

Dielectric Characterization of Relaxation and Curing Behavior of Oriental Lacquer

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ABSTRACT: Dielectric analysis was used to investigate the effects of temperature and humidity on the curing behavior of oriental lacquer and to characterize the dielectric properties of the lacquer film. It was found that the oriental lacquer could not cure to its hardened state at relative humidity less than 50% in ambient temperature and that the cure time could be shortened tremendously by increasing the curing temperature. In order to study the dielectric properties of oriental lacquer film, two films were prepared at different curing temperatures. The glass transition and secondary relaxation temperatures of ordinary oriental lacquer film, room temperature cured purified lacquer, were observed at 45 and -40°C , respectively. The high temperature cured purified lacquer film showed a secondary relaxation at around -50°C . The relationship between thermodynamic properties and chemical structures was explored based on the analysis of the dielectric relaxation behavior using Cole–Cole plots and the dielectric relaxation intensity $\Delta\epsilon$. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1804–1810, 2000

Key words: dielectric analysis; oriental lacquer; relaxation, curing; Cole–Cole

INTRODUCTION

Oriental lacquer is a natural product, which has been used for protective and decorative coatings since the 5th century, BC. The resinous sap of the *Rhus vernicifera* tree is obtained during the collection of natural rubber. After filtration and traditional purifying, the lacquer can be used directly as a coating material.¹ It is the hardening process of the oriental lacquer that distinguishes it from synthetic coatings. For oriental lacquer, solvent evaporation is not the primary drying mechanism. Instead, an oxidation-induced polymerization cures the film. Another unusual feature of the lacquering process is that the oriental

lacquer cures to its hardened state most efficiently at moderate temperature in the presence of air at relative humidity of greater than 70%.^{2–7} While the use of oriental lacquer dates back thousands of years, scientific studies of this complicated material are only now emerging.

In particular, cure monitoring of oriental lacquer has become increasingly important because it provides the technique for the control of the crosslinking process and hence the properties of the final product. It has become an essential part of oriental lacquer coating technology. Among the various techniques for monitoring the curing behavior of polymeric materials, the dielectric method has drawn considerable attention in recent years since it is amenable to coupling with electrical process control equipment. Dielectric analysis gives two fundamental electrical characteristics of material: capacitance and conductance

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as a function of temperature and frequency. While these electrical properties are important by themselves, they are even more significant when they are correlated to the molecular activity.⁸⁻¹⁰ In this study, an *in situ* dielectric experiment was carried out to characterize the curing behavior of the lacquering process. The effects of curing conditions on the dielectric relaxation of oriental lacquer film were also investigated.

EXPERIMENTAL

Chinese raw urushi was filtered using a traditional filter paper called *chilji*. To prepare the purified lacquer (PL, *jungeotchil*), the filtered raw lacquer (RL, *sangochil*) was stirred at 60 rpm in an open vessel [150 mm(*d*) x 150 mm(*h*)] for 1 h and then at 45°C for 3 h. The purification procedure for *jungeotchil* is based on the traditional method in which the main objective is to reduce water content in raw urushi from 25–35% to 3–6%. The HHPL (high humidity purified lacquer) and LHPL (low humidity purified lacquer) samples were obtained by applying *jungeotchil* to the remote single surface sensor and then were cured in an oven at relative humidity (RH) of 70 and 30%, respectively. The temperature was maintained to sustain the activity level of the enzymes. The RTCPL sample, coated on the poly(ethylene terephthalate) (PET) film with 60 μm thickness, was dried for one day at room temperature and at 75 ± 5% RH. The HTCPL sample was obtained by applying *jungeotchil* to the PET film and then was placed in an oven at 140°C for 4 h.

