Curing Behaviors of Korean *Dendropanax* Lacquer Determined by Chemical and Physical Measures

Byoung-Hoo Lee, Hyun-Joong Kim

Laboratory of Adhesion and Bio-Composites, Department of Forest Products, Seoul National University, Seoul 151-742, South Korea

ABSTRACT: This work was performed to investigate the curing behaviors of Korean *Dendropanax* lacquer and to determine its sufficient curing conditions. In FTIR and AFM analyses, the peak area of C=C (1644 cm^{-1}) and the microadhesion decreased with increasing curing time, attributed to oxidative thermal polymerization (or crosslinking). The magnitude of the microadhesion between the probe and the surface related to the surface tack of the lacquer indicates how well the lacquer was cured and crosslinked. The increased contact angle exhibited increasing lacquer hydrophobicity, due to polymerization, during the curing process. Changes in double bond peak, contact angle, and microadhesion were dependent on the curing temperature. The results obtained by chemical and physical measures showed that Korean *Dendropanax* lacquer can be effectively (economically) cured at 100°C for 150 min and at 110°C for 120 min. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 625–630, 2004

Key words: atomic force microscopy (AFM); coatings; crosslinking; curing of polymers; Korean *Dendropanax* lacquer

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 recent years, natural lacquers such as a cashew nut shell liquid (CNSL) lacquer and oriental (*Rhus vernicifera*) lacquer have attracted considerable interest because of the excellent protective and decorative properties. These have been used as surface coatings for wood, porcelain, metalware, and so forth.[2–13] Over the past 45 years, synthetic lacquers have competed with natural lacquers. However, natural lacquered wares retain a long-lasting, satisfying gloss, and beauty, whereas synthetic lacquered wares, although convenient and cheap, soon become dull and unattractive.[9] Moreover, natural lacquers are made of reproducible resources and are advantageous from the viewpoint of preservation of the environment.

CNSL is isolated from cashew nut shells that are chiefly grown in Brazil and India. The chemical, mechanical, and thermal properties of CNSL have been characterized by a number of techniques.[2–6] Oriental lacquer is made from the sap of lacquer trees, *Rhus vernicifera*, primarily in Korea, Japan, and China. A number of studies have been made on the chemistry, curing behavior, film properties, and viscoelastic and surface morphological properties.[7–13] More recently, many patents or studies related to the applications of CNSL and oriental lacquers have been published.[2–13]

In historic documents in Korea, Japan, and China, Korean *Dendropanax* lacquer has been described to produce coatings with excellent cured film properties with a brilliant golden yellow color on wooden and metallic substrates (armor suits, helmets, arrowheads, etc.).

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

However, little or no accumulated information is available because the coating technique of Korean *Dendropanax* lacquer has been largely a traditional, secretly guarded process and therefore is not known clearly today.

Recently, some research has been carried out to reestablish the coating technology of 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 thoroughly dry stage to achieve optimal film properties, curing at elevated temperatures may be required

because of the protracted curing time at atmospheric temperature.

This study was undertaken to investigate the curing behaviors of Korean *Dendropanax* lacquer with respect to time and temperature.

EXPERIMENTAL

Materials

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 acetone extraction followed by filtering or screening, and finally by concentrating the resin solution in a rotary evaporator under vacuum. Korean *Dendropanax* lacquer is a viscous, dark yellow liquid. To improve the brushability, 10 wt % solvent, based on the total amount of aqueous lacquer, was added to the lacquer. The solvent used was composed of turpentine, acetone, and ether (80, 10, and 10% by weight, respectively).

Sample preparation and the curing process

A glass plate (7.6 × 2.4 ×0.1 cm) was coated with 0.9 ± 0.1 g of Korean *Dendropanax* lacquer to measure contact angle with a contact angle measuring device and adhesion force by atomic force microscopy (AFM). A thin piece of aluminum foil (7.6 × 2.4 × 19 μm) was coated to measure the infrared (IR) spectrum by attenuated total reflection (ATR). The sample was coated with a bar coater (No. 22).

The coated glass and aluminum foils were oven-cured at 80, 90, 100, 110, and 130°C to a thoroughly dry state. The nonvolatile content of the lacquer was 55%. Samples were removed at regular time intervals to measure the degree of curing of the lacquer.

