

Effects of Aging and Moisture on the Dynamic Viscoelastic Properties of Oriental Lacquer (Urushi) Film

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ABSTRACT: The effects of aging and moisture on the dynamic viscoelastic properties of three oriental lacquer films were investigated. With aging over 1000 days at room temperature, the glass-transition temperature of the lacquer films (T_{α}) shifted to higher temperatures, the maximum loss tangent ($\tan\delta_{\alpha}$) decreased, and the storage modulus at 20°C (E) increased. These changes were analogous irrespective of lacquers. With increasing moisture content, E decreased and $\tan\delta$ increased at room temperature. Although the equilibrium moisture content of the virgin lacquer (sap) film was higher than that of the clear lacquer film, its E and $\tan\delta$ were more stable with an increase of moisture content. It was speculated that the polysaccharides aggregated in the sap film did not effectively contribute to the mechanical properties of the film, while their hygroscopicity resulted in higher moisture content. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2288–2294, 2002

Key words: Oriental lacquer; urushi; viscoelastic properties; aging; moisture

INTRODUCTION

The oriental lacquer (urushi) is a natural lacquer made from a sap of lacquer tree (*Rhus vernicifera*). It has been widely used as the coating of wooden crafts for several thousands of years, and its deep black color and beautiful luster are still symbolized as an oriental beauty. The oriental lacquer consists mainly of urushiol, water-insoluble glycoproteins, and water-soluble polysaccharides. The laccase-catalyzed oxidation and after

auto-oxidative polymerization of the urushiol have already been investigated in detail.¹

It should be noted that the previous stirring and heating of the sap, “kurome” treatment in Japanese, is an important procedure in the traditional lacquer work. According to Kumanotani,¹ the kurome treatment results in the evaporation of water, polymerization of urushiol, and reaction of glycoproteins with urushiol. At the same time, the lacquer constituents are homogenized and the polysaccharides disperse into the oil phase in which the urushiol–glycoproteins complex is formed. Consequently, each spherical grain of polymerized urushiol is surrounded by a thin wall of polysaccharides in the lacquer film. Such a fine “core-shell” structure is believed to be responsible for the excellent durability of the lacquer film

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owing to the high barrier of polysaccharides wall toward oxygen. In fact, Kumanotani has demonstrated that the density and viscoelastic profiles of the kurome-treated lacquer films remained almost unchanged with prolonged aging while those of a sap film changed remarkably even within a year.² However, there is little information about the viscoelastic properties of the oriental lacquer film in the early stage of its hardening, and no experimental result follows those of Kumanotani indicating the amazing effects of the kurome treatment.

By contrast, the effects of moisture should be considered to clarify the characteristics of the oriental lacquer film, because the lacquer includes hygroscopic polysaccharides that may affect the moisture sorption of the lacquer film. However, only a few investigations have focused on the effects of moisture on the dynamic viscoelastic properties of the oriental lacquer film.

This article describes the changes in the dynamic viscoelastic properties of three oriental lacquer films during aging over 1000 days. The effects of moisture are also discussed in relation to the characteristic morphology of the lacquer film.

EXPERIMENTAL

Materials

Three commercially available oriental lacquers, clear (C), virgin (V), and black (B) lacquers, were used. These were made from the sap of *Rhus verniciflua* harvested at Iwate (Japan). The C and B lacquers had lower moisture content (MC) of about 3%, and a higher degree of polymerization (DP), as a result of previous kurome treatment. Although the C lacquer gives dark brownish film, we call it "clear lacquer" in this article, according to its Japanese name, *suki sugurome urushi*, which means "clear kurome-treated lacquer." The B lacquer is specially colored with 1% (w/w) of iron powder.

The V lacquer was a neat filtered sap that has a naturally high MC of more than 20% and low DP. These lacquers were cast on a Teflon plate and dried at 20°C and 85% relative humidity (RH) for 3–10 days. This process was repeated 5 times to obtain a film thickness of 0.23 mm. Some films were pre-cured at 100°C for 12 h in a drying oven, 2 weeks after the formation of film. These films were then stored in a closed box at room temper-

ature and 60% RH before the viscoelastic measurements were made.

Measurements

The lacquer films were cut into strips of 70 mm × 5 mm, and their tensile storage modulus (E) and loss tangent ($\tan\delta$) were measured within the range of -150 – 300 °C at frequencies of 1, 3.5, 11, and 35 Hz, using a viscoelastometer, Orientec DDV-25FP. The programmed heating rate was 3°C/min, and the effective length of the strips was 55 mm.

