Effect of Water on Viscoelastic Properties of Oriental Lacquer Film

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ABSTRACT: We noticed the Urushi film, by which oriental lacquer wares are prepared. The effect of water on mechanical properties of oriental lacquer film was investigated in a tensile test and a stress relaxation test. These tests were conducted under the various degrees of humidity. Oriental lacquer film had a tendency to became brittle under dry condition and to toughen under wet conditions. On the other hand, the film becomes sticky and soft under high humidity or in water. The relaxation modulus for this film was determined under the various degrees of humidity. This behavior changed largely depending upon humidity. Master curves on the result of stress relaxation test were prepared by applying the rule of time–temperature superposition. The temperature dependence of shift factor on the various degrees of humidity could be represented by the Williams–Landel–Ferry equation by changing two parameters, C_1 and C_2. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 315–321, 1998

Key words: oriental lacquer film; water; stress relaxation; time–temperature superposition; WLF equation

INTRODUCTION

Oriental lacquer, that is, urushi,[1–3] has been widely utilized as the coating material from ancient times. This material is usually coated on wood and widely used as lacquer wares. Lacquer wares are not only in practical use but also in objects of craft work. Many of the wares are nowadays exhibited in museums in Japan, the U.S.A., and Europe. In the Shosoin temple in Japan, a great number of wares coated with oriental lacquer are exhibited, all having been preserved for more than a thousand years without having lost their original elegant beauty. Oriental lacquer is the sap obtained from lacquer trees (*Rhus vernicifera*). The sap is called raw lacquer. The raw lacquer is a natural resin that consists of the main constituent (urushiol), a gummy substance, nitrogen compounds, and other volatile components. The chemical structure of urushiol is shown Figure 1. When the raw lacquer has hardened, it has a deep luster and exhibits excellent resistance to weathering indoors.[4] It is indicated by the fact that lacquer wares can be preserved for long time without suffering any change in quality.[5] Because of such practical importance of oriental lacquer, many studies have been done on the chemical structure and reaction of urushiol, but articles on mechanical properties of oriental lacquer film are of a comparatively small number.[6–8]

In general, it is believed that oriental lacquer film is affected by water and light.[9–13] However, lacquer wares are often used in water or high humidity. When lacquer wares are used under these conditions, stress occurs between the lacquer and adherend, that is, usually wood. This stress makes bonding strength decrease in between the lacquer and adherend.[14,15] As a result of this stress, it is afraid that the lacquer is peeled off

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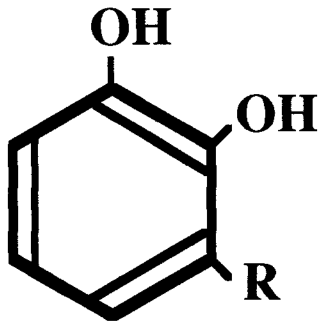

R=$(CH_2)_{14}$-CH_3	4%
=$(CH_2)_7$-CH=CH-$(CH_2)_5$-CH_3	21%
=$(CH_2)_7$-CH=CH-CH_2-CH=CH$(CH_2)_2$-CH_3	4%
=$(CH_2)_7$-CH=CH-CH_2-CH=CH-CH=CH-CH_3	70%
Other constituents	
Compound with C_{17}-side chain	1%

Figure 1 Typical chemical structure and composition of urushiol.

from adherend in an extreme case. Therefore, water is one of the most important factor to discuss the durability of lacquer ware.

A few studies have been carried out so far for the effect of water on the mechanical properties of oriental lacquer film, although it is already known that oriental lacquer wares are largely influenced by water. From these points of view, this subject is very important for practical use of lacquer wares.

In this study, stress relaxation and tensile tests were conducted under the various degrees of humidity, and the effect of water on these properties of the film was discussed in detail.

EXPERIMENTAL

We chose three different conditions on humidity, namely, dry (20% RH), normal (60% RH), and wet (100% RH). The stress relaxation test was conducted under the three different conditions on humidity.

