Dielectric Properties of Oriental Lacquer Coating Network

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In order to study the dielectric properties of the oriental lacquer films, three different films have been prepared differing purification and curing procedures. Dielectric properties were measured in the frequency range of 1 Hz to 10^5 Hz at various temperatures between -50 °C and 150 °C. The DEA using 1 Hz showed that glass transition and secondary relaxation temperatures of oriental lacquer film are very time dependent. In addition, the frequency-independent negative peak between 25 °C and 45 °C was observed, which could represent the formation of crosslink by laccase enzyme during heating. On the contrary, the high temperature cured film showed a hardly noticeable negative peak at the temperature range. The relationship between thermodynamic properties and chemical structures has been discussed based on the analysis of the dielectric relaxation behavior using the Cole-Cole plot and the dielectric relaxation intensity.

Introduction

The oriental lacquer is a natural product, which has been used for protective and decorative coatings since the fifth century B.C. The resinous sap of the Rhus vernicifera tree is 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 where solvent evaporation is not the primary drying mechanism but rather an oxidation-induced polymerization that 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.

Cure monitoring of coating material has become increasingly important because it provides the technique for the control of the crosslinking process and hence the properties of the final product and it has become an essential part of 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 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 activities.[8-10] Therefore, it would be useful to obtain the dielectric properties of various oriental lacquer films as well as to study the effect of enzyme content on the properties of lacquer coating network. In this study, dielectric experiment have been carried out on lacquer films obtained from different level of laccase enzyme content in coating formulation. The effects of curing condition and aging on the relaxations of the lacquer films will be investigated.

Experimental

Preparation of lacquer films. Chinese raw urushi was filtered using a traditional filter paper called *chilji*. The filtered raw lacquer (RL, *sangotchil*) was coated on slide glass substrates (thickness: 60 μm) and was dried for a week at room temperature and at 75±5% RH. The slide glasses were washed with surfactant and dried in an oven. To prepare the purified lacquer (PL, *jungjeotchil*), the filtered raw lacquer was stirred (60 rpm) in an open vessel (150 mm(d)×150 mm(h)) for one hour and then at 45 °C for three hours. The purification procedure for *jungeotchil* is based on the traditional method whose main objective is to reduce water content in raw urushi from 25-35% to 3-6%. The temperature was maintained to retain the activities of the enzymes. The PL, coated on the glass substrate with same thickness, was dried under the same condition of film RL. The high temperature cured lacquer (HTCL) film was obtained by applying PL to slide glass substrates and then was placed in an oven (120 °C) for 6 hours. The aged purified lacquer(APL) films and aged raw lacquer (ARL) films were obtained by aging films PL and RL for one year in a glass-windowed cabinet placed in dark area.

Measurements. A dielectric analyser DEA 2970 from TA Instruments coupled with a 2100 thermal analyser was used to obtain the dielectric parameters of the samples. The parallel plate sensors was used in the dielectric experiments. The DEA module provided real-time quantitative calculations of the parameters for 11 frequencies in the range of 1 Hz to 10^5 Hz from -50 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 δ) into permittivity and loss factor using

$$\varepsilon' = \frac{Cd}{A\varepsilon_0}, \quad \varepsilon'' = \frac{d}{RA\,2\pi f\varepsilon_o}$$

where d is the sample thickness, ε_0 is the permittivity of 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.
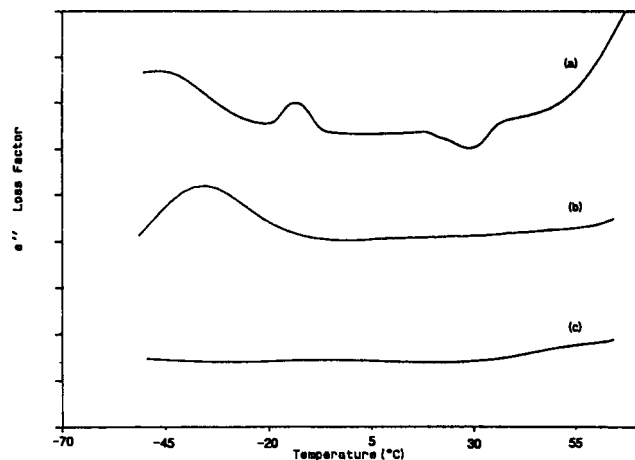
Figure 1. The dielctric loss versus temperature for (a) PL, (b) APL and (c) HTCL at 1 Hz.