MEASUREMENTS

TA Instruments dielectric analyzer DEA 2970 coupled with a 2100 thermal analyzer were used to obtain the dielectric properties of the samples. Parallel plate sensors were used in the dielectric experiments. The DEA module provided real-time quantitative calculations of the properties for 11 frequencies in the range of 1–10⁵ Hz from –70 to 150°C using 0.5 °C/min heating rate. Internally, it converted the measured sample response (capacitance *C*, conductance 1/*R*, and phase angle shift) into permittivity and loss factor using

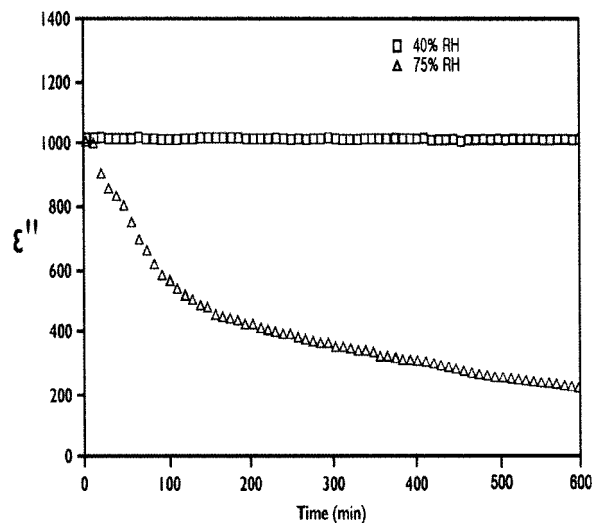


Figure 1 The dielectric loss factor versus time for oriental lacquer at different humidity.

$$\epsilon' = \frac{Cd}{A\epsilon_0} \quad \epsilon'' = \frac{d}{RA2\pi f\epsilon_0}$$

where *d* is the sample thickness, ϵ_0 is the permittivity of a vacuum (8.854×10^{-12} Fm⁻¹), *A* is the metallized electrode area, *f* is the frequency of the experiment, and *R* is the resistance of the sample.

Hardness was measured by pencil according to ASTM D3363 and ranged from 4B to 5H. Adhesion was checked by scoring a crosshatch pattern in the coating, applying adhesive tape, and then pulling the tape off with a sharp tug.¹¹

RESULTS AND DISCUSSION

The effect of humidity on the cure rate is shown in Figure 1 where the loss factor ϵ'' is plotted as a function of curing time. In the case of HHPL, the ϵ'' decreases with increasing curing time. The coating reaches its set-to-tough point as defined by ASTM D 1640-83 guidelines when the sensor output is $\log(2\pi f\epsilon'') = 4.2I$ after 500 min. The continual decrease in ϵ'' shows that the coating is still curing at 8 h after application, although the rate of crosslinking slows down markedly after 3 h. The LHPL sample is strikingly different from the HHPL sample, however. There is no detectable change in ϵ'' 8 h after application. These dielectric data clearly show that below 50% RH, the curing of oriental lacquer is totally inhibited in ambient temperature. To our knowledge, this

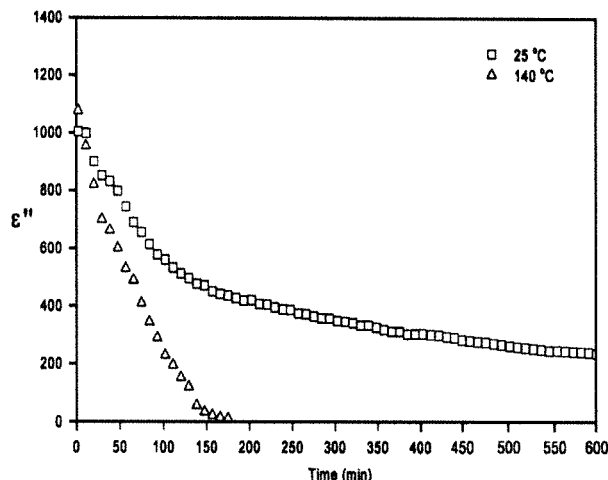


Figure 2 The dielectric loss factor versus time for oriental lacquer at different curing temperatures.

is the first *in situ* dielectric analysis of oriental lacquer curing demonstrating water's role in crosslinking.

To examine the effects of increased temperature, the curing process was monitored in an environmental chamber held at 25 and 140°C. Figure 2 shows the plot of the dielectric loss ϵ'' versus time at the different curing temperatures. Surprisingly, rapid decay of ϵ'' is observed for the high temperature curing and the set-to-tough point is reached at 100 min. This is approximately one-fifth the time required for a sample curing at moderate temperature. There is no further detectable change in ϵ'' 170 min after application. Therefore, the sample has obtained the fullest cure possible under 140°C.

