect to the raw urushi, which corresponded to 0.5 equiv with respect to urushiol. The solution was homogenized with an ultrasonic cell disruptor (Sonifier, Branson, Danbury, CT, USA). The homogenized solution was diluted with turpentine, and a vacuum-ultraviolet-treated Si substrate was spin-coated with the viscous liquid at 3000 r.p.m. for 60 s. The films were left to stand in air for 5 min and were then placed on a hot plate and baked at 100 °C for 10 min.

Surface texturing

A Si mold was brought into contact with an urushi liquid film, and the sample was pressed under a static pressure of 2.5 kN for 20 s with a nano-imprinter.

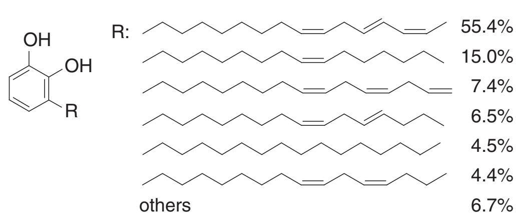

Figure 1 Typical chemical structure of urushiol.

The sample was heated to 100 °C for 10 min under pressure in air. The surface topography of the Si mold was replicated on the cured urushi thin film after it was released from the Si mold. The Si molds for imprinting were fabricated by photolithography. The typical mold pattern consisted of circular holes 2 μm in diameter and 1 μm deep with a pitch of 2 μm that were distributed over a 10 × 20 mm area. Before use, the surfaces of the Si molds were coated with a mold-release agent (Durasurf-DS5100, Harves Co., Ltd., Saitama, Japan).

RESULTS AND DISCUSSION

Surface morphology of urushi films

SEM and AFM observations were conducted to reveal the surface morphology of the cured urushi films. When a spin-coated film of raw urushi and iron(II) acetate mixture was thermally cured at 100 °C for 10 min, the surface finish was matte. SEM revealed that aggregates of particles were present on the surface of the film (Figure 2a). The AFM measurements confirmed that the surface roughness was several micrometers in magnitude. A raw urushi film cured by oxidative polymerization at room temperature for 12 h under 75% relative humidity showed similar surface morphology (Supplementary Figure S1). In contrast, the spin-coated urushiol and iron(II) acetate mixture produced a film with a flat glossy surface by thermal curing at 100 °C for 10 min. Raw urushi is a mixture of 60–65% urushiol and 20–25% water, with the remaining 15% consisting of other compounds such as water-soluble plant gums, polysaccharides and a small amount of lactase and other enzymes. A majority of the plant gum and the enzymes was dissolved in the water phase, and water/oil emulsions several microns in diameter were formed in the urushiol phase. Although the water evaporated during the drying process, the other compounds in the raw urushi lacquer made the surface rough.

There are three steps in the traditional refinement of urushi. The first step is the microparticulation of the emulsion (called *nayashi*), in which raw urushi is kneaded while stirring. In the second step (*kurome*), the amount of water is reduced by stirring the kneaded urushi in sunlight. Finally, the urushi is filtered to remove impurities and large particulates. The control of temperature and humidity is

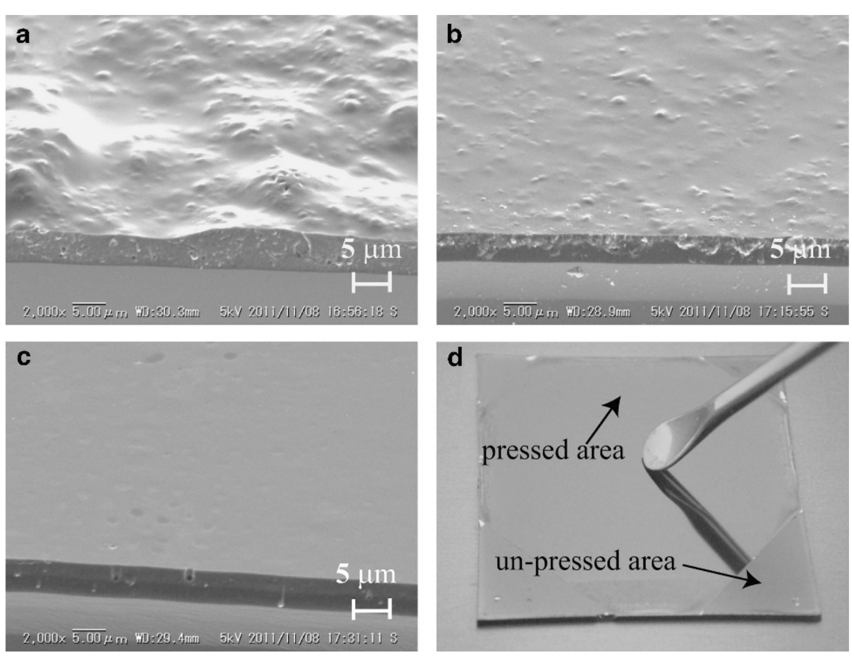

Figure 2 Images of the urushi thin films: SEM images of urushi films formed from (**a**) unhomogenized and (**b**) homogenized emulsions; (**c**) pressed with a flat Si mold and (**d**) digital photograph of a pressed sample. A full color version of this figure is available at *Polymer Journal* online.

