Characterization of natural coating materials using Fourier transform infrared spectroscopy and pyrolysis-gas chromatography/mass spectrometry

Noriyasu Niimura, Hiroshi Terashima

***Abstract*— Fourier transform infrared spectroscopy (FT-IR) with attenuated total reflectance (ATR) technique is one of the non-destructive analysis methods. Using this method, a Japanese lacquer film and a cashew resin film were characterized. Additionally, the results were compared with those obtained by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Cashew resin has been used as a substitute of the Japanese lacquer, because it dries quickly and the cost is lower.**

The absorption signals assigned to C-O stretching were detected at ca. 1260-1000 cm^{-1} in the respective FT-IR spectra. The signal at 1031 cm^{-1} is prominent in the Japanese lacquer film, but that in the cashew resin film is not. This prominent signal is attributed to plant gum. The Japanese lacquer film is composed of plant gum of which main constituent is polysaccharide, but the cashew resin film is not.

Using Py-GC/MS, the urushiol components were detected as the pyrolysis products from the Japanese lacquer film; however, cardanol components were detected from the cashew resin film. The OH, CH, C=C and C-O stretching absorption signals detected by FT-IR are attributed to these compounds, though the prominent signal at 1031 cm^{-1} in the Japanese lacquer film is done to the plant gum.

***Index Terms*— FT-IR, Py-GC/MS, Japanese lacquer, cashew resin.**

I. INTRODUCTION

Japanese lacquer has been used as the coating material for a long time. There are lots of historical artistic handicrafts, art objects and architectures coated with Japanese lacquer [1-5]. Some of them are designated as national treasures and others are registered on the World Heritage List.

In restoration work, it is important to identify the coating materials [5]. We reported that pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is efficient to analyze the coating material [6-10]. However, Py-GC/MS is the destructive analysis, and the less sample amount (0.5 mg) is required. To analyze the valuable sample, it is better to use non-destructive method.

Fourier transform infrared spectroscopy (FT-IR) with attenuated total reflectance (ATR) technique is one of the non-destructive analysis methods. Using this method, a Japanese lacquer film and a cashew resin film were characterized. Additionally, the results were compared with those obtained by Py-GC/MS. Cashew resin has been used as a substitute of the Japanese lacquer, because it dries faster and the cost is lower.

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II. EXPERIMENTAL

A. Japanese lacquer film

Toxicodendron vernicifluum lacquer was treated using the traditional Kurome and Nayashi methods, which are the mixing processes of the sap [11], and coated on a glass plate followed by hardening in a humidity-controlled chamber with a relative humidity of 70~90 % at 20°C for 7 days.

B. Cashew resin film [9]

Hexamethylenetetramine was added to the technical cashew nut shell liquid (CNSL) at lower temperatures to yield a benzylamine derivative. A secondary reaction occurs at higher temperatures involving the reaction of excess technical CNSL with benzylamines to form a methylene cross-linked structure with the evolution of ammonia. Metallic soap of manganese and cobalt was added to the methylene cross-linked structure to yield a cashew resin film.

C. FT-IR spectroscopy

An FT-IR spectrometer: JIR-WINSPEC50 (JEOL Ltd.) with a single reflection ATR accessory: Durascope (S. T. Japan Inc.) was used for the measurements. For each spectrum, 100 scans were accumulated at a resolution of 8 cm^{-1}. All spectra were recorded between 4000 cm^{-1} and 650 cm^{-1}.

D. Py-GC/MS

A stainless steel capillary column (0.25 mm i.d. x 30 m) coated with 0.25 µm of Ultra Alloy PY-2 (100 % methylsilicone) was used for the separation. The 50 mL/min He carrier gas flow at the pyrolyzer was reduced to 1 mL/min at the capillary column using a splitter. The sample (0.5 mg) was placed in a platinum sample cup. The cup was placed on the top of the pyrolyzer at near ambient temperature. The sample cup was introduced into the furnace at 400°C, and then the temperature programming of the GC oven was started. The GC oven was programmed at a constant temperature increase of 20°C per minute starting from 40°C to 330°C. The pyrolysis products were identified by mass spectrometry. The mass spectrometer: JMS-Q1500GC (JEOL Ltd.) ionization energy was 70 eV (EI-MS).