Although thermal curing can shorten curing time, a significant change in the curing mechanism and film properties would be expected. Therefore, it is necessary to investigate the effect of the curing temperature on the film formation of the oriental lacquer. The physical properties of the coating networks cured at the different curing temperatures are summarized in Table I. A com-

parison of RTCPL with HTCPL shows that the pencil hardness of HTCPL is higher than that of RTCPL. This is due to the high degree of crosslinking with thermal curing. HTCPL cures mostly through side chain crosslinking instead of enzyme related reaction with catechol. The contact angle of RTCPL is lower than that of HTCPL due to the existence of polysaccharides in the top layer of the oriental lacquer film. According to Kummanotani,¹ the coating network of the oriental lacquer is surrounded by hydrophilic polysaccharides, which decrease the contact angle of the surface film. One would expect that heating at temperatures higher than 60°C during the curing would eliminate the existence of the polysaccharides in the coating network, resulting in an increase of the contact angle. Although both systems show good adhesion to wood, RTCPL showed greater loss of adhesion to glass. HTCPL has a high gloss, which is not proper for the elegant application of the coating. Again, differences in adhesion and gloss properties seem to be related to the variation in polyssaccharide concentration in the film surface.

To explore the changes in microstructure resulting from different curing procedures, we investigated the loss factor ϵ'' of the oriental lacquer films as a function of temperature. Figure 3 represents the temperature dependence of the dielectric loss ϵ'' for RTCPL and HTCPL at a frequency of 1 Hz. There is a clear contrast in the relaxation behavior of the two materials. The relaxation peaks around -40 and 45°C are observed for RTCPL and the relaxation peak at -50 °C is observed for HTCPL. Figures 4 and 5 show the frequency dependence of ϵ' and ϵ'' for RTCPL and HTCPL, respectively. Both plots show the decrease in ϵ' with frequency and the maximum value of ϵ'' . The data were analyzed using the Havriliak-Negami equation¹²:

$$\epsilon^*(\omega) = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{\{1 + (i\omega\tau)^{\alpha}\}^{\beta}} \quad (1)$$

Table I Surface Properties of Various Oriental Lacquer Films

Sample	Pencil Hardness	Adhesion		Gloss (%)	Contact Angle (Degrees)
		On Wood	On Glass		
RTCPL	HB	100/100	40/100	62	14
HTCPL	2H	100/100	90/100	92	27

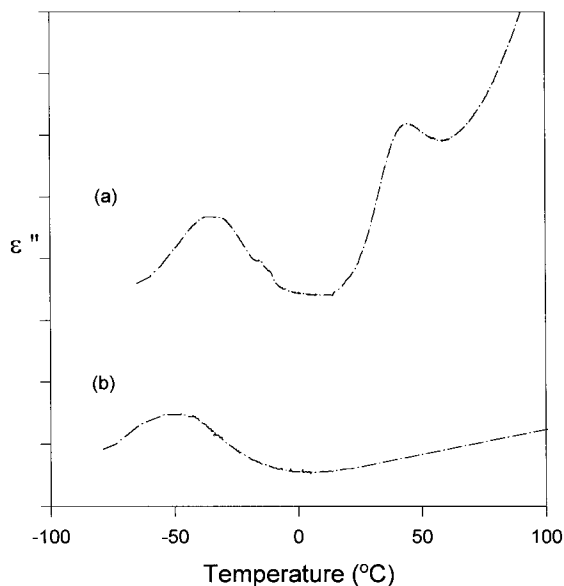


Figure 3 The dielectric loss versus temperature for (a) RTCPL and (b) HTCPL at 1 Hz.

where ϵ^* is the complex dielectric constant, ϵ_0 and ϵ_∞ represent the relaxed ($\omega \rightarrow 0$) and unrelaxed ($\omega \rightarrow \infty$) values of the dielectric constant, τ is the frequency, ω is the relaxation time, and α and β