critical for refining urushi because oxidative polymerization proceeds even at room temperature. We achieved the microparticulation of the emulsion by a simple homogenization process instead of the traditional kneading method, and the processed solution was spin-coated onto Si substrates. The surface roughness of the sample was improved by the processing (Figure 2b). AFM observation showed that the surface roughness of the homogenized urushi was ∼1 μm. Small uniform emulsions were formed by the processing.

The glossiest finish was obtained by curing the homogenized urushi while it was pressed in a flat Si mold (Figure 2c). The AFM image showed that the roughness of the film was ∼20 nm. Figure 2d) shows that the surface had a reflective mirror finish in the pressed area of the sample. The spectral reflectivity was quantitatively evaluated by absolute reflectance measurements. The reflectance absorption of the urushi film on the Si substrate was constant in the visible light region, and pressing the homogenized sample changed the value from 5 to 18% (Figure 3). The smooth surface of the pressed sample reduced the surface scattering and increased the reflectance of the sample. Traditionally, lacquerware is coated with urushi and then polished with charcoal powders; the process is repeated over 20 times to obtain a glossy finish. The final coat is applied carefully with a mixture of refined urushi and a drying oil that contains unsaturated long-chain fatty acids, such as tung oil (China wood oil). This makes the traditional manufacture of lacquerware very time-consuming. The simple pressing process for achieving a glossy finish may have interesting practical applications.

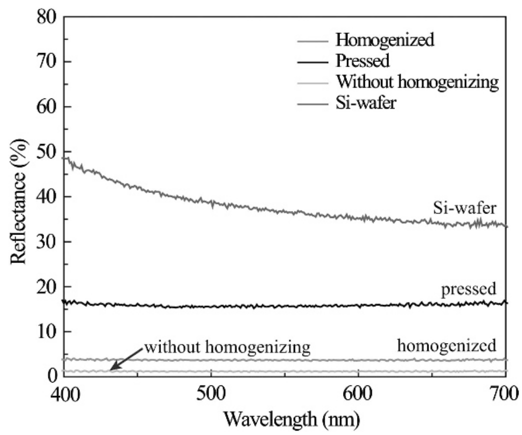

Figure 3 Absolute reflectance spectra of urushi thin films on a Si substrate. A full color version of this figure is available at *Polymer Journal* online.

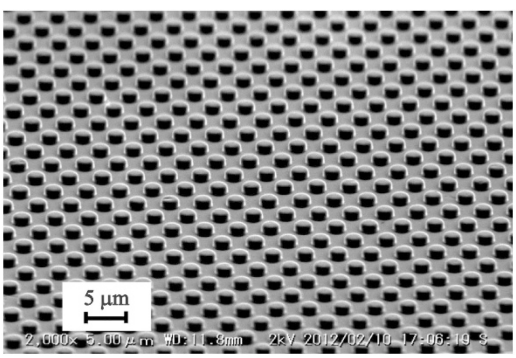

Figure 4 SEM image of a textured raw urushi lacquer film.

Surface texturing by imprinting

Surface texturing of urushi thin films was achieved by thermally imprinting urushi films with patterned molds. Figure 4 shows a typical SEM image of the processed film. Pillared structures 2 μm in diameter with a 1-μm height were obtained over the imprinted area, which replicated the hole pattern of the Si mold. Other topological patterns, such as line and space patterns, were also fabricated on the sample surface. It should be noted that conventional enzymatic oxidative polymerization was not suitable for imprinting. Because the supply of oxygen was restricted during the imprinting process, the film was not cured even when the sample was pressed for 12 h at room temperature. Surface texturing was only accomplished by thermal curing while the film was pressed in a patterned mold.