Analysis

In this study, FTIR, AFM, and contact angle techniques was used to investigate the curing behaviors. It should be possible to determine chemical and physical conversion at the microlevel by these more precise methods to identify sufficient curing time.

Gas chromatography–mass spectrometry (GC-MS)

The constituents of the Korean *Dendropanax* lacquer were separated using a GC-17A gas chromatograph (Shimadzu, Kyoto, Japan) fitted with a Hewlett–Packard HP-5 column (Hewlett–Packard, Palo Alto, CA). Samples were analyzed using GC-17A gas chromatograph connected to a QP-5000 (Quadrapole) mass spectrometer (Shimadzu). The Korean *Dendropanax* lacquer was injected dissolved in acetone. Initially, the
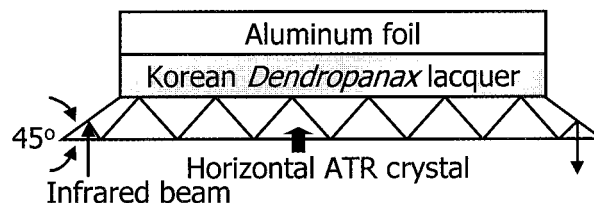

Figure 1 Schematic FTIR-ATR.

column oven temperature was maintained at 65°C for 1 min and then increased at 5°C/min to 250°C and held for 3 min. The splitless injector block and the detector were at 300 and 280°C, respectively. The carrier gas was helium at a gas flow of 0.9 mL/min in the column. The MS scan parameters included a mass range of 100–400, a scan interval of 0.5 s, a threshold of 1000, and a detector voltage of 1.5 kV. Compounds were identified by matching fragmentation patterns in mass spectra with the National Institute of Standards and Technology library (NIST12 and NIST62).

Baseline horizontal attenuated total reflection (ATR) spectroscopy

IR spectra were obtained using a Nicolet Magna 550 Series II FTIR (Nicolet Analytical Instruments, Madison, WI) equipped with attenuated total reflectance (ATR), which provides a means of investigating both the solid and liquid surfaces without altering the surface characteristics of the sample.[14,15] ATR spectroscopy is a versatile and powerful technique in infrared sampling because many types of samples can be analyzed with little or no sample preparation. ATR is ideal for samples that are too thick or too strongly absorbing to analyze by transmission techniques without extensive sample preparation. Internal reflection spectroscopy is a common technique, in which infrared radiation is passed through a crystal of high refractive index. As the radiation reflects internally at the surface of the crystal, an evanescent wave is created that extends beyond the surface of the crystal into the sample that is in contact with the crystal. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will interact with the sample and a spectrum is obtained.

IR from the spectrometer was directed at the beveled end of the ATR crystal as shown in Figure 1. The IR (probe) beam then passed through the crystal and penetrated the sample to short distances with each reflection at the surface. The beam was then directed out of the crystal at the other beveled end. Because the evanescent wave decays very rapidly with distance from the surface, it is important that the sample is in intimate contact with the crystal. In the normal design of the ATR accessory, the crystal is held in a vertical position with the sample clamped against one or both

sides. This design makes it difficult to achieve uniform sample contact with the crystal surface, which is necessary for acquiring reproducible data, and limits the type of sample that can be analyzed. Baseline ATR eliminates these problems by providing a horizontal surface for convenient and reproducible loading of most sample materials. The ATR crystal was of zinc selenide (ZnSe). It had a transmission range from 20,000 to 650 cm^{-1}, and its refractive index at 1000 cm^{-1} was 2.4. The resolution of the spectrum recorded was 4 cm^{-1}. The ZnSe crystal was covered with the coated thin aluminum plate, removed at regular time intervals from the oven to obtain the IR spectrum.

