Curing and thermal behaviors of Korean *Dendropanax* Lacquer made by acetone and wine spirit extraction methods

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Abstract

This study was performed firstly to investigate the curing mechanism of Korean *Dendropanax* Lacquer made by both the acetone and wine spirit extraction methods, and secondly to determine the minimum curing conditions.

The chemical, physical and thermal measurements obtained in this study showed that the Lacquer made by the wine spirit extraction method reacted faster at the same curing temperature. In addition, the Korean *Dendropanax* Lacquer made by the wine spirit extraction method can be effectively and economically cured at 100 °C for 150 min and 130 °C for 60 min.
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Keywords: Korean *Dendropanax* Lacquer; Curing mechanism; Wine spirit extraction; Acetone extraction

1. Introduction

Korean *Dendropanax* Lacquer is made from a resinous sap obtained from *Dendropanax morbifera* Lev., which is found in the southern part of the Korean peninsula. The Lacquer is called Hwangchil in Korea, Koshiabura in Japan and Jin-qi or Huang-qi in China [1].

In historic documents in Korea, Japan and China, Korean *Dendropanax* Lacquer has been described as producing coatings with excellent cured film properties and as creating a brilliant golden yellow color on wooden and metallic substrates (armor suits, helmets, arrowheads, etc.) [2–11].

Terada et al. showed that the chemical constituents of the Koshiabura varnishes in Japan contained conjugated diene compounds as the photopolymerizable monomers. They found that these monomers easily polymerized in sunlight to form golden-colored, hard-coating films in a short time, and that the films were waterproof and anticorrosive [1].

However, little or no accumulated information is available, because the coating technique used for Korean *Dendropanax* Lacquer has been largely a traditional affair and the technique was a guarded secret, which is not clearly known today.

Recently, some research has been carried out to re-establish the coating technology used for Korean *Dendropanax* Lacquer. Photooxidation may be one of the most important reactions in the chemistry of the Lacquer. Although Korean *Dendropanax* Lacquer air-dries to a through-dry stage to achieve optimal film properties, curing at elevated temperatures may be required, because of the protracted curing time at atmospheric temperature.

Generally, Korean *Dendropanax* Lacquer is made by removing impurities in the resinous sap using acetone as the extractant, followed by filtering or screening, and finally by concentrating the resin solution in a rotary evaporator under vacuum. However, acetone is harmful both to humans and to the environment.

In recent years, wine spirit has increasingly been used as an extractant, in place of acetone. Wine spirit is environmentally sound and emits virtually no volatile compounds that are known to pose a problem for humans or the environment.

This study was performed to investigate the curing mechanism of Korean *Dendropanax* Lacquer made by both the acetone and wine spirit extraction methods with respect to curing time and temperature.

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2. Experimental

Korean *Dendropanax* Lacquer is the resinous sap from *Dendropanax morbifera* Lev., which grows in the southern part of the Korean peninsula. Impurities in the resinous sap were removed by extracting them either with acetone (C_3H_6O) or with wine spirit (C_2H_5OH), followed by filtering or screening, and finally by concentrating the resin solution in a rotary evaporator under vacuum for 80 min. The Korean *Dendropanax* Lacquer obtained was a viscous, dark yellow liquid.

A glass plate was coated with ca. 0.08 g of Korean *Dendropanax* Lacquer to measure the contact angle with a contact angle-measuring device. A thin aluminum foil was coated with the Lacquer, in order to measure its infrared (IR) spectrum by attenuated total reflection (ATR). The sizes of the glass and aluminum foil were 7.6 cm × 2.4 cm × 0.1 cm and 7.6 cm × 2.4 cm × 19 cm, respectively.

The samples were coated with a bar coater (no. 22). The coated samples were placed in a dry-oven, which had a heat air circulating system. The coated samples were then cured at 80, 100 and 130 °C to a through-dry state and removed at regular time intervals to measure the degree of curing of the Lacquer.

In this study, FT-IR and contact angle techniques were used to investigate the curing mechanism. It should be possible to determine the degree of chemical and physical conversion at the micro-level by using such precise methods, in order to accurately measure the curing time required.

IR spectra were obtained using a Nicolet Magna 550 Series II FT-IR (NICOLET Co., Madison, WI, NICEM at Seoul National University) equipped with ATR, which provides a means of investigating both the solid and liquid surfaces, without altering the surface characteristics of the sample [12,13]. The ATR crystal was of zinc selenide (ZnSe), and had a transmission range from 3800 to 650 cm^{-1} with a refractive index at 1000 cm^{-1} of 2.4. The resolution of the spectrum recorded was 4 cm^{-1}. The ZnSe crystal was covered with the coated thin aluminum foil, which was removed at regular time intervals from the oven to obtain the IR spectrum.