Preparation of Lacquer Film

Oriental lacquer was obtained by evaporating water and carrying out a sugurome process[3] (a mildly oxidizing process and an enzymatically reacting process) with stirring the sap produced in the Republic of China. The sugurome process was conducted in 60 rpm for taking 60 min up to the maximum of 45°C. The lacquer obtained thus was spread on glass plate by using the applicator. Drying was achieved through the following three steps at 25°C; 4 h under 60% RH, 18 h under 70% RH, and 24 h under 80% RH. Films prepared thus was 50 μm in thickness. These films were preserved in a dark place for 3 months, while they were sufficiently hardened. These films obtained thus were used as test pieces, after peeling out them from the glass plates.

Tensile Test

A tensile test was carried out using a AGS-1000B tensile tester (Simadzu Co., Ltd., Japan) with a load cell 100 kg at the test speed of 2 mm/min. The test was conducted under the various degrees of humidity. Test pieces were 4 (width) × 35 (length) × 50 μm (thickness), and adopted values are the average of 5 measurements.

The amount of water absorption at equilibrium for oriental lacquer film is shown in Table I. This water was evaporated at a temperature less than 100°C when measured by differential scanning calorimetry (DSC) and is, therefore, not constrained.[6]

Stress Relaxation Test

The strain of 1.0% was given at first for the film. Subsequently, keeping the strain constant, the change of the stress with time was recorded for 100 h. The relaxation modulus, $E(t)$ was calculated according to eq. (1), where A is the cross-sectional area of the oriental lacquer film, ε is the strain, and $F(t)$ is the stress.

$$E(t) = \frac{F(t)}{A\varepsilon} \quad (1)$$

Table I Water Absorption of Oriental Lacquer Film at Equilibrium

Relative Humidity (% RH)	20	40	60	80	100
Water absorption (wt %)	0.932	1.50	2.13	3.11	5.78

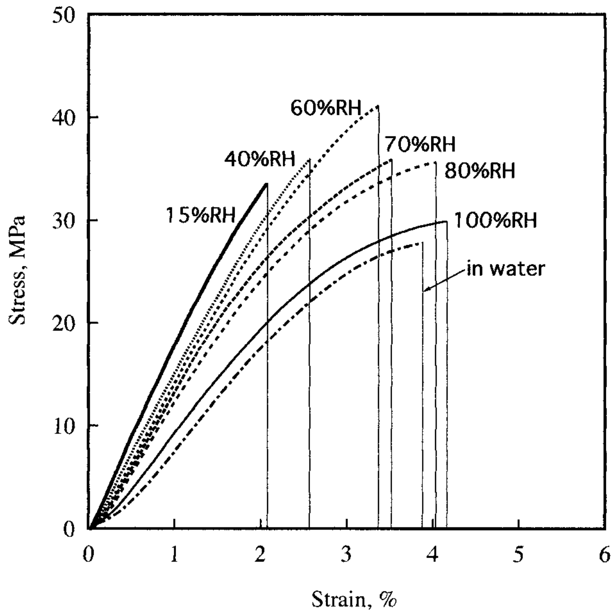

Figure 2 Tensile stress–strain curves of humidity.

This static experiment was conducted using a dynamic viscoelastometer Rheovibron DDV-II-C (Orientec Co., Ltd., Japan), though this instrument was originally designed for measuring dynamic properties. These experiments were carried out under a given temperature and humidity without giving any oscillation for the sample. The relative humidity was kept constant by supplying humid air at the flow rate 100 mL/min into the chamber of the viscoelastometer, even if the temperature changed.

RESULTS AND DISCUSSION

Tensile Test

Tensile stress–strain curves was obtained for oriental lacquer film under various conditions and are shown in Figure 2. The relationships between tensile properties and humidity are summarized in Figure 3. The strain at break increased with humidity. In general, the oriental lacquer films become flexible by water absorption, leading to an increase in the strain at break and an decrease the elastic modulus.[16] This will be caused by the fact that water serves the film as a plasticizer. In other words, this film becomes to be toughen with absorption of water.