Figure 3. Temperature dependence of the relaxation frequencies for α-, β-relaxations of five different lacquer films.

Results and Discussion

Figure 1a represents the temperature dependence of the dielectric loss for typical oriental lacquer film (sample PL) at a frequency of 1 Hz. The most interesting result is the frequency independent negative peak observed at temperature around 30 °C. Such a peak in DEA trace might appear when any volatile is evaporated from the material or when material undergoes polymerization or curing. However, The negative peak is not due to the evaporation of volatiles from the lacquer film since there is no volatile organic compound in the coating formulation. The transition peak around − 14 °C is frequency dependent and shifts to higher temperature region as the DEA measurement frequency is increased.

In order to get more information of negative peak, the DEA trace of sample APL (Figure 1b) was compared with that of PL. Instead of the transition of − 14 °C and negative peaks of PL, a new broad transition peak around − 34 °C appears. Figure 1c is the DEA trace for the lacquer film cured at 120 °C (HTCL) where neither noticeable negative peak nor transition in low temperature region is appeared.
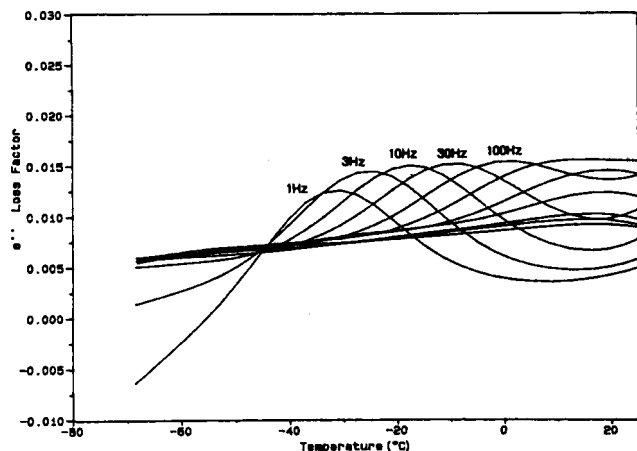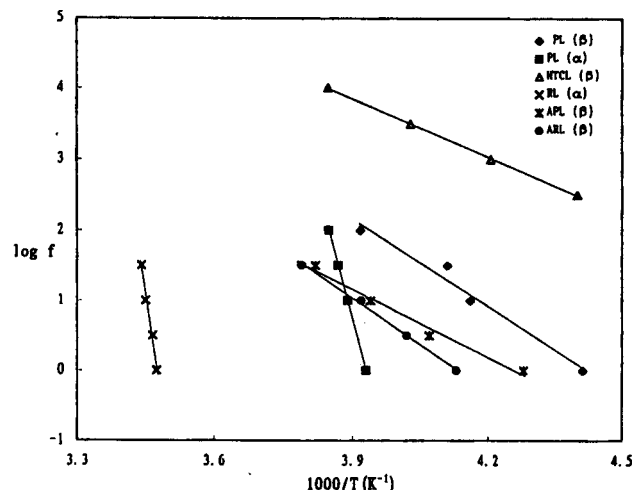
In order to assign the various transition and relaxation peaks in Figure 1, Arrhenius plots of log (frequency) *vs.* 1000/T_{max} were derived from the frequency dependent dielectric loss-temperature curves as typically shown in Figures 2. The activation energies of transitions for various lacquer films were determined from the slopes of plots (Figure 3) and summarized in Table 1. The activation energy of APL's transition peak at − 34 °C is 31.2 kJ/mol and that of PL's transition peak at − 14 °C is 216 kJ/mole. It suggests that the transition peak in Figure 1b is due to secondary relaxation peak while − 14 °C peak is due to glass transition. The data in Table 1 also demonstrate how purification affects the transition and relaxation behavior of the lacquer coating network. Well purified lacquer film has lower T_g and stronger secondary relaxation than unpurified raw lacquer film.