To monitor lacquer curing, the stretching vibration peak of C=C at 1644 cm^{-1} was chosen. The area of the vibrational peak was calculated in the 1654–1633 cm^{-1} region, which contained a peak at 1644 cm^{-1}. The reduction percentage in peak area of 1654–1633 cm^{-1} region, referred to as α, was calculated by eq. (1), as follows:

$$\alpha\ (\%) = \{[A_{T,\,t=0} - A_{T,\,t}]/[A_{T,\,t=0}]\} \times 100 \quad (1)$$

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

Contact angle measurement

The change of the contact angle of the Korean *Dendropanax* lacquer surface during the curing process was measured using an SEO 300A contact angle measuring device (Surface and Electro-Optics Co., Korea) at 20 ± 1°C and 57 ± 2% relative humidity. A single 10-μL drop of distilled water was placed on the surface of the samples, which were taken out at regular time intervals from the oven. The contact angle was measured at 1 min after the drop was placed on the surface.

Adhesion force by AFM

The curing behaviors of the *Dendropanax* lacquer were investigated using the force calibration mode of atomic force microscopy (AFM) programmed in Dimension SPM-3000 (Digital Instruments, Santa Barbara, CA) at 23 ± 1°C and 65 ± 3% relative humidity. The silicon nitride probe consisted of a cantilever with a sharp V-tip on the end. The spring constant of the cantilever was 0.12 N/m. In the conventional contact mode of AFM, the AFM tip touching the surface experiences the adhesive force. Adhesion force was measured by monitoring the deflection of the AFM cantilever.[16] Measurements were taken on the surface of the lacquer at regular intervals during oven curing.

In addition to imaging the surface topography and exploring the chemical and nonquantitative mechani-
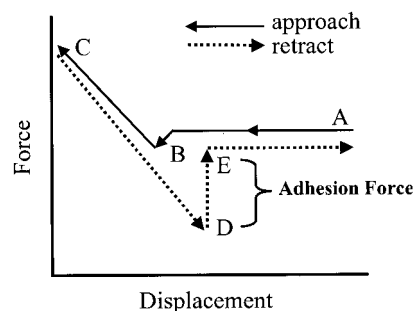

Figure 2 Plot of typical force–distance curve.

cal properties of samples, the AFM can be used to measure force–distance curves. These curves provide quantitative information of the force between the tip and the sample as a function of tip–sample distance.[17–19]

The AFM tip may be either attracted to or repelled by the sample surface.[19] Adhesion decreased with increased curing time and temperature. The magnitude of the adhesion, or pull-off, force gives a measure of the surface tackiness of the Korean *Dendropanax* lacquer, and provides an indication of how well the Korean *Dendropanax* lacquer was cured and crosslinked.

Figure 2 shows a typical force–distance curve between the AFM tip and the surface of the lacquer. When the tip approaches the sample surface, the cantilever is deflected from its original position. For distances typically >10 nm electrostatic and hydrophobic interactions are dominant between the tip and the sample. If the force between the tip and the sample is attractive, the cantilever bends toward the sample (A–B). For tip–sample distances < 10 nm the bending is mainly caused by the attractive van der Waals forces in the nontouching regime. If the tip is nearer the sample surface, the cantilever jumps at a certain distance to the surface and a rapid tip–sample contact is established (jump-in contact/touching regime).

This happens if the attractive force becomes larger than the spring constant of the cantilever. If the tip surface distance is further reduced, cantilever deflection is increased (B–C). Depending on the force applied, elastic or plastic deformation may occur to the tip, cantilever, and/or the sample (indentation).

If the tip is subsequently retracted, the bending of the cantilever is reversed beyond the distance of the initial jump in contact (C–D). The tip "sticks" to the sample surface because of adhesion force and the capillary force until an abrupt transition from the contact to the noncontact regime called "pull-off" occurs (D–E). Capillary force is an important factor in the force measurements in ambient air, but not in aqueous environments or in high vacuum. Because the capillary force may be larger than the intermolecular force one
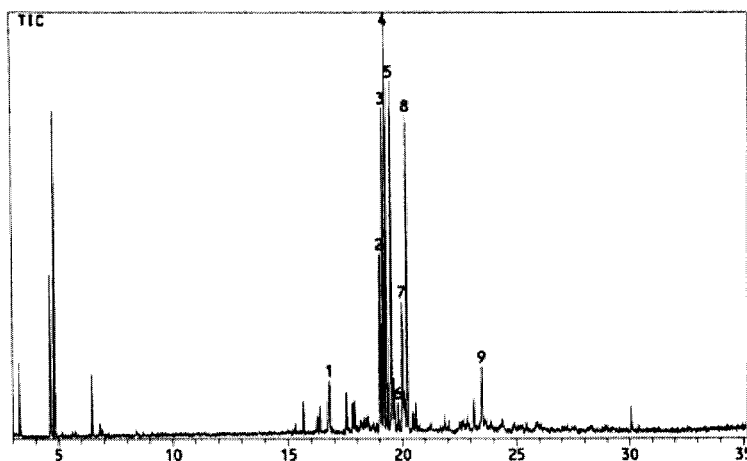
Figure 3 Gas chromatogram of Korean *Dendropanax* lacquer.[20] Constituents of Korean *Dendropanax* lacquer as identified by GC-MS analysis: (1) β-elemene; (2) copaene; (3) α-cubebene; (4) naphthalene; (5) β-selinene; (6) δ-cadinene; (7) γ-cadinene; (8) β-cadinene; (9) junipene.