III. RESULTS AND DISCUSSION

A. FT-IR measurements

FT-IR spectra of the films are shown in Fig. 1. The absorption signals assigned to O-H, C-H and C=C stretching were detected at ca. 3550-3100, around 2925, 2855 and 1625 cm^{-1} in the respective spectra. Additionally, the absorption signals assigned to C-O stretching were detected at ca. 1260-1000 cm^{-1} in the respective spectra. The signal at 1031 cm^{-1} is prominent in the Japanese lacquer film, but that in the cashew resin film is not. This prominent signal is attributed to plant gum. The Japanese lacquer film is composed of plant gum of which main constituent is polysaccharide [12], but the cashew resin film is not.

The detection of the prominent signal is effective to discriminate the Japanese lacquer film from the cashew resin film.

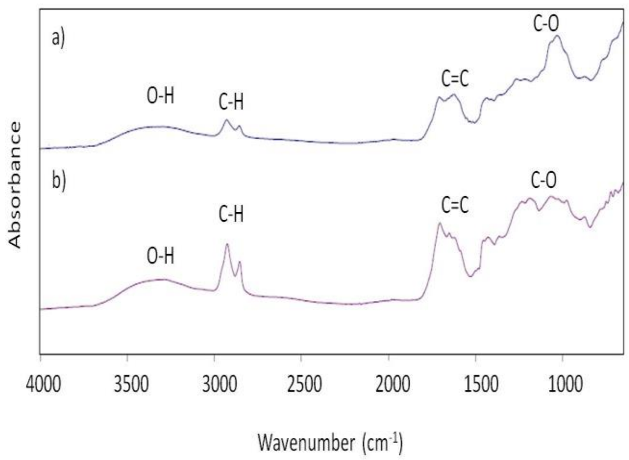

Fig. 1 FT-IR spectra of the films

a) Japanese lacquer film
b) Cashew resin film

B. Py-GC/MS measurements

The total ion current chromatogram (TICC) of the Japanese lacquer film is shown in Fig. 2. The peaks 1 and 2 were assigned to 3-pentadecenylcatechol and 3-pentadecylcatechol by mass spectra shown in Fig. 3, respectively. These are urushiol components, which are the monomers of the Japanese lacquer film [4]. The Japanese lacquer film is terminated with these compounds [6]. The OH, CH, C=C and C-O stretching absorption signals detected by FT-IR are attributed to these compounds, though the prominent signal at 1031 cm^{-1} is done to the plant gum.

