Plastic Shape Material "*Urushi-Nendo*" Applying Lacquer Tree Paint

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A new material for use in shaping has been created using *urushi* (Japanese lacquer) as a matrix, with natural fibers, such as cellulose as a filler and a primary amine as an additive, to promote the lacquer curing reaction. The cured material is characterized by exhibiting a strength comparable to that of wood.

Urushi, or Japanese lacquer, a liquid obtained in the form of sap from the Japanese lacquer tree (*Rhus vernicifera*), contains the enzyme laccase. In general, this enzyme becomes extremely active under temperature and humidity conditions of 20–30 °C and 70–80% RH and an oxidation–reduction reaction begins. Through this reaction, the principal component of urushi, called urushiol, polymerizes and forms a coating.[1,2] Under these conditions, the molecular structure of urushiol is thought to adopt a reverse micelle form. The authors have made a proposal as to the mechanism driving this reaction.[3,4] In addition, the primary amine is known to display good reactivity with catechol compounds at normal temperatures.[5–7]

Accordingly, the authors sought to engineer a curing reaction by making use of urushiol's catechol ring, and adding the primary amine, which has two or more 2-aminoethylene groups, to urushi sap as an additive. It was predicted that this would lead to a promotion of the curing reaction, leading to a closer binding of the cured material due to a cross-linking effect. The effect of the reaction was to expand a urushi's curing condition range, while also giving the urushi sufficient cohesiveness to allow it to be used as a binder. By exploiting this reaction, the authors attempted to develop a new complex material.

A diagram of the manufacturing method is shown in Fig. 1. A hybrid mixer is used for the mixing and degassing operations. The volume of the container used is 200 mL.

With regard to the composition ratio, cellulose as a filler together with some clay as a viscosity adjuster made up 75–80 wt %, while urushi as a matrix made up 20–25 wt %, and the primary amine as a curing accelerator for the urushi sap was on the order of 1 wt %. The amount of this additive with respect to the urushi sap, which included 82.3 wt % urushiol, was equivalent to 0.01 mol% of urushiol (the average molecular weight was 315.6).[3] Once the constituents were added and allowed to mix, the material became clay-like through uniform mixing alone. We later named this material *urushi-nendo* (meaning literally "urushi clay").

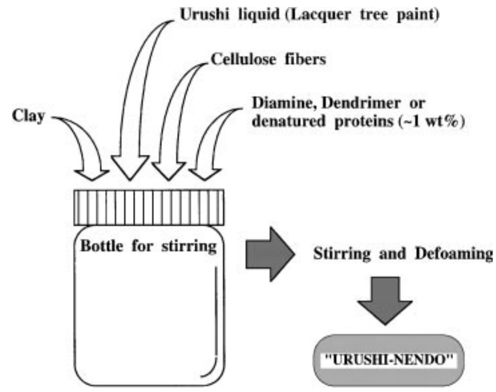

Fig. 1. Manufacturing process of "*Urushi-Nendo*".

Table 1. Curing Properties of "*Urushi-Nendo*"

Testing material	Curing time at dwelling room/h	Color difference[b]		
		L*	a*	b*
"*Urushi-Nendo*"	24	30.14	5.34	8.19
Without additive[a]	72	39.77	7.37	14.02
Without urushi liquid and additive	—	88.85	1.41	7.29
Urushi liquid contained additive	5	28.63	9.29	2.18
Urushi liquid only	20	33.81	19.72	11.07

a) $H_2N–(CH_2)_n–NH_2$/diamine. b) L*/lightness, a* and b*/saturation.

A comparison of the data related to the curing and color of *urushi-nendo* and of urushi film is given in Table 1.

Firstly, the curing time should be considered. The mixture without an additive took almost three days to cure, while compared to the *urushi-nendo* cured in about one day, as shown in Table 1. This was due to the effect of the additive's action in accelerating the urushi curing process under normal conditions, a conjecture that can be assumed from the results of data obtained from measuring the curing rates of urushi films both with and without the additive being present, and as such it can be considered to be a valid result. In addition, although the two types of samples displayed a number of properties in common, the *urushi-nendo* tended to exhibit a great deal less exudation of urushi, as compared to a mixture with no additive present.

Next, the color difference should be considered. Because the curing reaction of urushi proceeds favorably in the presence of an enzyme, we were able to confirm decreases in both the saturation level and the lightness of the mixture.[4] With the additive present, the curing reaction of the urushi was accelerated through the same effect, and the color of the mixture became darker, in line with the measurement results given in Table 1. By observing this color change, we were able to confirm the progress of the urushi curing process.