The resolution of this process is currently limited to ∼1 μm. Interfacial delamination from the substrate was observed when an equally spaced 500 nm line and space pattern with a height of 500 nm was transferred (Supplementary Figure S2). This was caused by the

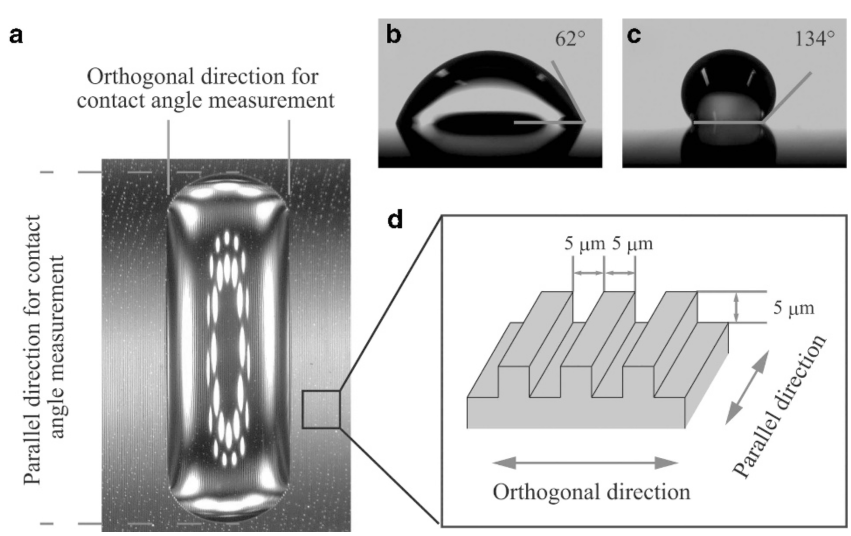

Figure 5 Water droplet on a textured urushi film with 5-μm line and space patterns: (**a**) optical micrograph, top view, (**b**) drop shape from the parallel direction to the pattern, (**c**) drop shape from the orthogonal direction to the pattern and (**d**) schematic illustration of the geometry of the pattern. A full color version of this figure is available at *Polymer Journal* online.

characteristics of urushiol; an urushiol thin film with no additives showed similar delamination. The superior adhesive properties of the catechol derivative[22] may induce peeling behavior even though the surface of the mold was coated with fluorinated materials to decrease the surface energy of the material. Further optimization of the process conditions is necessary to improve the resolution.

Wettability of textured urushi films

Subsequently, the wettability of the processed material was evaluated. The static water CA of urushi film was enhanced from $70 \pm 0.5^\circ$ to $112 \pm 3^\circ$ on a 2-μm pillared pattern with a 1-μm height. The enhancement of the CA can be simply explained using the Cassie–Baxter model, which describes the wetting regime on a heterogeneous (rough) surface. The calculated value of the apparent CA using the Cassie–Baxter model is in good agreement with the experimental results (see the Supporting Information). When the pattern was a 5-μm line and space pattern with a 1-μm height, the surface showed anisotropic wettability (Figure 5). The CA values were $62 \pm 2^\circ$ and $134 \pm 1^\circ$ for the parallel direction of the pattern and the orthogonal direction of the pattern, respectively. The CA hysteresis ($\Delta\theta$) of the direction was $\sim 72^\circ$.

Because the patterned surface is in a Cassie–Baxter state, air is trapped within the groove of the line and space patterns. The air-trapped region pins the advancement of a contact line of droplets in the orthogonal direction, and the contact line must jump the energy barrier to spread the liquid. In contrast, in the parallel direction, there are no such energy barriers to pin the contact line. This is why the CA in the orthogonal direction is higher than that in the parallel direction.[23] The pinning also provided sliding angle anisotropy. Sliding angles were estimated by tilting the samples until a droplet started to move. We measured the average of five readings. A 20-μl sample of water droplets slid with a tilting angle of $\sim 8^\circ$ when the sample was tilted parallel to the direction of the pattern. It is clear that the patterned surface showed strong water repellency. In contrast, water droplets did not slide down even though the sample was tilted over 80° in the orthogonal direction to the pattern.

CONCLUSIONS

Surface texturing of urushiol was achieved using a thermal imprinting technique. An indented surface was obtained by thermal curing while pressing an urushi film with a patterned mold. The indented surface enhanced the static water CA in comparison with the flat urushi film. Moreover, the line and space patterns cause strong anisotropic wetting that is useful for various applications, such as microfluidic devices, evaporation-driven alignment of materials, ink-jet processes and easy-clean coatings.[16,24] Recently, several researchers reported that catechol derivatives act as a scaffold for the immobilization of initiating species for polymer grafting.[25–28] The combination of the texturing of urushi thin films and the polymer grafting method would produce a unique material because surface properties are determined by the surface topography and its chemical composition. Our results demonstrate that the texturing of urushi thin films is a useful technique that reinforces the value of the urushi thin film as a natural thermosetting polymer.

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Author contributions: H. Watanabe and A. Takahara contributed equally to this work.

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Supplementary Information accompanies the paper on Polymer Journal website (http://www.nature.com/pj)