To monitor the Lacquer curing, the stretching vibration peak of C=C at 1644 cm^{-1} was chosen. The area of the vibration peak was calculated to be in the 1633–1657 cm^{-1} region, which contained a 1644 cm^{-1} peak. The percentage reduction in peak area of the 1633–1657 cm^{-1} region, referred to as α, was calculated by means of:

$$\alpha = \frac{A_{T,t=0} - A_{T,t}}{A_{T,t=0}} \times 100 \tag{1}$$

where A is the peak area of the vibration band, T the curing temperature, and $t = 0$ represents the initial curing time and t the current curing time.

The change in the contact angle of the Korean *Dendropanax* Lacquer surface during the curing process was measured using an SEO 300A contact angle measuring device (Surface & Electro-Optics Co., Korea) at 26 ± 1 °C and 71 ± 1% relative humidity. A single 10 cm drop of distilled water was placed on the surface of the samples, which were taken out of the oven at regular time intervals. The contact angle was measured 1 min after the drop of distilled water was placed on the surface of the sample.

The viscoelastic properties of the Korean *Dendropanax* Lacquer were measured using a dynamic mechanical thermal analyzer (DMTA; Rheometric Scientific DMTA IV, NICEM at Seoul National University) set at rectangular tension mode. In order to investigate the viscoelastic properties of the viscous Lacquer using the rectangular tension mode, the Lacquer was impregnated into the rectangular shaped filter paper (8 mm × 0.5 mm × 272 mm). The weight of the impregnated Lacquer was 183 mg. The measurements were performed at a frequency of 1 Hz. The temperature range was from 45 to 350 °C at a heating rate of 5 °C/min. The results were presented in terms of storage modulus (E') and loss modulus (E'').

In addition, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to investigate the thermal properties of the Korean *Dendropanax* Lacquers.

DSC analysis with a TA Instrument DSC Q 1000 (NICEM at Seoul National University) equipped with a Thermal Analysis Data Station enabled the curing exotherm of the Korean *Dendropanax* Lacquer to be determined. This study was done using a sealed aluminum capsule pan, under a nitrogen atmosphere, at five different heating rates of 2, 5, 10, 20 and 40 °C/min, between 30 and 300 °C.

3. Results and discussion

3.1. FT-IR analysis

Fig. 1 shows the IR spectra of the uncured Lacquer and the Lacquer cured at 100 °C for 300 min, with the wine spirit extraction method. In Fig. 1, the peaks at 3386, 2927–2856
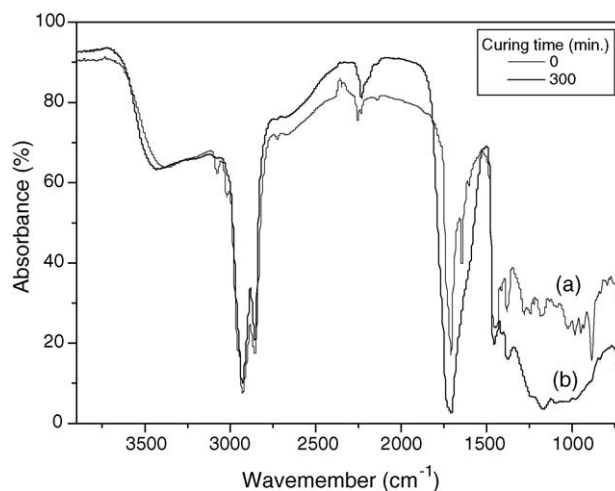

Fig. 1. IR spectra of Korean *Dendropanax* Lacquer cured at 100 °C for (a) 0 min and (b) 300 min, with the wine spirit extraction method.
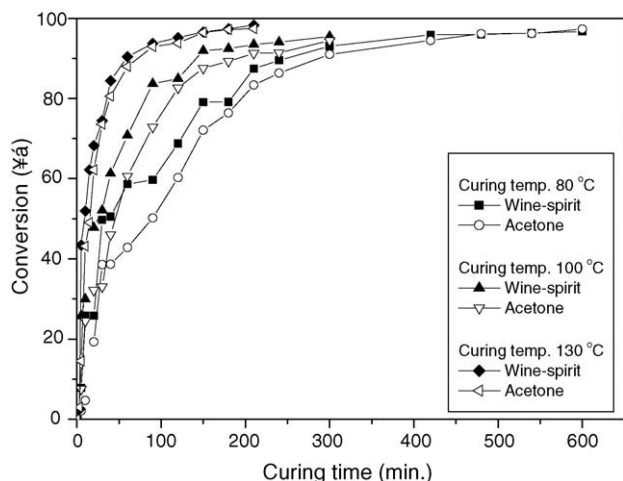
Fig. 2. Changes in the C=C ATR peak area as a function of curing time at each curing temperature.