Based on these observations, it is believed that the magnitude of the negative loss factor peak is related to the crosslinking of the lacquer coating network. In fact, oriental lacquer is known to be crosslinked *via* laccase enzyme whose optimum activity temperature is between 20 and 50 °C. It is also known that the laccase loses its activity above 60 °C. This explanation is supported by the fact that the Figure 1c shows no transition around 30 °C. It has been known that the oriental lacquer keeps curing for a long period of time longer than one year, although curing time depends on the curing environment and film thickness. In case of film

Figure 2. The dielectric loss versus temperature at different frequencies for APL.

Table 1. Activation Energies (kJ/mol) of α-, β-Relaxations for five lacquer films observed at 1 Hz. -: the relaxation frequency could not be observed clearly

	sub-Tg		Tg	
	T (°C)	Ea (kJ/mol)	T (°C)	Ea (kJ/mol)
PL	− 43	35.3	− 14	216
APL		31.2		-
RL	-	-	− 3	366
ARL	− 31	35.3		-
HTCL	-	21		-

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PL, Figure 1b shows that T_g disappeared and broad secondary relaxation peak appeared after 1 year aging, indicating that the lacquer film of PL has been fully cured within 1 year. The fact that sample PL is composed of single coated layer and general oriental lacquer film is composed of more than five coats supports above explanation.

By examining the shape of the Cole-Cole plots of ε'' and ε', valuable information about the dielectric relaxation process can be obtained.[11,12] The frequency- and temperature complex dielectric constant is given by

$$\varepsilon^*(\omega,\ T)=\varepsilon'(\omega,\ T)-i\varepsilon''(\omega,\ T) \tag{1}$$

with ω the angular frequency, T the temperature and $i=\sqrt{(-1)}$. It is common practice to characterize a dielectric parameters by the real part of the dielectric constant and by the imaginary part of the dielectric loss factor. In general, the dielectric constant as a function of the frequency at a given temperature can be described mathematically by the empirical Harviliak-Negami equation,[13,14] which is applicable to the dielectric relaxation process for most polymers:

$$\varepsilon^* =\varepsilon_\infty+\frac{\varepsilon_o-\varepsilon_\infty}{\{1+(i\ \omega\tau)^\alpha\}^\beta} \tag{2}$$

