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Development of bio-based hybrid resin, from natural lacquer

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ABSTRACT

Preparation and structure analysis of a bio-based hybrid material composed of natural lacquer, epoxy, and organic silane compounds were investigated using liquid and solid-state nuclear magnetic resonance. The good composition of additives in the hybrid was determined by the drying, hardness, and resin-molding properties. Although natural lacquer alone cannot form thick resins, this bio-based hybrid material showed good resin formation at room temperature without thermal treatment. This result could be based on the enhancement of curing by the sol–gel reaction between natural lacquer and the organic silane compound, and a crosslink reaction between organic silane and epoxy groups. At the same time, oxidative polymerization at the unsaturated side chains in the urushiol was enhanced by the sol–gel reaction because the catechol hydroxyl groups, which have an antioxidative property, reacted with the organic silane. In addition, this bio-based resin possesses a thermoset property because curing of the hybrid was improved by thermal treatment. Based on the structure analyses, the sol–gel reaction between urushiol and organic silane compound proceeded immediately, indicating the high reactivity of this sol–gel reaction. On the other hand, the reaction between bisphenol A-type epoxy resin and the organic silane seems to progress slowly after the epoxy ring opening. In addition, a sol–gel reaction occurred between the amine group in the organic silane and the hydroxyl group formed after the crosslink reaction of the epoxy group. These results suggested that the improvement in drying and molding properties of the hybrid was based on the chemical reactions among all components (*i.e.*, natural lacquer, epoxy, and organic silane).

1. Introduction

Many functional polymer materials such as film and resin have been synthesized to make more comfortable and convenient in our daily life. Most of these polymer materials are derived from oil and require large amounts of energy to produce. Therefore, an alternative to oil-based industrial products using renewable resources is desired due to recent environmental problems, global warming, and depletion of fossil fuels. Development of polymers from natural products, such as plant oils and non-food materials, is one of the very attractive ways to solve such environmental problems economically and ecologically.

Natural lacquer (urushi) is one of the traditional natural polymers in Japan that has a beautiful glossy appearance and high durability [1]. Lacquer sap consists of urushiol, which has C15 unsaturated hydrocarbons at 3 or 4 catechols, water, a gummy substance, a nitrogenous material, and laccase [2,3]. One advantage of natural lacquer is that it is polymerized enzymatically in the presence of moisture and laccase without any organic solvent, making natural lacquer, bio-based coating material. Therefore, polymer materials using natural lacquer have been investigated for use as resins [4,5], hybrids [6–8], and composites [9,10].

The laccase in lacquer sap plays an important role in this polymerization. The autoxidation of natural lacquer occurs at unsaturated side chains of urushiol [1]. However, because these reactions progress slowly, the curing of natural lacquer generally takes longer than that of conventional organic coatings. The drying of natural lacquer is strongly affected by the environmental conditions such as humidity and temperature. This enzymatic oxidation reaction requires a highly moist environment (70–80% RH) for activation of laccase [11]. Furthermore, it is difficult to fabricate thick resin products from natural lacquer alone. Therefore, fabrication of thick resin material using natural lacquer is also important to expand the use of natural lacquer application as effective utilization of renewable resources.

We previously developed hybrid lacquers composed of natural lacquer and amine-functionalized organic silane compounds that show good drying property at low relative humidity [8,12,13]. Hybridization by the sol–gel reaction between OH groups in the lacquer and organic silane compounds considerably improves the film properties such as drying speed and hardness [12,14]. In addition, we recently reported hybrid microwave-adsorption materials

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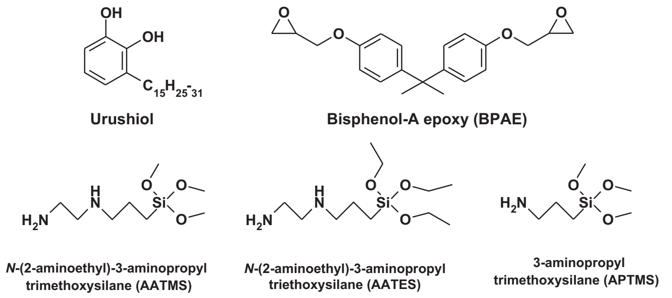

Fig. 1. Chemical structure of urushiol, bisphenol-A epoxy (BPAE), and organic silanes, *N*-(2-aminomethyl)-3-aminopropyl trimethoxysilane (AATMS), *N*-(2-aminomethyl)-3-aminopropyltriethoxysilane (AATES), and 3-aminopropyltrimethoxysilane (APTMS).

prepared from natural lacquer, epoxy, and organic silane compounds [9]. However, the chemical structure of these hybrids has not been described. Therefore, the chemical structure of a bio-based hybrid resin fabricated by chemical reactions among natural lacquer, epoxy, and organic silane compounds and optimization of additive components were investigated in terms of the drying, hardness, and molding properties of the hybrids.