Fig. 3. Variation in contact angle as a function of curing time at each curing temperature.

and 1709 cm^{-1} are due to O–H, C–H and C=O stretching vibrations, respectively. In particular, the peak at 1644 cm^{-1} is due to C=C stretch. This peak decreased with increased curing time (see Fig. 2). The decrease in the area of the peak at 1664 cm^{-1} is due to the decrease in the number of C=C chemical bonds caused by the oxidative thermal polymerization (or cross-linking) process.

Korean *Dendropanax* Lacquer includes an unsaturated chain responsible for the polymerization properties, either thermal or oxidative, of the Lacquer [14,15]. The unsaturated chains have one, two, three or more double bonds, and their position is thought to vary. The number and position of the double bonds is important. Double bonds separated by a single bond are called conjugated bonds and they dry more rapidly than isolated double bonds.

In addition, the decrease in area of the peak at 1664 cm^{-1} may have been caused by heat, which is thought to cause the migration of the carbon double bonds to conjugated positions. This conjugation facilitates cross-linking by a Diels–Alder type of mechanism [14]. Thus, the Lacquer is polymerized by either thermal or oxidative means to give a solid or semi-solid structure. The typical changes occurring in the C=C peak area during the curing process are shown in Fig. 2, which shows the decrease in the peak area with increasing curing time, resulting from thermal oxidative polymerization.

The changes in the C=C peak area are dependent on curing temperature; the area increases with increasing temperature. In particular, both peak areas decreased sharply during the first stage, irrespective of the curing temperature, and the C=C peak area of the Lacquer made by the wine spirit extraction method decreased more dramatically than that of the Lacquer made by the acetone extraction method. In the wine spirit extraction method, the C=C peak area reached a minimum after 300 min at 80 °C, 150 min at 100 °C and 60 min at 130 °C, which represented ca. 90% decrease in peak area. In the acetone extraction method, the C=C peak area reached

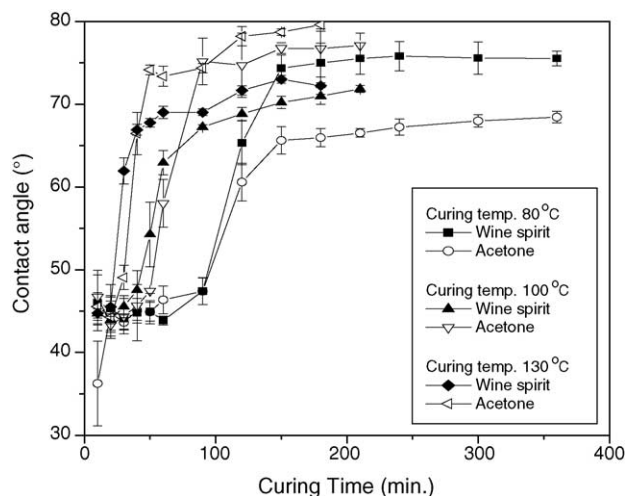a minimum after 420 min at 80 °C, 210 min at 100 °C and 90 min at 130 °C.

3.2. Contact angle

The variation in contact angle as a function of curing time and temperature is shown in Fig. 3. The contact angle increased with increasing curing time and temperature. Previous studies have shown that a large contact angle is related to low surface free energy and stronger hydrophobicity [15]. The contact angle increased dramatically during the earlier stage of the curing process, in parallel with changes in the C=C peak area, as measured by ATR.

Knowledge of the hydrophilic/hydrophobic behavior is very important for understanding the surface curing behavior. Generally, contact angles are related to the surface morphology/reorientation or the mobility of the surface segments, which all contribute to the surface free energy [16]. Previous studies have shown the existence of a clear relationship between contact angle and surface energy [16,17].

The decreased C=C peak area and increased contact angle demonstrate that the Korean *Dendropanax* Lacquer can be cured by thermal oxidative polymerization [14].

The number of hydrophilic sites, which are able to react with the liquid in the Korean *Dendropanax* Lacquer, decreased with increasing curing time and temperature. In addition, the film permeability to liquid may have decreased as the amount of cross-linking of the cured film increased.