is interested in, care must be taken in the interpretation of force measurements obtained in an ambient air environment. More controlled experimental conditions such as force measurements in fluid can solve this problem.

A prerequisite for obtaining exact force–distance relationships is the use of calibrated cantilevers with known force constants. The force applied to the cantilever is calculated using the following equation:

$$F = \kappa z \tag{2}$$

where F is the adhesion force (nN); κ is the spring constant of the cantilever, which was equal to 0.12 N/m in this study; and z is the deflection (nm) of the cantilever, which in Figure 2 is the vertical distance between D and E, in the z-direction defined to be perpendicular to the sample surface.[17–19]

RESULTS AND DISCUSSION

GC-MS and FTIR ATR measurements

The gas chromatogram of the *Dendropanax* lacquer is shown in Figure 3. Its compounds, as analyzed by GC-MS, are given in Figure 3. Major compounds were found to be naphthalene (21.8%) and β-selinene (19.2%).[20]

Figure 4 shows IR spectra of the uncured lacquer and that of cured at 100°C for 220 min. In Figure 4(a), the peaks at 3411, 2856–2926, and 1709 cm^{-1} are attributed to O—H, C—H, and C=O stretching vibrations, respectively. In particular, the peak at 1644 cm^{-1} is attributed to C=C stretching. This peak decreases with increased curing time [see in Fig. 4(b)]. The decrease in the peak at 1644 cm^{-1} is attributed to the decrease of C=C chemical bonds by the oxidative thermal polymerization (or crosslinking) process.

Korean *Dendropanax* lacquer includes an unsaturated chain responsible for polymerization properties, either thermal or oxidative, of the lacquer.[21,22]

The unsaturated chains have one, two, three, or more double bonds, and their position may vary. The number and position of the double bonds are important. Double bonds separated by a single bond are called conjugated and they dry more rapidly than isolated double bonds.

In addition, a decrement of the peak at 1644 cm^{-1} may be caused by heat, which is thought to be attributed to the migration of carbon double bonds to the conjugated positions. The conjugation facilitates crosslinking by a Diels–Alder type of mechanism.[21] Thus, the lacquer is polymerized by either thermal or oxidative means to give a solid or semisolid structure.

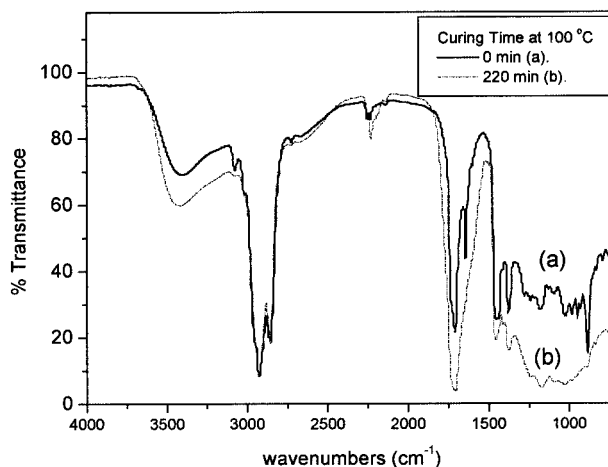Typical changes in the C=C peak area during the curing process are shown in Figure 5, which shows