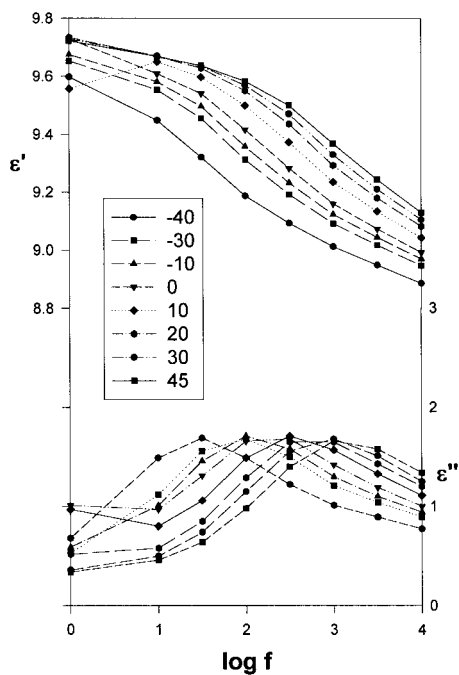


Figure 4 Plots of the permittivity (ϵ') and the loss factor (ϵ'') against the frequency logarithmic scale for RTCPL at 8 different temperatures.

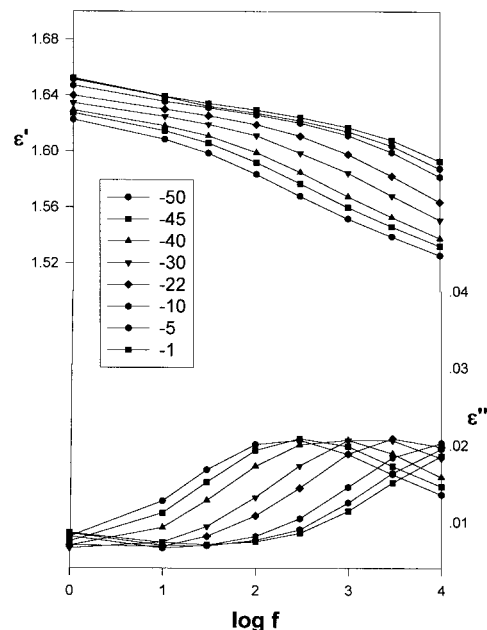


Figure 5 Plots of the permittivity (ϵ') and the loss factor (ϵ'') against the frequency logarithmic scale for HTCPL at eight different temperatures.

represent the broadening and skewing parameters, respectively. When $\alpha = 1$, eq. (1) reduces to the Davidson–Cole expression corresponding to a dispersion in the shape of a skewed semicircle, while for $\beta = 1$, a symmetric arc results (Cole–Cole form). When both α and β are equal to unity, the Debye expression is recovered.¹³

The Cole–Cole plots were constructed at selected temperatures in the vicinity of relaxation regions and are shown in Figures 6 and 7 for RTCPL film and HTCPL film, respectively. In the case of RTCPL film, the Cole–Cole plots are well fitted by the Havriliak–Negami equation. The shape of the Cole–Cole plot at -40°C for RTCPL film is asymmetrical and broader in the high-frequency region, suggesting that another relaxation mode exists below -40°C . This relaxation, however, is too weak and too close to the relaxation at -40°C to be characterized. The shape of the Cole–Cole plot at 45°C is also asymmetrical, although it is more symmetrical than that of the relaxation at -40°C . For the relaxation of HTCPL film, however, a symmetric response is observed so that the dispersion can be described by the Cole–Cole form of eq. (1) ($\beta = 1$; see Fig. 7). These results suggest that the relaxation behavior of HTCPL film is very different from that of RTCPL due to the microstructural differences between the two coating networks.

