Studies on the Fast Drying Hybrid Urushi in Low Humidity Environment

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Four kinds of hybrid urushi, fast drying in a low humidity environment, have been synthesized with an organic silicone compound. Their characteristics and drying mechanism have been analyzed based on IR and RPT measurements.

Urushi sap, known as "raw urushi," consists of urushiol, laccase, water, and polysaccharides.[1] The partial structure of a Chinese urushi polysaccharide has been revealed by methylation analysis[2] and NMR measurement,[3] previously. Urushiol is a mixture of many isomers of 1,2,3-tri-*O*-, or 1,3-di-*O*-substituted catechols having a long alkyl chain with double bonds,[4–6] as shown in Scheme 1. Laccase is a copper-glycoprotein and functions as the polymerization catalyst of urushiol,[7] so the activity of laccase by which urushiol polymerizes significantly affects the process. In order to maintain the optimum activity of laccase, a high relative humidity (70–90% RH) is required for the polymerization of urushiol to form a high polymer. However, winter in Japan always has a low humidity (low than 40% RH).

Herein we developed a hybrid urushi that dries fast in a low relative humidity environment, named NDU-40 (drying in 40% RH), and NDU-30 (drying in 30% RH), i.e. "Transparent urushi" (Tp, Suki-urushi), and "Black urushi" (Bl, Kuro-urushi), respectively. Because raw urushi has more moisture (20–30%)[8] and the organic silicone would be analyzed by water, the "Kurome" urushi was used in this test.

The "Kurome" processes when the raw urushi is stirred in an open vessel at room temperature for about one and a half hours, and then at a temperature increasing from 20 to 45 °C for 2–4 h until the water content is reduced to 2–5%.[9]

Kurome urushi (100 g) was mixed with an organic silicone $(X–R–Si–(OCH_3)_3, R=(–CH_2)_n–)$ in different proportions, and the Fe ion act as a catalyst in drying, as in Table 1. After storing
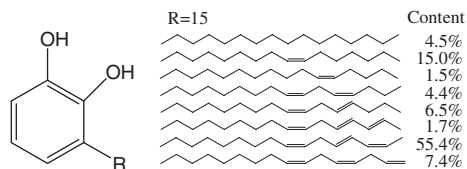
Scheme 1. Structure of typical urushiol.

Table 1. The composition of hybrid urushi

Name	X=Amino	X=Epoxy	X=Isocyanet	Naph.Fe[a]
NDU-40 (Tp)	5 g	5 g	-	-
NDU-40 (Bl)	5 g	5 g	-	10 g
NDU-30 (Tp)	5 g	-	5 g	-
NDU-30 (Bl)	5 g	-	5 g	10 g

[a] Iron naphthenate.

Table 2. The MW distribution of Kurome and hybrid urushi

Name of urushi	High polymer	Polymer	Oligomer	Monomer
Kurome urushi	0	6.64	29.35	64.01
NDU-40 (Tp)	5.54	9.75	31.06	53.65
NDU-40 (Bl)	3.18	16.40	29.15	51.27
NDU-30 (Tp)	1.69	10.97	35.40	51.94
NDU-30 (Bl)	1.47	13.80	36.55	48.18

High polymer: MW $\geq$ 36000, Polymer: 10000 $\geq$ MW > 3000, Oligomer: 3200 $\geq$ MW $\geq$ 640, monomer: MW = 316–320.

in a tube for one month (rt), the characteristics of the hybrid urushi have been tested. The viscosities of the four kinds of hybrid urushi were from 2000–6000 mPa/s, at 20 °C, suggesting that the urushi hybridized with the organic silicone compound in this study were stable.[10,11] The GPC data for the high polymer, polymer, oligomer, and monomer of urushiol of the hybrid urushi and Kurome urushi are shown in Table 2. A few monomer, more oligomer and polymer content are favorable for drying.

The IR spectra (figure not showed) of the hybrid urushi revealed that the 982 cm^{-1} for the dienes obviously decreases and the 993 cm^{-1} for the trienes increases compared with Kurome urushi, implying that the hybrid urushi dries faster than the Kurome urushi.[11,12]

The drying process of urushi can be divided into three steps: dust free dry (DF), touch free dry (TF), and harden dry (HD).[13] NDU-40, and NDU-30 have been tested for drying in an auto dry desiccators at 38–42% RH and 28–32% RH, respectively. Because the desiccators is small, automatic drying time recording and RPT measurement were carried out at 55% RH. The drying time at 25 °C, 55% RH of Kurome and hybrid urushi was measured in an automatic time recorder (figure not showed). The drying time was summarized in Table 3.