Here, both α and β are fitting parameters characterizing the functional form of the dispersion relation. The parameter β (having a numerical value between 0 and 1) is related to the skewness of the dispersion; if $\beta=1$, equation (2) reduces to the Cole-Cole relation (single relaxation time). The parameter α ($0\le\alpha\le1$) is related to the width of the dispersion; equation (2) reduces to the Cole-Davidsion relation if $\alpha=1$. In a polt of ε'' versus ε' such a dispersion gives a
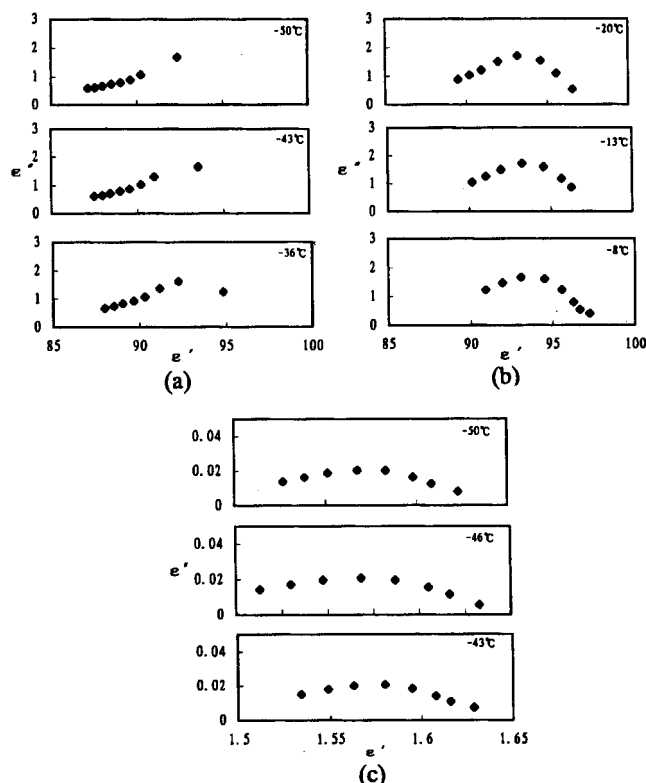
semi-circle with its centre below the ε' axis. The relaxation of side chains, functional groups and chains segments in polymers is usually described very well by the Havriliak-Negami equation.[13,15,16]

As shown in Figure 4, the Cole-Cole diagrams are constructed at a selected temperature in the vicinity of relaxation regions for the PL film and the HTCL film. The shape of the Cole-Cole arcs in the vicinity of the β relaxation region for PL film, shown in Figure 4a, is asymmetrical and broader on the high-frequency region. It suggests that another relaxation mode exists below the temperature of β-relaxation.[17] This relaxation, however, is too weak and close to the β-mode to be characterized. The shape of Cole-Cole arcs in the α-relaxation region in Figure 4b is also asymmetrical, being a more symmetrical than that of β-relaxation. In the transition region of HTCL films, Figure 4c shows a broad symmetric response where the dispersion can be described by the Cole-Davison form of eq. 2 ($\alpha=1$), in contrast to the skewed appearance of the relaxation for PL. These results suggest that relaxation behavior of samples PL is very different from that of HTCL due to the different microstructure between two coating networks.

It is important to note that the activation energy for the β-relaxation of HTCL film is 21 kJ/mol which is relatively lower than those of the other lacquer films. This means that the β-relaxation process in the HTCL is attributed to the local motion of side chains or groups which may exhibit ther-

Figure 4. Cole-Cole plots of (a) β- and (b) α-relaxations for PL, (c) β-relaxation for HTCL at different temperatures.
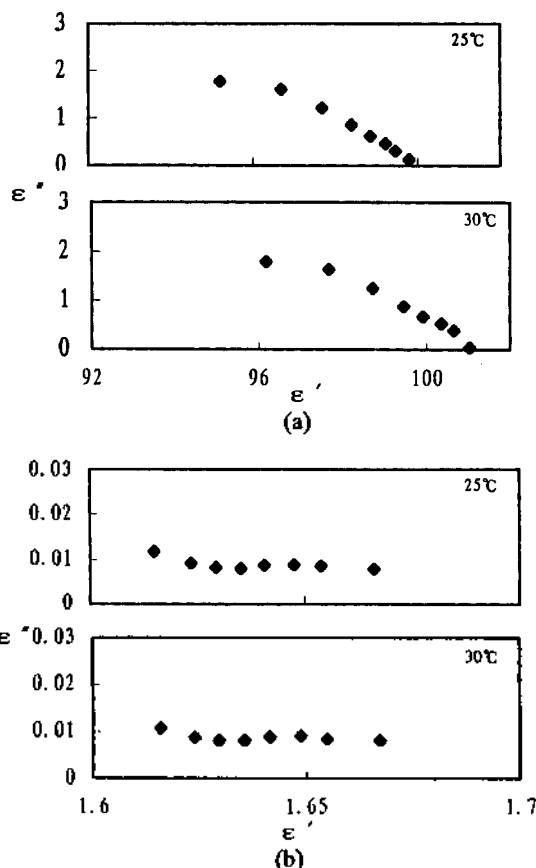