Figure 4 IR spectra of Korean *Dendropanax* lacquer cured at 100°C for (a) 0 min and (b) 220 min.
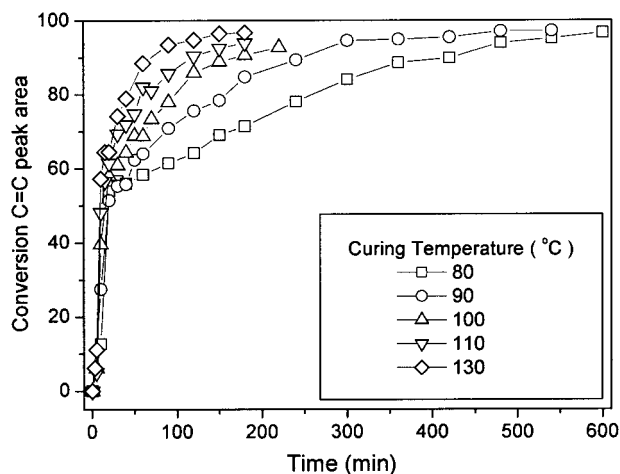
Figure 5 Changes of the C=C ATR peak area as a function of curing time at each curing temperature.[20]

Figure 7 Changes of adhesion force as a function of curing time at each curing temperature.

peak area decrement with curing time, attributed to thermal oxidative polymerization.[20] Changes in the C=C peak area are dependent on curing temperature and increase with temperature. In particular, the peak area decreased sharply during the first 30 min, irrespective of the curing temperature. However, the decrements of C=C peak area were minimal after 420 min at 80°C, 240 min at 90°C, 150 min at 100°C, and 120 min at 110 and 130°C, which represented an approximately 90% decrement in the peak area.

Contact angle

Changes of contact angle versus curing time and temperature are shown in Figure 6. 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 stron-
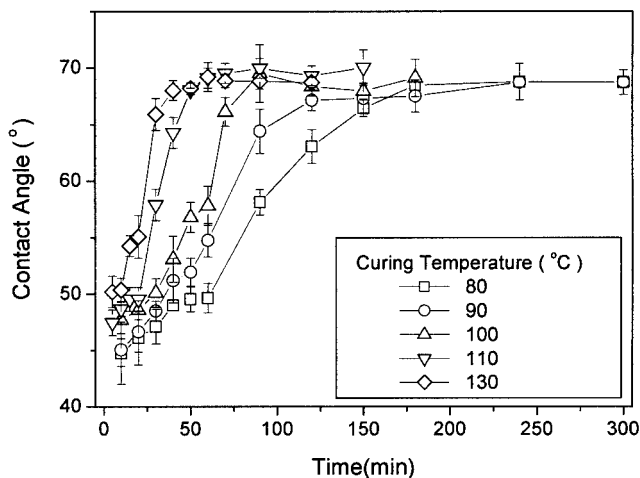

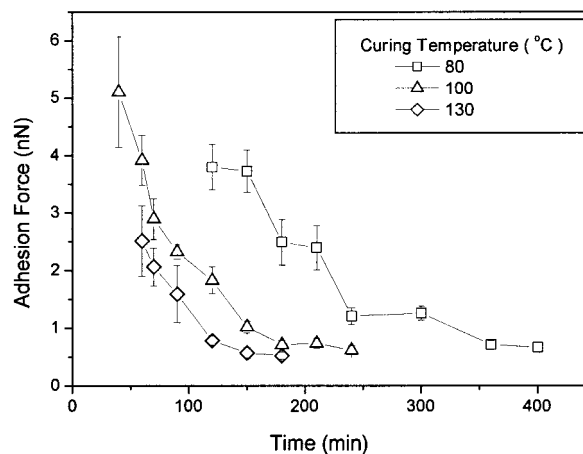**Figure 6** Changes of contact angle as a function of curing time at each curing temperature.

ger hydrophobicity.[23] The contact angle increased dramatically during the earlier stage of the curing process and in parallel with changes in the C=C peak area as measured by ATR.