Relaxation Behavior

The relaxation moduli $E(t)$ at 60% RH were measured and are shown on the left side of Figure 4. The master curve under this condition was obtained by applying the principle of time–temperature superposition[17] when we adopted 293 K (20°C) as a reference temperature. The result is shown on the right side of Figure 4, where the long-term region above the temperature of 333 K was neglected because the chemical structure of the film changed during the experiment. At any rate, we can predict the relaxation modulus for a very long or short term from this curve. In practical use of lacquer wares, the relaxation rate is not fast under this humidity. Relaxation modulus curves similar to Figure 4 were obtained under dry and wet conditions. The master curves are shown in Figure 5. From this figure, it is clear that the modulus of this film in a wet condition decreases with time at a high rate. The behavior in this film is similar to highly viscous liquid. The percentage of crosslinking of the film would be small as compared with usual thermosetting polymers.

The temperature dependence of shift factor log a_T was determined experimentally under the 3 different conditions on humidity. Actually log a_T was determined according to the following equation:

$$\log a_T = \log\left(\frac{t_T}{t_{293}}\right) \tag{2}$$

where t_{293} means the time when the relaxation mod-

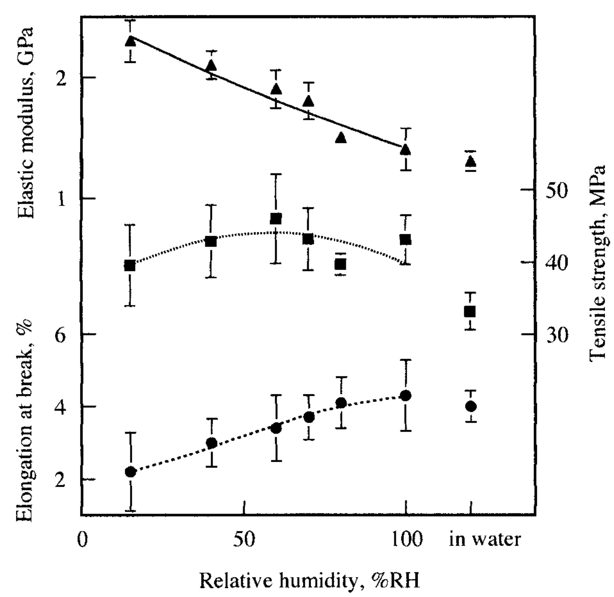

Figure 3 Relationship between stress–strain properties and relative humidity: (▲) elastic modulus, (■) tensile strength, and (●) strain at break.