Comparison data on the mechanical properties, such as the strength and hardness of *urushi-nendo*, its related materials, and wood as a control, are given in Table 2. In addition, com-

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Table 2. Mechanical Properties of "*Urushi-Nendo*"

Testing material	Flexural stress at break/MPa	Durometer hardness/HDD[b)]	Specific gravity (dry condition)	Cross cut friction test/Point
"*Urushi-Nendo*"	37.1	70.5	1.27	—
Without additive[a)]	13.8	62.0	1.18	—
Without urushi liquid and additive	5.7	51.3	0.97	—
Wood ("KIRI"/*paulownia*)	34.7	37.4	0.38	—
Wood ("SUGI"/*cryptomeria*)	63.7	33.2	0.29	—
Urushi paint on "*Urushi-Nendo*"	—	—	—	4
Urushi paint on ABS resin	—	—	—	0–2
Urushi paint on a wooden bowl (on the market)	—	—	—	2–4

a) $H_2N–(CH_2)_n–NH_2$/diamine. b) 100–40 h/h: depth of dimple (mm).

parison data for adhesion when a coating of urushi film is applied to typical molding materials are shown.

First, the mechanical strength should be considered. A comparison test of each material's flexural stress at breaking was performed. Flat plates were cut and 5 × 10 × 100 mm test pieces were made in order to compare the effects of the individual components in the *urushi-nendo*. The test began with a cured specimen made using only a filler and a quantity of viscosity adjuster (but with neither urushi sap nor additive) as a standard. Then, a specimen in which urushi sap was impregnated into this mixture and the strength of the resulting cured specimen (without the additive) were compared with that of the standard specimen. This revealed that with the addition of urushi the strength of the material was almost doubled. Next, the strength of the *urushi-nendo* (to which the additive had been added) was measured and compared against the standard specimen, with the result that this material was found to have almost seven-times the standard specimen's strength. Conversely, a distinctive feature of *urushi-nendo* is that it exhibits constant strength independently of the load's orientation, distinct from the wood.

The reasons why the material's strength increases with the addition of an additive are as follows. The fact that adding an additive results in a harder coating has been confirmed by comparing cases in which an additive was and was not added to urushi film.[8,9] This effect is due to the increased density of the urushiol's reverse micelle particle structure and the tighter binding of the coating. Looking at comparison data with respect to the surface hardness and density reveals that both sets of data display an increase in values when using a binder for the urushi, and that these values increase further with the addition of an additive. A comprehensive analysis of these results indicates that curing urushi sap in the presence of an additive produces a cross-linking effect that increases the resulting material's density, and also improves the adhesion with the filler, which can be interpreted as being linked to an increase in strength. Through this, the closer binding of the cured urushi material due to the cross-linking effect was confirmed.

Urushi-nendo is a material created through a curing reaction in the presence of an enzyme at room temperature and under low-humidity conditions, which is one of the factors that makes urushi such a difficult substance to handle. Thus, one of its features is that it eliminates the difficulties in handling urushi. Moreover, *urushi-nendo* is a new material made by using natural substances and that uses urushi not only as a paint, but as a new forming material.

Experimental

Materials. The urushi sap used in this experiment was obtained from China, and nothing was added to the urushi after sap collection. In this experiment, dodecamethylenediamine was used as the primary amine, although the same effect has been confirmed with similar types of diamine, dendrimer (generation 1.0 (MW 316.54); DAB-Am-4/*N*,*N*,*N′*,*N′*-tetrakis(3-aminopropyl)-1,4-butanediamine),[5] with different numbers of methylene chains.

Test Piece Production. A sample used to measure the curing time of the *urushi-nendo* was spread uniformly to a thickness of 2 mm on a glass plate.

To prepare test pieces for tests concerning the physical properties, a quantity of *urushi-nendo* was formed into a flat plate measuring 5 × 50 × 100 mm and made in the manner previously mentioned.

Measurements. The curing time for the *urushi-nendo* was set as the time when the maximum hardness became constant, as determined using a durometer, known as a type-A hardness tester.

For the flexural stress at a breaking test, 3-point bending was measured using a universal testing machine with the distance between fulcrums set at 40 mm and a head speed of 2 mm/min.

The durometer hardness was measured using a type-D hardness tester durometer based on JIS K7215 tests.

A cross-cut stripping test was performed with one hundred squares at a clearance interval of 1 mm based on JIS K5600 (ISO 2409) tests.

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