The hydrophilic/hydrophobic behavior is very important in the understanding of surface curing behavior. Generally, contact angles are related to surface morphology/reorientation or mobility of surface segments, all of which lead to the surface free energy.[23] Previous studies have shown a clear relationship between contact angle and surface energy.[23–25]

It is obvious that the Korean *Dendropanax* lacquer can be cured by thermal oxidative polymerization because of decreased C=C peak area and increased contact angle.[21]

Hydrophilic sites, which react with liquid in the Korean *Dendropanax* lacquer, decrease with increased curing time and temperature. In addition, film permeability to liquid might decrease with increasing the crosslinking of the cured film. Thus, the sufficient curing time and temperature can be determined by determining the contact angles, attributed to increased hydrophobicity. Changes in the contact angle were slight after 180 min at 80°C, 150 min at 90°C, 90 min at 100°C, and 60 min at 130 and 110°C.

Adhesion force

Adhesion force was used to measure the adhesion between the surface and the AFM tip. The influence of curing time and temperature on the adhesion force is shown in Figure 7.

A previous study showed that strong attractive surface forces occur in a very humid environment, but not in a dry environment. These results explain why an adsorbed liquid on the surface may cause a strong attractive force in the force–distance curve: the adhesion force was always greater than the jump-to-contact
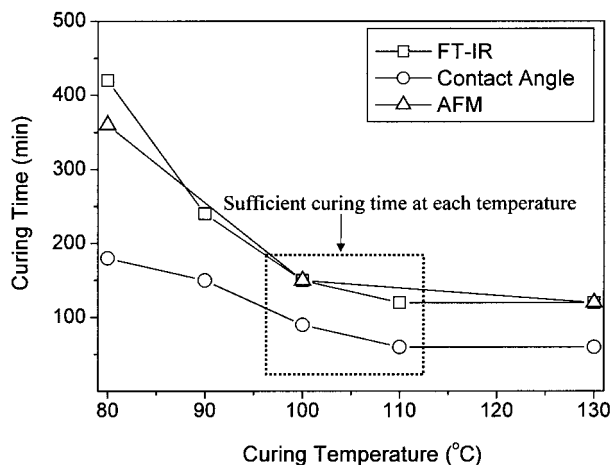
Figure 8 Sufficient curing time at each curing temperature determined by FTIR, contact angle, and AFM.

force.[25] In the present study, the surface condition of uncured Korean *Dendropanax* lacquer is consistent with that of the lacquer with an adsorbed liquid film, as reported in the previous study. As energy (heat) was supplied to the lacquer, the viscosity increased because of the thermal oxidative polymerization and solvent evaporation.[21] Thus, the attractive surface force and the adhesion force between the surface and AFM tip decreased when the surface was cured. The sufficient curing time and temperature were determined by monitoring the adhesion force.[21,26] The adhesion force reduced with increased curing time and temperature, and was weak after 360 min at 80°C, 120 min at 130°C, and 150 min at 100°C.

Figure 8 shows the sufficient curing time at each curing temperature determined by FTIR, contact angle, and AFM. As shown in Figure 8, the decrease of the curing time was slight over curing temperature at 100°C and FTIR determinations include results of both contact angle and AFM. Thus, FTIR results were satisfied with curing chemically and physically.

The results obtained by chemical and physical measures show that Korean *Dendropanax* lacquer can be effectively (economically) cured at 100°C for 150 min and at 110°C for 120 min.

CONCLUSIONS

This work was performed to investigate the curing behaviors of Korean *Dendropanax* lacquer and to determine its sufficient curing conditions.

The lacquer of the major compounds was naphthalene (21.8%), and β-selinene (19.2%). In FTIR and contact AFM analyses, the peak area of C=C (1644 cm^{-1}) and the microadhesion decreased with increasing cur-

ing time, attributed to oxidative thermal polymerization (or crosslinking). The magnitude of the microadhesion between the probe and the surface related to the surface tack of the lacquer indicated how well the lacquer was cured and crosslinked. The increased contact angle exhibited increasing lacquer hydrophobicity, attributed to polymerization.

In addition, changes in double bond peak, contact angle, and microadhesion were dependent on the curing temperature. The results obtained by chemical and physical measures show that Korean *Dendropanax* lacquer can be effectively (economically) cured at 100°C for 150 min and at 110°C for 120 min.

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