The water sorption isotherms of strips aged over 1000 days were determined at 30°C. The moisture dependence of their E and $\tan\delta$ were also measured at 0.5 Hz and 30°C within the range of 10–90% RH, using a viscoelastometer, DMS 6100, Seiko Instruments. The effective length of the strips was 20 mm.

RESULTS AND DISCUSSION

Changes in the Viscoelastic Properties of Lacquer Films During Aging

Figure 1 shows the temperature variations of E and $\tan\delta$ at 11 Hz for the C lacquer film. With respect to the $\tan\delta$ peaks, three relaxation processes labeled α , β , and γ were detected. These were attributed to the glass-transition of polymerized urushiol, the motions of water molecules remaining in the film, and the molecular motions of methylene groups in the side-chains of urushiol, respectively.³

Figure 2 shows the temperature location of the α loss peak (T_α) and its peak value ($\tan\delta_\alpha$) plotted against the aging duration (t). The T_α increased and $\tan\delta_\alpha$ decreased with an increase of aging duration irrespective of lacquers. These changes reflected the oxidative polymerization of urushiol and the formation of crosslinking between their side-chains.⁴ The B and V lacquer films showed lower T_α and higher $\tan\delta_\alpha$ values than the C lacquer film at the same t . As the chemical components of these three lacquers were almost identical, the variations in the T_α and $\tan\delta_\alpha$ should be attributed to the effects of previous treatments, the kurome treatment and the addition of trace iron. The lower DP and higher MC of the V lacquer might be responsible for its slower hardening. By contrast, sufficient explanation cannot be given for the slower hardening of the B lacquer

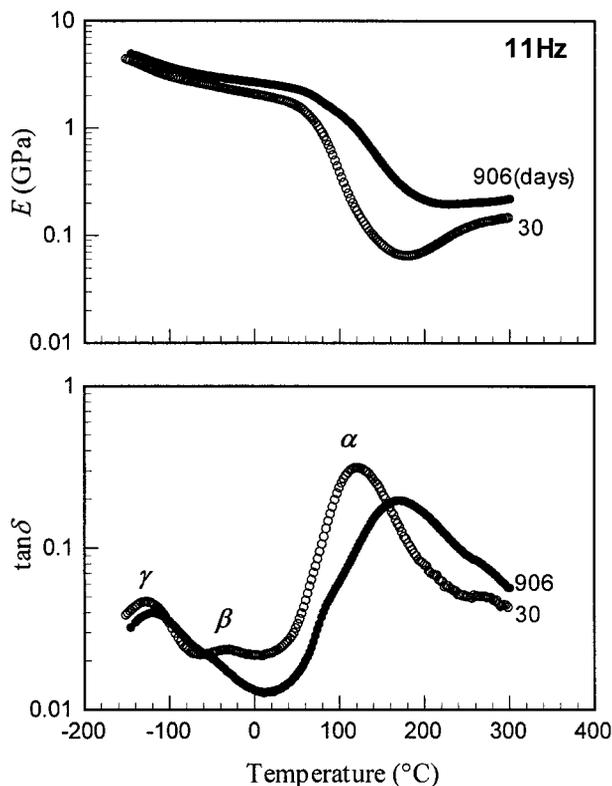


Figure 1 Temperature variations of storage modulus (E) and loss tangent ($\tan\delta$) at 11 Hz for the clear oriental lacquer films aged for 30 days (○) and 906 days (●).

film. The iron–urushiol complexes formed in the B lacquer might affect the oxygen permeation to retard its hardening.⁵

In Figure 3, the $\tan\delta_{\alpha}$ are plotted against the T_{α} . All plots lay on the same line. This fact indicated that the α loss peak shifted with aging analogously irrespective of lacquers, at the same time it implied that the kurome treatment did not result in considerable structural changes in the lacquer constituents but affected the initial DP and/or degree of crosslinking.

