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Design and characterization of modified urethane lacquer coating

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Abstract

A new series of natural lacquer/polyurethane (LPU) blended films were synthesized. The new lacquer/polyurethane films have very good visual color and detected gloss, fast drying time, strong weather resistance, especially against UV light and water, and a better pencil lead hardness (8H). The gel ratio increases with drying time and becomes stable after 6 months (more than 99%). The surface glass transition temperature (T_gs) obtained from a rigid-body pendulum physical properties testing (RPT) instrument showed that the new LPU films dried for 6 months have higher T_gs than polyurethane (PU) films in the following order: LPU 100 > LPU 90 > LPU 80 > LPU 70 > LPU 60 > LPU 50 > PU. Differential scanning calorimeter (DSC) results showed the same tendency as T_g but without a great gap in the LPU series except for polyurethane. Thermogravimetric analysis (TGA) showed that when the ratio of natural lacquer is more than 50%, the 50% weight loss temperatures increase about 100 °C. In addition, the reaction between lacquer and polyurethane is discussed based on the IR and NMR measurements.

Keywords: Lacquer; Urethane; Anti-UV; Coating; RPT

1. Introduction

Lacquer is a complex compound that includes urushiol (60–65%), gummy substance (5–7%), glycoprotein (∼2%), and water (20–30%) [1]. It is a natural and reproducible polymer product obtained from lacquer trees and an excellent green coating film when catalyzed by laccase. The history of lacquer in China goes back 5000–6000 years [2]. The famous ZhuQi MuWan (Vermilion Lacquer Wooden Bowl) found at the Hemudu site, in Zhejiang Province of China, was produced 7000 years ago, in the Neolithic Age [3], which proves that the Chinese began using lacquer to produce highly creative artwork more than 6000 years ago [4]. Lacquer spread across the countries of Asia, especially Japan, and to Europe via the Silk Road for about 1000 years ago [5,6]. Lacquer is valued for its high thermostability, water impermeability, adhesive power, insulating qualities, and durability. Until now, no artifical paint or coating has been able equal its comprehensive properties. However, it has also found to have some disavantages: low yields and high prices, deep and dark color, poor resistance to ultraviolet light, alkali-resistance, the need for strict drying conditions, and limited application in industry.

The structures of urushiols—the main components of lacquer—have been studied thoroughly [7–12], as shown in Scheme 1. Urushiols play a main role as the matrix and skeleton of lacquer films, which are catalyzed by *Rhus* laccase in the drying process.

Due to the environmentally friendly nature and biocompatibility and the versatile structure–property relationships of polyurethane [13–15], polyurethane products offer desirable properties such as high setting speeds, low viscosity, good flexibility, and thermal and ultraviolet stability [16], and their application is rapidly extending to fields such as coatings and paints, automotive, apparel, medical, and window treatment products [17,18].

Polyurethane is typically composed of isocyanate-capped macromolecular chains containing urethane groups in their backbones, usually with a 1–15 wt.% free isocyanate concentration [19], obtained by reaction of a polyol with a molar excess of di- or polyisocyanate:

$$\mathrm{R{-}N{=}C{=}O + HO{-}R' \rightarrow R{-}NH{-}COOR'} \quad (1)$$

$$\mathrm{R{-}N{=}C{=}O + R{-}NH{-}COOR' \rightarrow R{-}N(COOR){-}COOR'} \quad (2)$$

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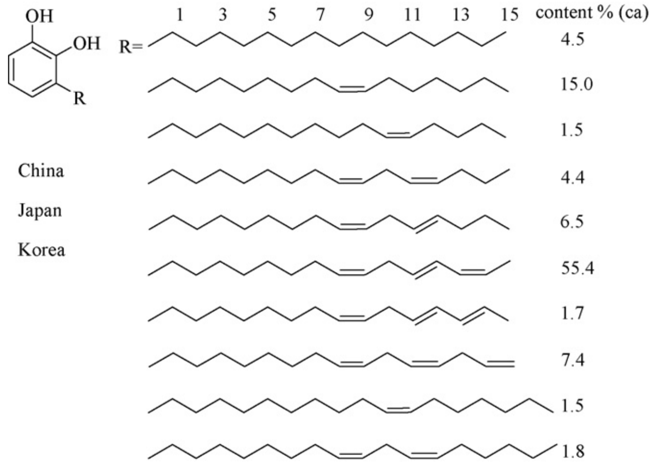

Scheme 1. Typical structures and components of urushiol from China, Japan, and Korea.

where reaction Formulas (1) and (2), R and R′, represent many different organic compounds such as alcohols or other hydroxy-containing compounds.