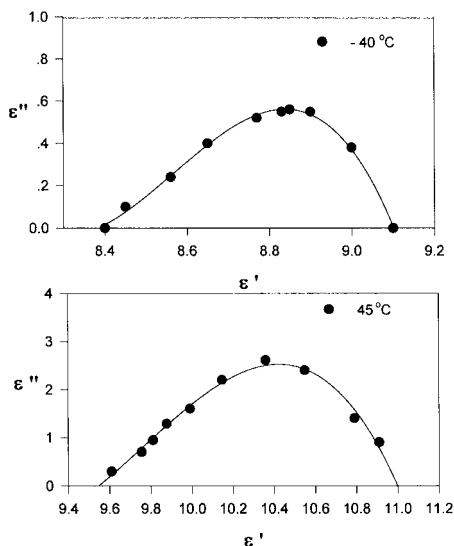


Figure 6 Cole–Cole plots of RTCPL at different temperatures.

In order to investigate the origin of the relaxation, the relaxation time τ has been estimated by fitting the experimental data to the Havriliak–Negami equations. This relationship is shown in Figure 8. The activation energies of transitions for the HTCPL and RTCPL samples were determined from the slopes of the fitted lines in Figure 8 and summarized in Table II. It is common practice to plot the frequency at which ϵ'' has a maximum value as a function of reciprocal temperature.¹⁴ However, it is known that this procedure might lead to erroneous results. Therefore, we used the relaxation time obtained by using the Havriliak–Negami equations to get a more exact value of the activation energy for the relaxation of oriental lacquer. The activation energies of RTCPL's transition peaks at -40 and 45°C are 12 and 60 kcal/mol, respectively, suggesting that the transition peak at -40°C is due to secondary re-

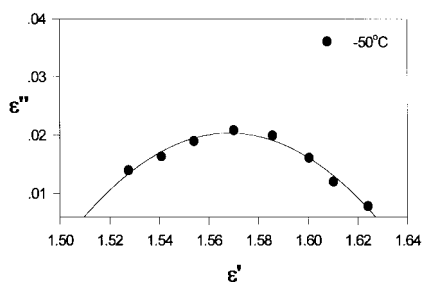


Figure 7 Cole–Cole plots of HTCPL at -50°C .

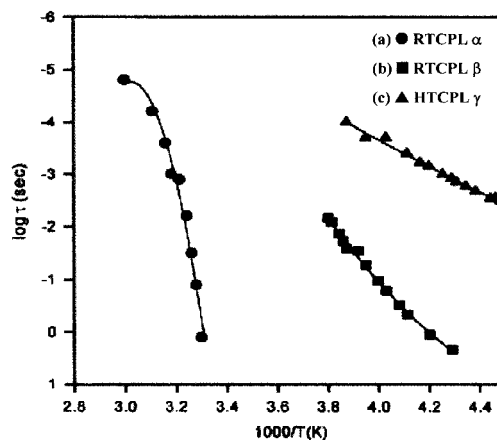


Figure 8 $\log \tau$ from the Cole–Cole relation as a function of reciprocal temperature.

laxation (β relaxation) while the peak at 45°C is due to glass transition (α relaxation). The activation energy of the transition peak for HTCPL at -50°C is 5 kcal/mol and is regarded as γ relaxation. It is important to note that the activation energy for the γ relaxation of HTCPL film is lower compared to those of the other lacquer films. This suggests that the γ relaxation process in the HTCPL is attributable to the local motion of side chains or groups, which may exhibit thermal motion almost independent of that of the main chain. This also suggests that the dielectric results for the γ relaxation of HTCPL are consistent with highly localized, noncooperative motion along the main chains. Here, the interaction with neighboring molecules restricts the process because of high crosslinks density and a decreasing amount of the dipoles.

The parameters included in eq. (1) were determined at each temperature of interest by a least squares curve fitting approach, with initial values for the parameters¹⁵ and summarized in Table III. For the low-temperature region of RTCPL, the broadening parameter increases with increas-

Table II Activation Energies of Relaxations for RTCPL and HTCPL

Sample	Sub- T_g		T_g	
	T ($^\circ\text{C}$)	ΔE (kcal/mol)	T ($^\circ\text{C}$)	ΔE (kcal/mol)
RTCPL	-40	12	45	60
HTCPL	-50	5	—	—

Table III Values of the Parameters Given by the Model (Havriliak–Negami Equation) for RTCPL and HTCPL

