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Solvent influence on crosslinking and surface characteristics of Urushi films

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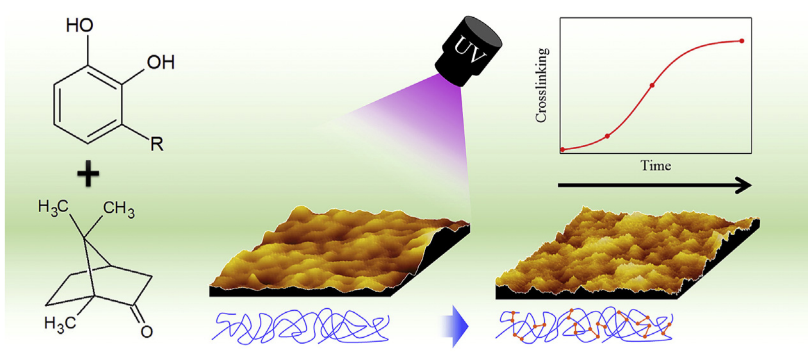
HIGHLIGHTS

- Photodegradation and crosslinking of Urushi film.
- This research focused on the solvent effect of Urushi films.
- AFM images showed the change of surface morphology by solvents and UV irradiation.
- Surface roughness is influenced by UV irradiation time.

GRAPHICAL ABSTRACT



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ABSTRACT

We here demonstrate the effects of solvents on crosslinking and surface characteristics of Urushi (Oriental lacquer) films. We aimed to clarify the influence of solvents on crosslinking of Urushi by comparing normal Urushi films with Urushi films blended with three types of solvents, camphor, turpentine, and methanol, by using differential scanning calorimetry (DSC). In addition, we evaluated the effects of ultraviolet (UV) irradiation on crosslinking and surface characteristics of Urushi films using scanning probe microscopy (SPM) and Fourier transform infrared (FTIR) spectroscopy. The DSC results showed that Urushi films blended with camphor had large amounts of non-crosslinked parts compared to films blended with turpentine and methanol. From the results of SPM observations, it was found that surface roughness increased with an increase in UV irradiation time. Furthermore, FTIR results indicated that C=O stretching peaks attributed to the curing reaction increased with an increase in UV irradiation time. This tendency of increasing peak intensity is consistent with the change in surface roughness induced by UV irradiation.

1. Introduction

Natural polymeric materials such as natural fibers [1–3], natural rubbers [4–6], hydrogels [7–9], and natural resins [10–13] have received growing attention in environmental viewpoints, because

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these materials achieve zero emissions and contribute to sustainable society. Urushi (Oriental lacquer), a sap collected from Toxicodendron verniciflua lacquer trees, is a natural polymer that can form coating films with high robustness and flexibility. In general, curing of Urushi is influenced by the temperature and humidity [14]. Urushi film formation occurs through the enzymatic oxidation of laccase enzymes in Urushi solutions, followed by aerobic oxidation of the double bonds of the unsaturated hydrocarbon side chains of urushiol [15–17]. Urushi film has also characteristics of thermosetting [18–20]. Despite its high durability, Urushi is easily affected and degraded by ultraviolet (UV) radiation [21–27]. Therefore, UV resistance is one of the criteria to evaluate the characteristics of Urushi.

Urushi used as a coating material is typically refined. Since its liquid has a higher viscosity than other coating materials, solvents are used to adjust its viscosity in case of a needed viscosity adjustment. Camphor and sometimes turpentine are used as solvent for this purpose [16,28–30]. Although camphor and turpentine are generally considered to have negligible effects on the Urushi film, no detailed studies exist on the influence of solvents on the crosslinking and surface characteristics of Urushi.

The appearance and durability of Urushi are highly prioritized, since it is mainly used to coat tableware and furniture [31–35]. On the other hand, urushiol, the main component of Urushi, can cause allergic contact dermatitis in some people [36]. For these reasons, it is very important to clarify the influence of solvents on Urushi both in terms of its quality as a coating material and its effects on human health. In general, the crosslinking of thermosetting polymers needs crosslinking agents. Therefore, the progress of thermosetting polymers is controlled by adjusting amount of crosslinking agent. However, Urushi is a natural polymer that can be crosslinked without any agents because it has an enzyme for crosslinking. Thus, a new utilizing method of Urushi, such as the creation of flexible-Urushi film, is expected if the progress of crosslinking of Urushi is controlled by using solvent or UV irradiation. The utilization of natural polymers would be contributed to the efforts to environmental problems, an increase of carbon dioxide, an energy resource issue, and so on.