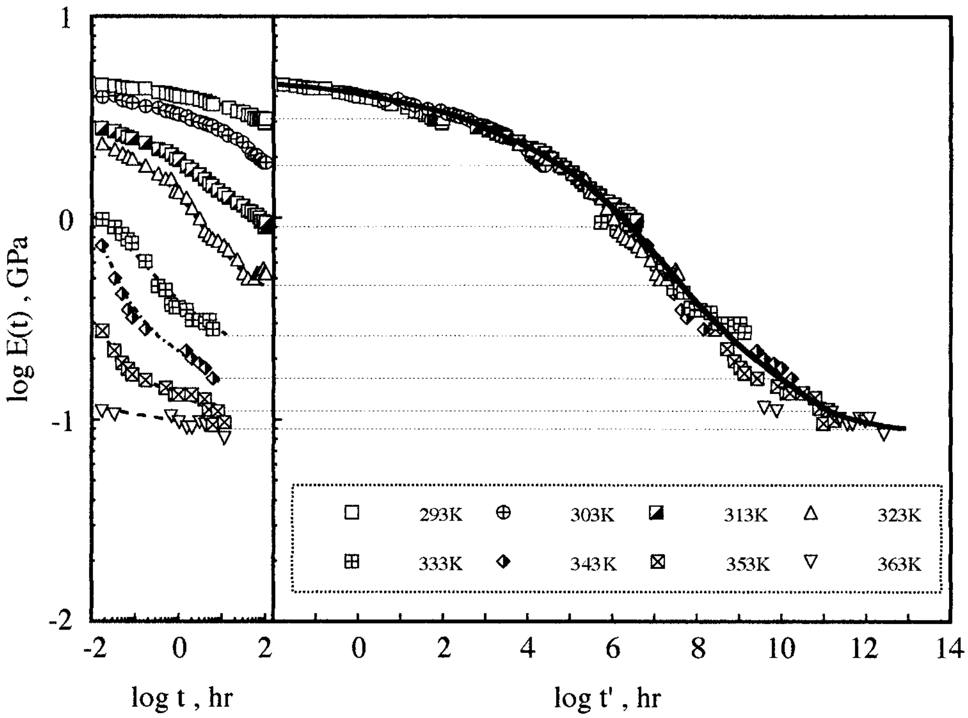

Figure 4 Relaxation modulus of oriental lacquer film and master curve for oriental lacquer film at 60% RH.

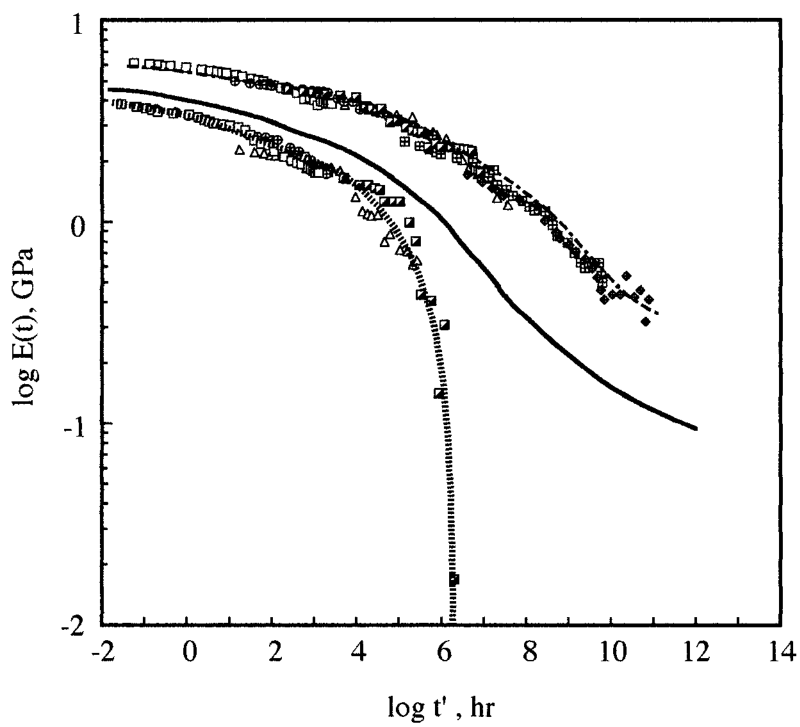

Figure 5 Master curves for oriental lacquer film under various humidities: (– —) 20%, (———) 60%, and (– – —n) 100% RH; □ 293, ⊕ 303, ♦ 308, ◪ 313, △ 323, ⊞ 333, ◈ 343 K.

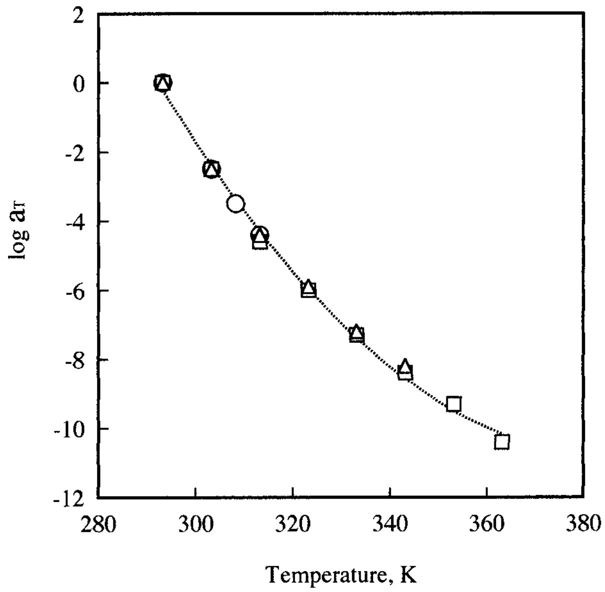

Figure 6 Temperature dependence of shift factor when the reference temperature was fixed at 293 K (20°C): (△) 20%, (□) 60%, and (○) 100% RH.