Thus, the minimum curing time and temperature can be determined by measuring the contact angles, due to the relationship between the increased hydrophobicity and the extent of curing.

In the wine spirit extraction method, only slight changes in the contact angle were observed after 40 min at 130 °C, 90 min at 100 °C and 150 min at 80 °C. In the acetone extraction method, slight changes in the contact angle were
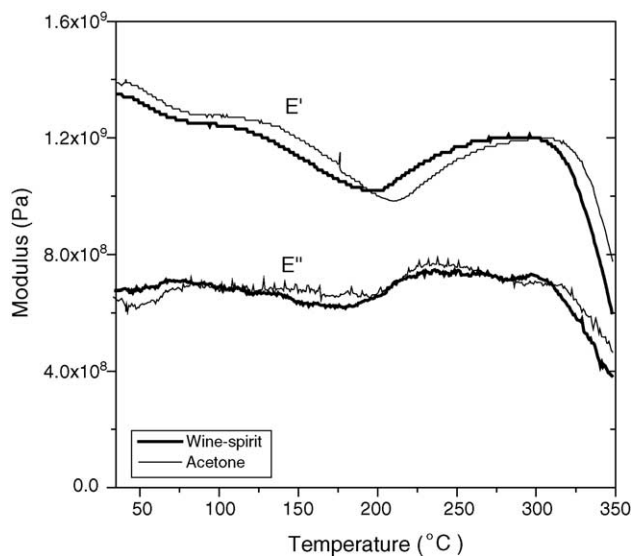
Fig. 4. Variation in viscoelastic properties as a function of curing time at each curing temperature.

observed after 60 min at 130 °C, 90 min at 100 °C and 180 min at 80 °C.

However, at an earlier stage, the contact angle of the Lacquer made by the wine spirit extraction method increased more than that of the Lacquer made by the acetone extraction method.

3.3. Viscoelastic properties

In Fig. 4, the viscoelastic properties of the Korean *Dendropanax* Lacquer are presented. In the rectangular tension mode of DMTA, filter paper as a support was used to investigate the viscoelastic properties of the viscous Lacquer. In the case of the Lacquer made by the wine spirit extraction method, E' increased gradually at around 204 °C, due to thermal oxidative polymerization. Compared with the Lacquer made by the acetone extraction method, the onset temperature of increasing E' was lower. The observed decrease in E', after the maximum value was attained, was explained by the thermal degradation of the constituents of the filter paper and the Lacquer [18]. The chemical and physical measurements obtained in this study show that the Lacquer made by the wine spirit extraction method reacted faster at the same curing temperature.

3.4. Thermal properties

As reported in the literature [19], nth order and auto-catalytic kinetics are the two reaction mechanisms used to describe the curing reaction. The nth order kinetics are expressed as:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \qquad (2)$$

where α is the extent of the curing reaction, is defined by $\alpha = \Delta H_t / \Delta H_{\text{Total}}$, and the enthalpy of the curing reaction at

time t and at the end of the curing can be determined from the DSC thermograms.

The rate constant can be expressed as:

$$k = A\,e^{-E_a/RT} \qquad (3)$$

where A is the frequency factor and E_a the activation energy. Then,

$$\ln k = \ln\left[\frac{d\alpha/dt}{(1 - \alpha)^n}\right] = \ln A - \frac{E_a}{RT} \qquad (4)$$

When the order of this reaction is properly assumed, a plot of $\ln k$ versus $1/T$ allows us to predict A and E_a.

Kissinger [20] proposed that,

$$E_a\beta(RT^2) = A\,e^{-E_a/RT_p} \qquad (5)$$

where β is the heating rate and can be expressed as $\beta = dT/dt$. By taking the logarithm of Eq. (4), the Kissinger equation is obtained as follows:

$$-\ln\left(\frac{\beta}{T_P^2}\right) = -\ln\left(\frac{AR}{E_a}\right) + \left(\frac{1}{T_p}\right)\left(\frac{E_a}{R}\right) \qquad (6)$$

A and E_a can be obtained by plotting $-\ln\left(\beta/T_P^2\right)$ versus $1/T_p$. The curing kinetic with DSC at different heating rates, required to obtain the fundamental kinetic constants of E_a, is obtained from plotting $-\ln\left(\beta/T_P^2\right)$ against $1/T_p$.

The DSC curing curves of the Lacquer made by the wine spirit extraction method as a function of the heating rate are shown in Fig. 5. It can be seen that there is an endothermic peak in the curing process. As shown in Fig. 5, the peak temperature increased as the heating rate was increased. Using the same process, the DSC curing curves of the Lacquer made by the acetone extraction method were obtained.