Sample	Temperature (°C)	$\Delta\epsilon$	α	β	Relaxation Time (s)
RTCPL	-41	0.72	0.29	0.18	7.4×10
	-40	0.75	0.32	0.19	6.0×10
	-39	0.81	0.40	0.21	5.5×10
	44	1.23	0.54	0.25	2.5×10^{-3}
	45	1.42	0.49	0.27	2.1×10^{-3}
	46	0.98	0.46	0.30	1.8×10^{-3}
HTCPL	-51	0.15	0.43	1	1.1×10^{-3}
	-50	0.12	0.45	1	1.9×10^{-3}
	-49	0.1	0.47	1	2.6×10^{-3}

ing temperature. This result reflects a gradually narrowing distribution of the relaxation time,¹⁶ which demonstrates that the molecular mobility of each molecular segment reaches the same level. In the high temperature region of RTCPL, however, the broadening parameter decreases with increasing temperature, due to the increase of the thermal energy. This causes a disruption of the orientational dipoles. The skewing parameter β is also temperature dependent and increases with increasing temperature. This indicates that the relaxation times become narrower even to the extent of approaching a single relaxation time. At this stage, it is interesting to compare the skewing parameter value of RTCPL with that of HTCPL. The skewing parameter value of RTCPL is lower than that of HTCPL, suggesting that different relaxation modes exist in the coating networks of RTCPL and HTCPL.

The dielectric intensities were obtained by determining the intersection point of the circle with the ϵ' axis in each of the Cole–Cole plots at the different temperatures.¹⁷ The dielectric relaxation intensity $\Delta\epsilon$ is defined in eq. (2)

$$\Delta\epsilon(T) = \epsilon_0(T) - \epsilon_\infty(T) \quad (2)$$

where $\Delta\epsilon$ is the difference between ϵ_0 , the relaxed dielectric constant for the low frequency region and ϵ_∞ the unrelaxed dielectric constant for the high frequency region. This characterizes the mobility and number of molecular dipoles. The relaxation intensities $\Delta\epsilon$ of the low temperature region for RTCPL film increase with increasing temperature. An increase in the molecular mobil-

ity causes the dipoles to reorient toward the alternating electric field, thereby resulting in an increase of the relaxation intensities. In contrast to the above result, the relaxation intensities of the high temperature region for RTCPL and the low temperature region for HTCPL decrease with increasing temperature. This is caused by a gradual decrease in the orientational polarizability of the responding dipoles with increasing thermal energy leading to a randomization in the orientation of the dipoles relative to the alternating electric fields.¹⁸ In addition, consideration of the dielectric intensity values of both samples reveals a stronger dipolar response for the RTCPL as compared to the HTCPL film. This means that HTCPL film has weak relaxation, signifying that this relaxation involves fewer dipoles than that in RTCPL. This is consistent with the fact that the molecular chains must pass through high potential barriers, so they have many difficulties to overcome in reorienting their dipoles.¹⁹

CONCLUSION

In situ dielectric analysis demonstrates that the oriental lacquer cannot be cured at lower than 50% RH and that oriental lacquer can be cured 5 times faster if cure temperature is increased from ambient temperature to 140°C. The film RTCPL, cured by the traditional process, shows sub- T_g relaxation at -40°C and α relaxation at 45°C. However, the film HTCPL, cured at 140°C shows only one sub- T_g relaxation at -50°C. The experimental data fit the Havriliak–Negami equation well. For both RTCPL and HTCPL, this analysis gave the temperature-dependent values of the relaxation time and relaxation strength $\Delta\epsilon$, respectively. The results show that $\Delta\epsilon$ of HTCPL is lower than that of RTCPL, revealing that the relaxation of HTCPL film involves fewer dipoles than that of RTCPL. The activation energy for sub- T_g relaxation of HTCPL is 5 kcal/mol, which is lower than that of RTCPL. This means that the sub- T_g relaxation in HTCPL is attributable to the local motion of side chains or groups, which may exhibit thermal motion almost independent of that of the main chain. Consequently, it is suggested that the excellent toughness of well-purified and traditionally cured oriental lacquer film come from the special microstructure of the coating network where various secondary relaxation

modes permit sufficient subgroup motion to allow deformation.

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