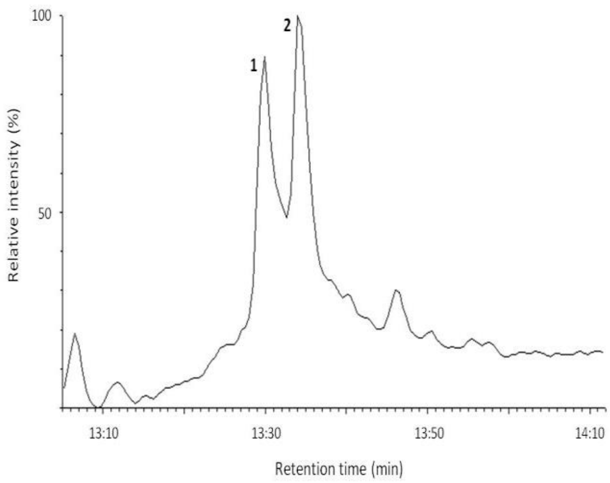

Fig. 2 TICC of the Japanese lacquer film

1: 3-pentadecenylcatechol
2: 3-pentadecylcatechol

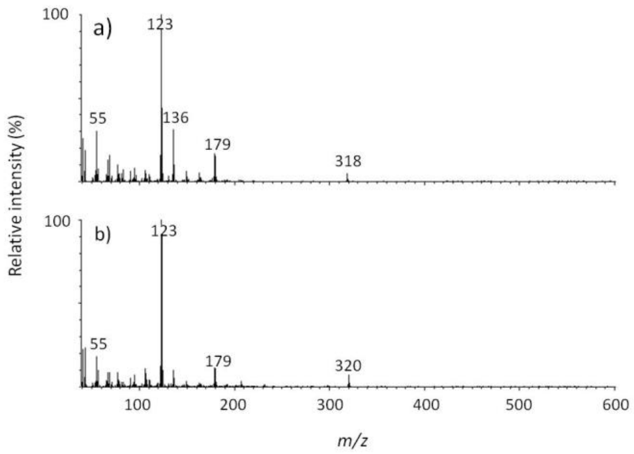

Fig. 3 Mass spectra of the peaks 1 and 2 shown in Fig.2

a) peak 1 (3-pentadecenylcatechol)
b) peak 2 (3-pentadecylcatechol)

The TICC of the cashew resin film is shown in Fig. 4. The peaks 1 and 2 were detected in the chromatogram. These were assigned to 3-pentadecenylphenol and 3-pentadecylphenol by the mass spectra shown in Fig. 5, respectively. These are cardanol components, which are the monomers of the cashew resin film [13]. The OH, CH, C=C and C-O stretching absorption signals detected by FT-IR are attributed to these compounds.

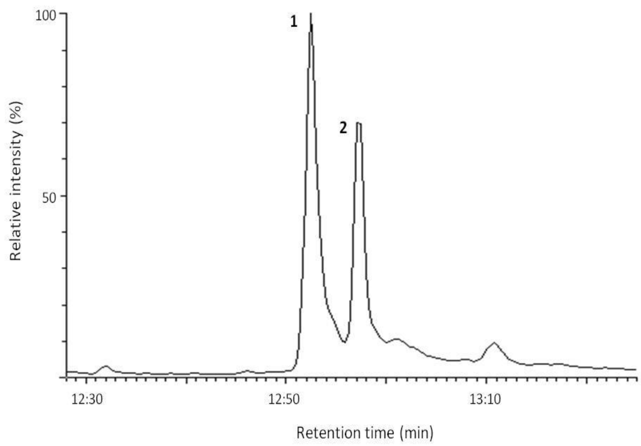

Fig. 4 TICC of the cashew resin film

1: 3-pentadecenylphenol
2: 3-pentadecylphenol

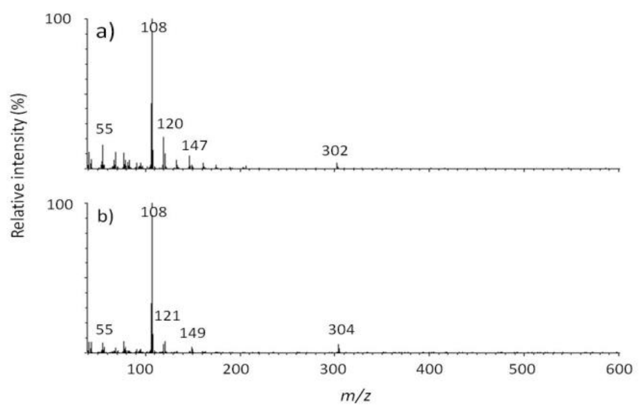

Fig. 5 Mass spectra of the peaks 1 and 2 shown in Fig.4
a) peak 1 (3-pentadecenylphenol)
b) peak 2 (3-pentadecylphenol)

IV. Conclusion

A Japanese lacquer film and a cashew resin film were characterized using FT-IR and Py-GC/MS. In the respective FT-IR spectra, the absorption signals assigned to O-H, C-H, C=C and C-O were detected, being attributed to urushiol and cardanol, respectively. On the one hand the prominent signal was detected at 1031 cm^{-1} in the spectrum of the Japanese lacquer film, but on the other hand it was not detected in that of the cashew resin film. The detection of this signal is effective to discriminate the Japanese lacquer film from the cashew resin film. Additionally, the urushiol and cardanol components were detected from the respective films by using Py-GC/MS. These results support those obtained by using FT-IR, characterizing the respective films.

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