The plots of $-\ln(\beta/T^2_p)$ against $1/T_p$ for the Lacquer made by the acetone and wine spirit extraction methods are shown in Fig. 6.
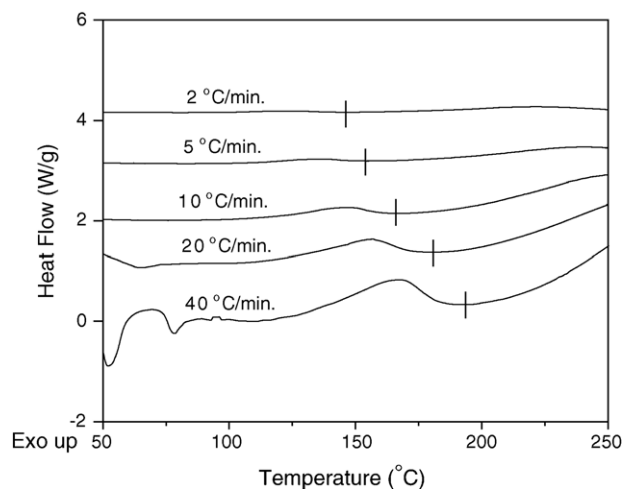

Fig. 5. Comparison of the curing peak of the Lacquer made by wine spirit extraction method at different heating rates.
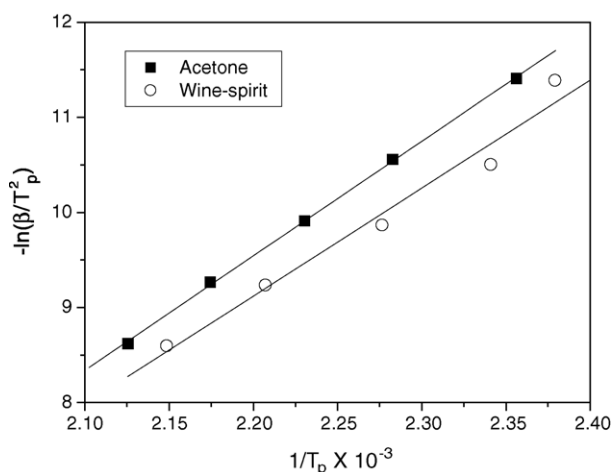
Fig. 6. Plot of $-\ln(\beta/T^2_p)$ vs. $1/T_p$ for the Lacquer made by the acetone and wine spirit extraction methods.

The curing kinetics with DSC at different heating rates, used to obtain the fundamental kinetic constants of E_a, are obtained from plotting $-\ln(\beta/T^2_p)$ against $1/T_p$.

The obtained value of E_a is 99.9 kJ/mol for acetone and 93.4 kJ/mol for wine spirit.

4. Conclusion

This study was performed firstly to investigate the curing mechanism of Korean *Dendropanax* Lacquer made by both the acetone and wine spirit extraction methods and secondly to determine their minimum curing conditions.

According to the FT-IR results and the contact angle analysis, the peak area of the C=C ($1644\,cm^{-1}$) stretch decreased with increasing curing time, due to oxidative thermal polymerization (or cross-linking). The Lacquer with an increased contact angle exhibits increasing hydrophobicity, due to the polymerization, which occurs during the curing process. The changes in the area of the double bond peak and the contact angle were dependent on the curing temperature. In DMTA analysis, the changes observed in E' and E'' were due to thermal oxidative polymerization and thermal degradation. When the Lacquer made by the wine spirit extraction method was compared with that made by the acetone extraction method, the onset temperature of increasing E' was lower for the former.

The curing kinetics with DSC at different heating rates, required to obtain the fundamental kinetic constants of E_a in the Kissinger equation, were obtained from plotting $-\ln(\beta/T^2_p)$ against $1/T_p$. The obtained value of E_a was 99.89 kJ/mol

for the Lacquer made by acetone extraction method and 93.43 kJ/mol for that made by the wine spirit extraction method. Therefore, the Lacquer made by the wine spirit extraction method undergoes faster curing than that made by the acetone extraction method under the same curing conditions.

The chemical, physical and thermal measurements obtained in this study showed that the Lacquer made by the wine spirit extraction method reacted faster at the same curing temperature. The Korean *Dendropanax* Lacquer made by the wine spirit extraction method can be effectively and economically cured at 100 °C for 150 min and 130 °C for 60 min.

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