In this study, a commercial polyurethane product used as a coating was mixed with *kurome* lacquer. The aim of this study was to investigate blends of these two coatings, both of which have good qualities. Until now, no effort to combine these two components has been reported to our knowledge.

2. Experimental

2.1. Materials

2.1.1. Preparation of kurome lacquer

The raw lacquer was collected in 2005 from a Chinese lacquer tree in Chengkou, Sichuang Province, China, and purchased from Tohityu Co. Ltd. in Osaka, Japan. The *kurome* procedure for lacquer was as follows: 20 g raw lacquer was stirred in an open vessel (bottom diameter, 80 mm; capacity, 100 mL) at room temperature for about 1.5 h, then the temperature is increased from 20 to 40 °C for 2–4 h until the water content was reduced to about 3–5% (determined at 120 °C by an AND MX-50 moisture analyzer, AND, Japan), and was used for the experiments. Polyurethane resin (R′ = main phenyl group and minor alkyl group) and its hardener were purchased from Cashew Co. Ltd., Saitama, Japan, and used as received. The components of polyurethane resin are shown in Table 1.

Table 1
The components of commercial polyurethane resin

Component	Polyurethane resin A (%)	Polyurethane hardener B (%)
Xylene	14.4	3.3
Butylacetate	12.3	9.0
Propylene glycol monoethyl ether acetate	3.0	–
Ethylbenzene	11.8	2.7
Ethylacetate	–	18.0
Toluene	–	4.0

2.1.2. Preparation and drying procedures of the blends of kurome lacquer and urethane

The lacquer/polyurethane (LPU) blends of *kurome* lacquer and polyurethane were mixed in various ratios in glass sample cups with or without a hardener by hand stirring 5 min at room temperature (20–25 °C). In each case, the ratio of polyurethane to its hardener was 2:1. According to the concentrations of lacquer used in the experiments, the blends were named LPU 100 (0% polyurethane), LPU 90 (10% polyurethane), LPU 80 (20% polyurethane), LPU 70 (30% polyurethane), LPU 60 (40% polyurethane), LPU 50 (50% polyurethane), and LPU 0 (100% polyurethane).

Kurome lacquer and the blends were uniformly coated on glass sheets (23.5 mm × 245 mm × 2 mm) and square glass plates (70 mm × 70 mm × 1.3 mm), respectively, with a 76 μm thickness, and hardened in a humidity-controlled chamber at 20–25 °C. After 7 days, the sample coated glass sheets were removed from the chamber and stored at room temperature for 6 months.

2.2. Material characterization

The process of lacquer drying can be divided into three stages: dust-free dry (DF), touch-free dry (TF), and hardened dry (HD) and is measured using an automatic drying time recorder (RC auto-recorder of painting drying time, TaiYu Co. Ltd., Osaka, Japan). The hardness of pencil lead is described by letters and numbers determined according to the current national standard of GB/T6739-1996: the meanings of H and B designate how hard or soft the tested films are, respectively. A higher number with H or B expresses the hardness or softness of the tested films, respectively; F and HB indicate medium hardness, while F is a slightly harder film than HB. The pencil lead hardness was determined by a Yoshimitsu C-221 instrument (Tokyo, Japan).

Infrared spectra (IR) were taken on a JASCO FTIR 460+ spectrometer under drying air at 25 °C. Because it is possible that moisture in the lacquer sap would melt a KBr or NaCl disk, polyvinylidene chloride (PVC) film (Saran Wrap, Asahi Kasei, Japan) was used to form the IR sample. The lacquer was thinly coated on the PVC film with a spatula, and the same kind of PVC film was used as a blank. Spectra of samples were acquired at 2 cm^{-1} resolution ranged from 400 to 4000 cm^{-1} under the same scanning and temperature conditions.

^{1}H NMR and ^{13}C NMR were recorded on a 500 MHz JEOL JNM α-500 spectrometer. Samples were dissolved in DMSO–d_6 and acetone–d_6 with chemical shifts referenced from tetramethylsilane (TMS).

A rigid-body pendulum physical property-testing (RPT) instrument (AND, Japan) was used to determine the drying time of the blended films. The RPT oven was programmed to rise at a rate of 2 °C/min from 25 to 250 °C [20].

A DSC-60 furnace (Shimadzu, Japan) was programmed at a constant heating rate rise of 10 °C/min in the temperature range from 30 to 300 °C. DTG-60 equipped with a TA-60 WS apparatus (Shimadzu, Japan) was also used to analyze the thermal behaviors of the blended films at a constant heating rate rise of 20 °C/min in the temperature range from 30 to 600 °C.