ulus reaches a given value at 293 K and t_T is the time at a given temperature T. The result is shown in Figure 6, where the reference temperature is 293 K. These temperature dependencies of shift factor are very similar to each other. This fact means that the network structure of oriental lacquer film does not change under the various degrees of humidity.

We discussed the temperature dependence of the shift factor based on the Williams–Landel–Ferry equation. The WLF equation is given by eq. (3).[17]

$$\log a_T = -\frac{C_1(T - T_S)}{C_2 + T - T_S} = \log \frac{t_T}{t_S} \tag{3}$$

where C_1 and C_2 are constants, T_s is the reference temperature, and T is the experimental temperature. When we adopt glass transition temperature for T_S, it is well known that $C_1 = 17.44$ and $C_2 = 51.6$.[17] When we adopt a temperature other than T_g as the reference one, the shift factor $\log S_T$ is given as follows.

$$\log S_T = \log \frac{t_T}{t_S} \tag{4}$$

$$= \log \frac{t_T}{t_g} - \log \frac{t_S}{t_g}$$

$$= -\frac{17.44(T - T_g)}{51.6 + T - T_g} + \frac{17.44(T_S - T_g)}{51.6 + T_S - T_g} \tag{5}$$

We determined the glass transition temperature from loss modulus or thermomechanical analysis (TMA) thermograms for the oriental lacquer film under different conditions on humidity, where loss modulus was determined from the loss factor and storage modulus of this film. The glass transition temperature T_g at 20% RH was 361 K, that at 60% RH was 348 K, and that at 100% RH was 333 K. Thus, the temperature dependence of according to eq. (5) is shown in Figure 7. As shown by experimental points, the experimental shift factors are very different from curves predicted by the usual WLF equation. So we tried to change the parameters C_1 and C_2 in eq. (3).

Equation (4) is generally rewritten as follows. In addition, new parameters C_1' and C_2' correspond to C_1 and C_2, respectively, as follows:

$$\frac{(T - T_g)}{\log S_T + \log S_S} = \frac{C_2'}{C_1'} - \frac{(T - T_g)}{C_1'} \tag{6}$$

where $\log S_S$ is given by equation (7).

$$\log S_S = -\frac{C_1'(T_s - T_g)}{C_2' + T_S - T_g} = \log \frac{t_S}{t_g} = \text{Constant} \tag{7}$$

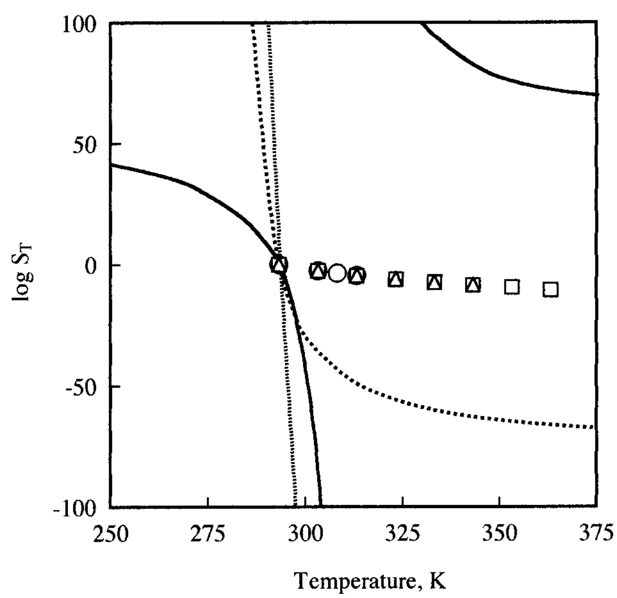

Figure 7 Relationship between experimental shift factors and curves predicted by the WLF equation in which the usual parameters ($C_1 = 17.44$, $C_2 = 51.6$) and different T_g were used. WLF equation: (———) $T_g = 361$ K, (-----) $T_g = 348$ K, and (– – –) $T_g = 333$ K. experimental shift factors: (△) 20%, (□) 60%, and (○) 100% RH.