This research therefore aims to clarify the influence of solvents on the crosslinking and surface characteristics of Urushi by comparing regular Urushi films with Urushi films blended with three kinds of solvents: camphor, turpentine, and methanol. First, calorimetry was performed to confirm crosslinking of each sample. Secondly, observation, shape measurements, and Fourier transform infrared (FTIR) spectroscopy were performed on the sample surface before and after UV irradiation.

2. Experimental

2.1. Materials and samples

Kuro-roiro Urushi manufactured in 2016 was used to make samples. Three kinds of solvents, camphor (Wako 1st grade, Wako Pure Chemical Industries, Ltd., Japan), turpentine (Wako 1st grade, Wako Pure Chemical Industries, Ltd.), and methanol (Wako 1st grade, Wako Pure Chemical Industries, Ltd.) were used for blending into Urushi. Methanol is normally not used as a solvent for Urushi, but was used in this study for comparison with other solvents because it has a higher polarity the other solvents. The chemical structure and molecular weight of urushiol [16] and each solvent are shown in Fig. 1. Solvents were used at 10 or 40 wt% in Urushi. Each solvent was uniformly stirred with a magnetic stirrer. The experimental conditions for each sample are shown in Table 1. Urushi films were prepared on mica substrates using a casting method. All samples were kept in a container at 60% relative humidity and 25 °C after preparation.

2.2. Measurement methods

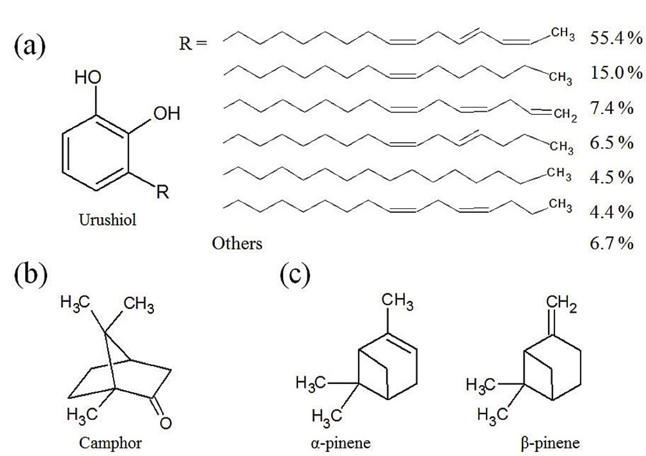
Calorimetry was performed first with the 40 wt% samples since those samples were affected by solvents more than the ones with 10 wt% solvent. Then, surface observations, shape measurements, and FTIR were performed of the sample surfaces before and after UV irradiation with a UV lamp (385 nm, 9 W) to confirm its influence. Differential scanning calorimetry (DSC)analysis was carried out using nitrogen gas from 30 to 200 °C at a heating rate of 10 °C/min (Pyris 1, PerkinElmer, Japan). The amount of sample used for DSC was approximately 10 mg. The calorific value of curing was calculated from 105 to 195 °C. Scanning probe microscopy (SPM, AFM5100N, Hitachi High-Tech Science Corporation, Japan) was used to observe and measure the surface of each sample, and measurements were made using dynamic force mode (DFM). Infrared spectra of sample surface were obtained using a Spectrum GX 2000FTIR instrument (Perkin-Elmer) by attenuated total reflectance (ATR). The surface chemical structures of the samples were measured by Laser-Raman confocal microscopy (LabRAM HR-800, HORIBA, Ltd., Japan) with 633 nm excitation laser source.

3. Results and discussion

DSC curves and ΔH (J/g) of each sample are shown in Fig. 2. The increase in temperature was carried out twice, with the DSC curves in Fig. 2 showing the first temperature increase, because the exothermic peak disappeared during the second temperature increase.

From the DSC results, C-40 had the highest ΔH (J/g), followed by Normal, M-40, and T-40 in decreasing order. An exothermic reaction occurs when crosslinking of the thermosetting resin takes place [37,38]. The corresponding exothermic peak can be seen between 110 and 180 °C for the Urushi films in this study. The higher ΔH (J/g) is, the more non-crosslinked areas exist. Thus, the Normal samples and the samples containing camphor had more non-crosslinked areas than those containing turpentine or methanol. In addition, the samples containing camphor had more non-crosslinked parts than the Normal samples.

As mentioned above, both camphor and turpentine are typically used to adjust the viscosity of Urushi. However, our result here



Solvent	Camphor	Turpentine	Methanol
Chemical structure	$C_{10}H_{16}O$	$C_{10}H_{16}$	CH_3OH
Molecular weight	152.24	136.00	32.04

Fig. 1. Chemical structure and molecular weight of urushiol and solvents.