Figure 5. Cole-Cole plots (a) PL and (b) HTCL at 25 °C and 30 °C.

mal motion almost independent of that of the main chain.[18,19] This suggests that the dielectric results for the β relaxation of HTCL are consistent with highly-localized, non-cooperative motion along the main chains where interactions with neighboring molecules restrict the process because of high cross-links density. Consequently, the dielectric process for the HTCL exhibits a broad relaxation characteristics.

Figure 5 shows the Cole-Cole plots of films PL and HTCL in the vicinity of 25 °C. In case of film PL, the ε" decreases toward zero on the low frequency region at 25 °C and 30 °C. The film HTCL shows that ε" is not frequency dependent. These observation can be explained by the fact that laccase enzyme is responsible for the curing of oriental lacquer film around 30 °C. In case of film HTCL, heating the PL at 120 °C make laccase inactive, subsequently make crosslinking impossible through typical oriental lacquer curing method. Instead, crosslinking would be possible by side-chain reaction.

In an effort to investigate the mechanism of relaxation behavior of oriental lacquer film, dielectric relaxation intensities have been measured. The dielectric relaxation intensities have been obtained according to the circle intersection with the ε' axis in the Cole-Cole plot at different temperatures.[20-22] The dielectric relaxation intensity Δε is defined in eq. (3)

$$\Delta\varepsilon(T) = \varepsilon_o(T) - \varepsilon_\infty(T) \qquad (3)$$

where Δε is the difference between ε_o, the relaxed (for the low frequency region) and ε_∞, unrelaxed dielectric constants (for the high frequency region) and characterizes the mo-

bility and number of molecular dipoles. The relaxation intensities as a function of temperature are shown in Figure 6. The Δε for the α-mode of film PL increases steeply around T_g with increasing temperature. The decrease of Δε with a further increase of temperature above T_g is presumably due to the 1/T dependence predicted by the thermal perturbation in the reorientation of dipoles.[11,23-25] For the β-mode of PL, Δε increases slowly with increasing temperature. Results of dielectric relaxation intensities as a function of polymer composition and temperature reveals a stronger dipolar response for the PL as compared to the HTCL. The sample HTCL displays a decrease in the β relaxation intensity with increasing temperature. It is also shown that film HTCL has the weak relaxation intensity (ε_o-ε_∞), representing that this relaxation involves fewer dipoles than that in film PL. 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.[26,27] In the temperature region between 20 °C and 45 °C (Figure 6c), its dielectric properties of film PL can be changed due to the change in the equilibrium properties. As the cross-linking occurs, the PL increases the chain length and the macroscopic density, and changes the net dipole moment per unit volume.[28] Therefore, Δε, the contribution to permittivity from orientation polarization, changes continuously.[29,30]

Finally, it is appropriate to discuss the structure-property relationship of the oriental lacquer coating network. The film PL gives tough and relatively hard coating, but the film HTCL gives brittle and high gloss coating. We believe
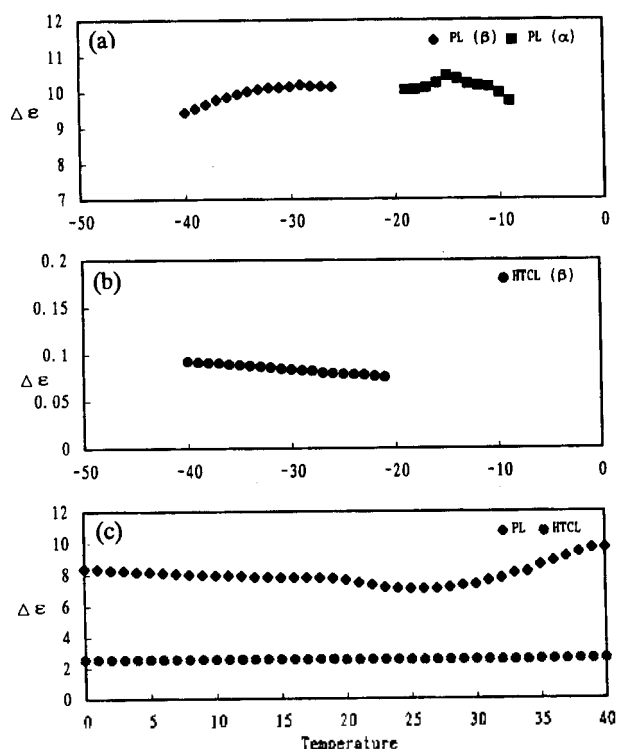