2. Experimental

2.1. Chemicals

The natural lacquer used in this study was purchased from Doityu Shoten, Co. Ltd., Osaka, Japan. Urushiol and lipid component of the lacquer were extracted from raw lacquer sap according to the previous study [14]. Bisphenol A-type epoxy resin (BPAE, Epoxyclear 305114) was purchased from I-Resin Co., Ltd., Tokyo, Japan, and used without further purification. Organic silane compounds, *N*-(2-aminomethyl)-3-aminopropyl trimethoxysilane (AATMS), and 3-aminopropyltrimethoxysilane (APTMS) were purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. *N*-(2-aminomethyl)-3-aminopropyltriethoxysilane (AATES) was kindly supplied by Shin-Etsu Polymer Co., Ltd., Tokyo, Japan. These chemical structures of compounds used in this study are presented in Fig. 1.

2.2. Preparation of hybrid lacquer and resin

Ten grams of natural lacquer and given ratios of additives such as BPAE and organosilicon compounds were mixed for 5 min at room temperature. After fabrication of a hybrid lacquer, the mixture was uniformly coated on a square glass plate (70 mm × 70 mm × 1.3 mm) at 23 °C ± 1 °C using a 76 μm thickness applicator (Yoshimitsu Seiki, Tokyo, Japan) which has ± 10 μm deviation. This lacquer was stored in the dark at 25 °C and 50% RH to evaluate the drying and hardness properties. For preparation of the thick resin, the mixture of natural lacquer, BPAE, and organosilicon compounds was poured into a fluororesin tube (outside diameter: 16 mm, inside: 14 mm, and thickness: 20 mm) at room temperature. After three days, formed thick resin was taken from the tube. The effect of thermal treatment on the curing property of hybrids was also investigated.

2.3. Characterization

The molecular weight of the hybrid was determined at 40 °C by aqueous phase gel permeation chromatography (GPC; TSK-gel column α-3000, α-4000 and α-M, ϕ7.8 mm × 300 mm × 3, Tosoh Co. Ltd., Tokyo, Japan) using dimethylformamide (DMF) as an eluent with 0.01 mol LiBr on a high-performance liquid chromatography system with an RI-8012 refractive-index detector with polystyrene standards. The elution rate was 0.8 ml/min.

The drying process of the epoxy coatings at 23 °C ± 1 °C can be divided into three stages: dust-free dry, touch-free dry, and harden dry (HD). Each stage was measured using an automatic drying time recorder (RC auto-recorder of painting drying time, TaiYu Co. Ltd., Osaka, Japan) at 23 °C ± 1 °C and 60% relative humidity.

The pencil hardness is performed based on the current national standard of GB/T6739-1996. H and B indicate the hardness and softness, respectively, of tested coatings, and higher numbers express the relative hardness or softness of the tested coatings. F and HB indicate medium hardness. However, F is a slightly harder coating than HB. In the present study, pencil lead hardness was determined using a C-221 (Yoshimitsu Seiki, Tokyo, Japan) at 23 °C ± 1 °C.

The gel content of the epoxy coating was determined. Coatings were immersed in acetone at 23 °C ± 1 °C for 24 h, and the non-soluble parts were filtered and dried in a Taiyo muffle furnace (Isuzu, Tokyo, Japan) for 1 h at 50 °C, cooled, and subsequently examined at room temperature to remove residual solvent before weighing. The gel content was calculated using the following equation:

$$\text{gel content}(\%) = \frac{M_1}{M_0} \times 100 \qquad (1)$$

where M_1 and M_0 are the weight of the insoluble fraction and the original weight of the completely dried epoxy coating, respectively.

The structural analysis was conducted *via* liquid-state proton and carbon nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectroscopies using a JNM-ECA500 spectrometer (JEOL Ltd., Tokyo, Japan). Samples were dissolved in deuterated dimethyl sulfoxide (DMSO) solution with chemical shifts referenced from tetramethylsilane (TMS). Cross-polarization/magic angle spinning (CPMAS) solid-state ^{13}C-, ^{29}Si-, and ^{15}N-NMR experiments were performed on a JNM-ECA400 NMR spectrometer (JEOL Ltd., Tokyo, Japan) using a zirconium sample tube (ϕ6 mm).

3. Results and discussion

3.1. Molecular weight distribution

GPC was conducted to determine the molecular weight distribution of hybrids, and the results are summarized in Table 1. As the organic silane content increased, the molecular weight and molecular weight distribution tended to increase. This result could be based on the sol–gel reaction between organic silane and urushiol, as previously reported [12]. On the other hand, the increase in the molecular weight for hybrids using AATES seemed to be lower than that of other silane compounds such as AATMS and APTMS. This result indicates that the organic silane reactivity of the sol–gel reaction in the methoxy group seems to be higher than that in ethoxy group. Therefore, the molecular weight of hybrids was affected more by the use of organic silane compounds other than BPAE.

3.2. Drying and hardness properties

To determine the suitable addition ratios of organic silane and BPAE, we measured the drying and hardness properties of various bio-based hybrid lacquers. The drying property of the lacquers is summarized in Table 2. The addition of BPAE and silane compound to the natural lacquer significantly improved the drying property at room temperature. The hybrid lacquers prepared with 20 wt% of BPAE (Entries 3, 6, and 9) dried more rapidly than natural lacquer (Entry 1). On the other hand, an BPAE at higher concentration (*i.e.*, 30 wt%) decreased the drying property, indicating that the excess BPAE could prevent the sol–gel reaction between urushiol and the