It can be seen that the drying time gradually decreases from kurome urushi to NDU-30 (Bl) urushi. Urushi has only application in craft till present, because of its severe drying condition demand. For example, fixed temperature and about 80% of humidity require a special room (Urushi Muro). However, the hybrid urushi in this study can be applied not only in craft but also in industry because of its fast drying characteristics.

Measurement using the Rigid-body pendulum Physical properties Testing instrument (RPT, A&D Co. Ltd., Japan) is

Table 3. The drying time of hybrid urushi (h:min)

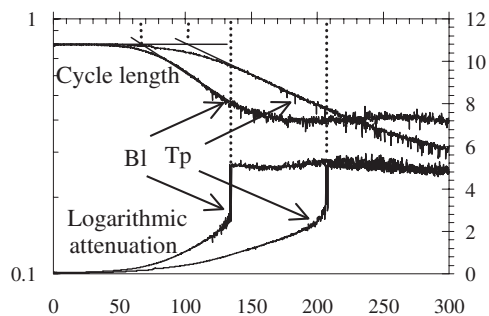| Name of urushi	DF	TF	HD
Kurome urushi	2:10	5:50	8:30
NDU-40 (Tp)	1:25	4:55	7:20
NDU-40 (Bl)	0:40	3:30	4:30
NDU-30 (Tp)	0:30	2:50	3:40
NDU-30 (Bl)	0:20	1:50	2:20

Figure 1. RPT spectrum of NDU-30 (Tp, and Bl) urushi.

shown in Figure 1 (figure only shows Tp and Bl of NDU-30, 25 °C, 55% RH). The cycle length decrease means that the cross-linkage reaction of urushiol occurred. A steady change in the logarithmic attenuance means that the harden dry is over. The cycle length decreases in 265 min for Kurome urushi, 200 min for NDU-40 (Tp), 188 min for NDU-40 (Bl), 105 min for NDU-30 (Tp), and 70 min for NDU-30 (Bl) urushi. The steady state of the logarithmic attenuation value of Kurome, NDU-40 (Tp), NDU-40 (Bl), NDU-30 (Tp), and NDU-30 (Bl) urushi were 550, 425, 270, 208, and 135 min, respectively, consistent with the HD data in Table 3.

In general, the urushi film is formed via the oxidation of urushiol catalyzed by laccase, and then followed by a coupling reaction as well as an autoxidation reaction on the long aliphatic unsaturated side chain. We have reported that the autoxidation of the side chain of urushiol occurred after the urushiol monomer decreases to fewer than 30%.[11] In a high humidity, laccase has the optimum conditions to catalyze the monomer of urushiol into a dimer, trimer, etc. The drying process displayed as enzymatic polymerization. When the content of the urushiol monomer decreased under 30%, the autoxidation begin to occur in the side chain.

In a low humidity environment, water in the urushi evaporated in a low vapor pressure. As the diffusion and osmosis of oxygen decreased, the reduced En–Cu$^+$ in laccase would not be oxidized into En–Cu^{++}, and the polymerization of laccase could not be continued, as in Scheme 2.

However, for the hybrid urushi, the reaction between urushiol and the silicone compound occurred, although in a low humid-
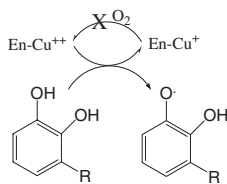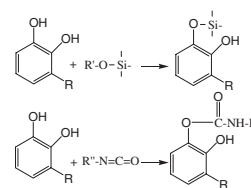
Scheme 3.

ity.[14,15] Silicones with isocyanato residue not only react to urushiol but also react with the hydroxyl group of urushiol through its –SiO– residue (scheme 3).[16] As the hydroxy group in urushiol was consumed, the anti-oxidization of urushiol monomer decreased, then the urushiol monomer was less than 30% in the urushi sap, initiating the autoxidation of the olefin in the side chain of urushiol, and then formed a high polymer.

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Scheme 2.