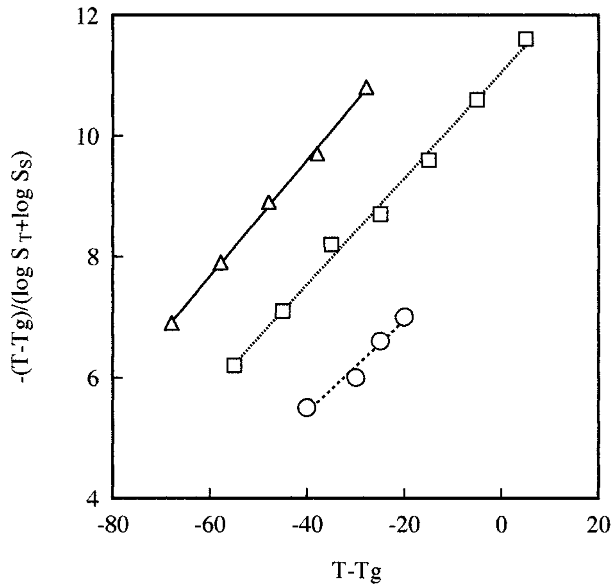

Figure 8 $-(T - T_g)/(\log S_T + \log S_S)$ versus $(T - T_g)$ plot at $T_S = 293$ K according to eq. (6). Experimental points: (△) 20%, (□) 60%, and (○) 100% RH.

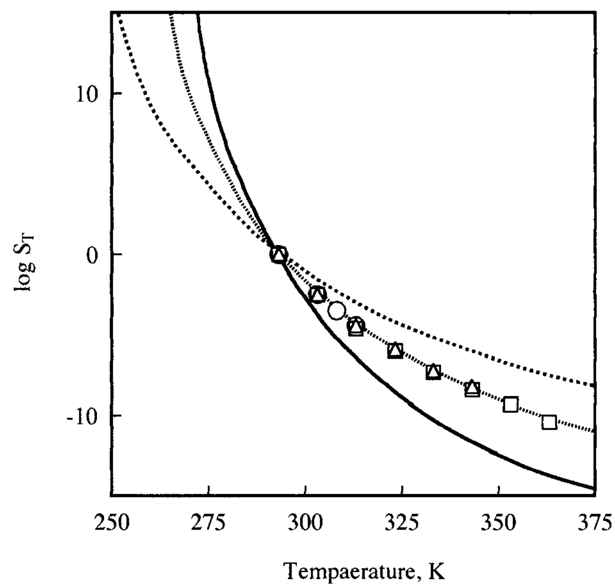

Figure 9 Relationship between experimental shift factors and curves predicted by the WLF equation in which one pair of modified parameters ($C_1'' = 11.5$, $C_2'' = 125.8$) was used. WLF equation: (———) $T_g = 361$ K, (-----) $T_g = 348$ K, and (– – –) $T_g = 333$ K. experimental shift factors: (△) 20%, (□) 60%, and (○) 100% RH.

where t_g means the time when the relaxation modulus reaches a given value at glass transition temperature T_g, and t_s is the time at a given reference temperature T_S. In other words, $\log S_S$ is the actual shift factor from T_g to T_S. Then the value of $\log S_S$ at 20% RH is 9.8, that at 60% RH is 8.9, and that at 100% RH is 7.3. The slope α and the intercept β of the lines in Figure 8 can be correlated with C_1' and C_2', as follows.

$$C_1' = \frac{1}{\alpha} \quad (8)$$

$$C_2' = \frac{\beta}{\alpha} \quad (9)$$

The result is shown in Table II. Thus, C_1' and C_2' were determined so as to follow the experimental points. However, as shown Figure 9, when we adopt a fixed pair of parameters in the WLF equation, the experimental shift factors are different from the curves predicted by the WLF equation. Therefore, we have to choose the parameters according to T_g.