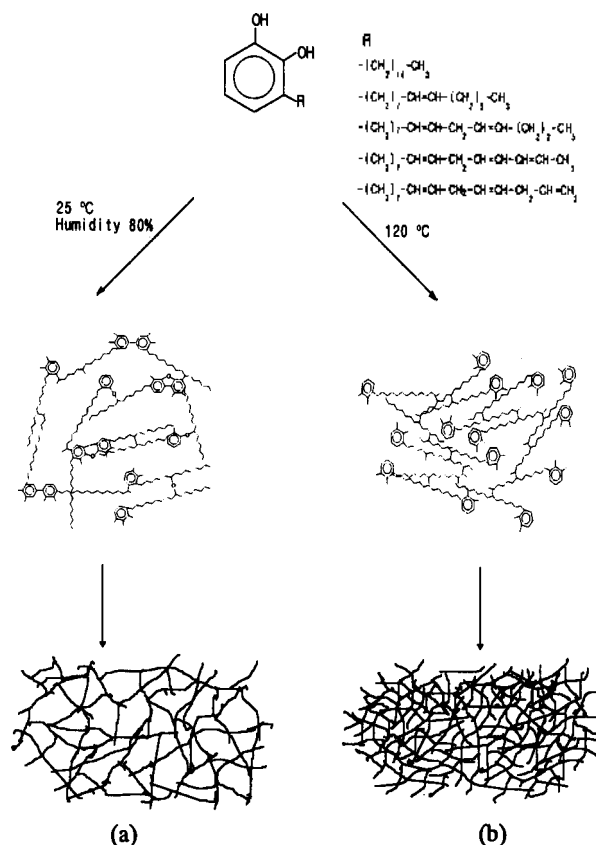
Figure 6. The relaxation intensity as a function of temperature (a) β-, α- of PL (b) β-relaxation of HTCL (c) between 0 and 40 °C for PL and HTCL.

(a)   (b)

Figure 7. Schematics of the coating network for PL (a) and HTCL (b).

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that excellent toughness of films PL and APL is originated from the special microstructure of coating network where strong secondary relaxation permit sufficient subgroup motion. Suggested development of coating networks for films PL and HTCL is schematically presented in Figure 7. It is clearly shown that both dielectric properties and mechanical properties of two coating networks will be different due to the different morphologies resulting from different curing procedures.

Further understanding of oriental lacquer curing requires additional experiments such as DEA isothermal study and spectroscopic analysis and such experiments are underway.

Conclusions

The dielectric properties of various oriental lacquer films have been investigated by examining the transition and relaxation behavior of coating network. Preliminary results show that curing temperature is the most important key parameter affecting dielectrical properties of coating film. The film PL, obtained by the traditional curing process, shows strong sub-Tg relaxation below -45 °C, α relaxation around -14 °C and the negative peak between 25 and 45 °C. However, the film HTCL, obtained by the curing at 120 °C, shows weak sub-Tg relaxation below -50 °C and does not show negative peak. This suggests that the excellent toughness of well purified and traditionally cured oriental lacquer film is originated from the special microstructure of coating network where strong secondary relaxation permits sufficient subgroup motion to allow deformation.

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