Table II Parameters in WLF Equation for Oriental Lacquer Film

Relative Humidity	T_g (K)	C_1'	C_2'	$C_1'C_2'$
20% RH	361.05	13.0	110.4	1435.2
60% RH	348.15	11.5	125.8	1446.7
100% RH	333.15	10.3	138.9	1430.7

As shown in Table II, the product of C_1' and C_2' is almost constant even if T_g varied. This result is given, as follows:

$$C_1'C_2' = C_1''C_2'' = \text{Constant} \quad (10)$$

Therefore, new parameters C_1'' and C_2'' for a new $(T_g(\cong T_g')$ can be given by the following equations.[17]

$$C_1'' = C_1'C_2'/(C_2' + T_g - T_g') \quad (11)$$

$$C_2'' = C_2' + T_g - T_g' \quad (12)$$

So we can determine C_1'' and C_2'' from C_1', C_2' and T_g for the arbitrary glass transition temperature T_g'. The shift factor $\log S_T$ for any T_g can be repre-

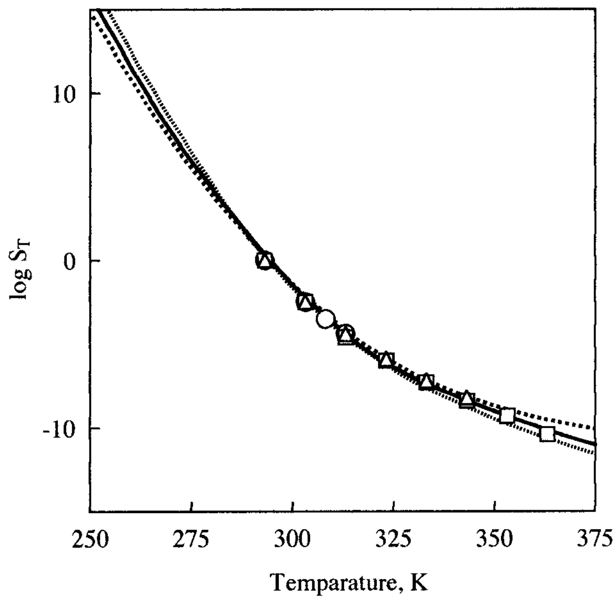

Figure 10 Relationship between experimental shift factors and curves predicted by the WLF equation in which modified parameters C_1'', C_2'' were used. WLF equation: (———) T_g = 361 K, (-----) T_g = 348 K, and (– – –) T_g = 333 K. Experimental shift factors: (△) 20%, (□) 60%, and (○) 100% RH.

sented once C_1' and C_2' are known for a given T_g. Thus, C_1'' and C_2'' are generally given as a function of T_g' in the case of oriental lacquer film.

$$C_1'' = \frac{1438}{474.0 - T_g'} \tag{13}$$

$$C_2'' = 474.0 - T_g' \tag{14}$$

The relationships between experimental shift factors and the curve predicted from WLF equation using C_1'' and C_2'' are shown in Figure 10. The experimental shift factors are in good agreement with the predicted curves. Thus, we can predict the relaxation modulus of oriental lacquer film for any humidities and temperatures.

CONCLUSIONS

Oriental lacquer film has a tendency to become brittle by water desorption and to be toughen with absorption of water. Relaxation modulus of this film changed largely depending upon humidity. The temperature dependence of shift factor on the relaxation modulus could be represented by WLF equation, in which the parameters were modified. In addition, we can determine the two parameters in the WLF equation for arbitrary glass transition temperature. Thus, the relaxation modulus of oriental lacquer film can be determined for any humidities and temperatures.

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