Kumanotani has reported that the viscoelastic profiles of kurome-treated lacquer films remained unchanged over 19 years, while those of a sap film changed drastically even within a year. He has also found an additional relaxation process, α' , in the sap film at a temperature higher than the α process.^{1,2} In our results, however, the viscoelastic profile of the V lacquer film, i.e., the sap film were analogous to those of the kurome-treated lacquer films, and no α' relaxation process was detected. Strictly speaking, our V lacquer was not a fresh sap, but rather a commercially provided

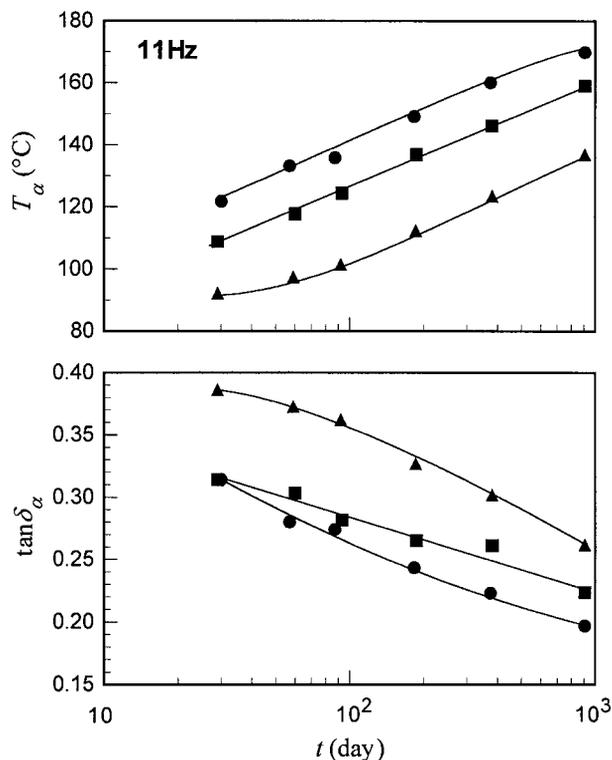


Figure 2 Changes in the peak temperature (T_{α}) and peak value ($\tan\delta_{\alpha}$) of the α relaxation process detected in the clear (●), black (▲), and virgin (■) oriental lacquer films with the elapse of time (t).

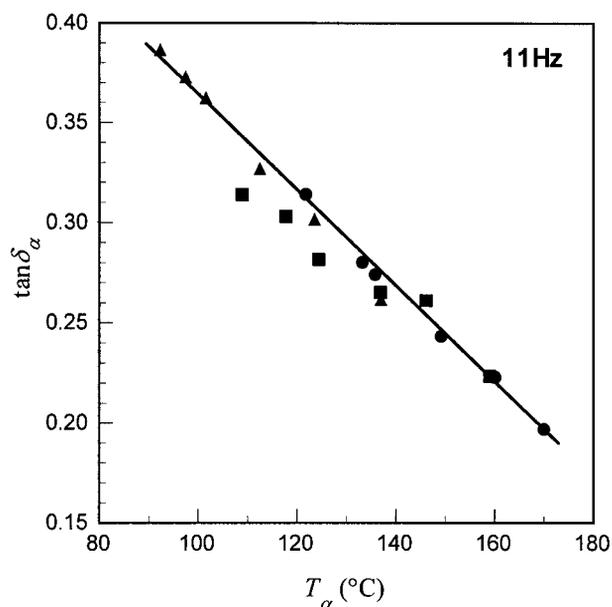


Figure 3 Relationship between the $\tan\delta_{\alpha}$ and T_{α} for the oriental lacquer films. For keys, see Fig. 2.

one that had been purified, packed, and stored for a year before the experiments. These previous "treatments" might involve the polymerization of urushiol and dispersion of lacquer constituents, as induced by the kurome treatment. If so, it is a question of whether the active kurome-treatment is really responsible for the stable viscoelastic properties of the lacquer film.

At any rate, the straight line between the $\tan\delta_\alpha$ and T_α indicates that the changes in the α process of the lacquer films are analogous. Let's assume that the faster initial hardening corresponds to longer aging duration, and these can be represented by a , a hypothetical shift factor. When the C lacquer film is regarded as a base material ($a = 1$), 0.125 and 0.5 were given for the a values of the B and V lacquer films, respectively. Figure 4 shows the changes in the T_α and $\tan\delta_\alpha$ plotted against the reduced aging duration (at). Furthermore, the E and $\tan\delta$ of lacquer films at 20°C and 11 Hz are plotted against t and at in Figure 5. All plots could be superposed in success and gave smooth curves. These curves can represent the general characteristics of the lacquer films examined in this study. From the curves in Figure 5(b),

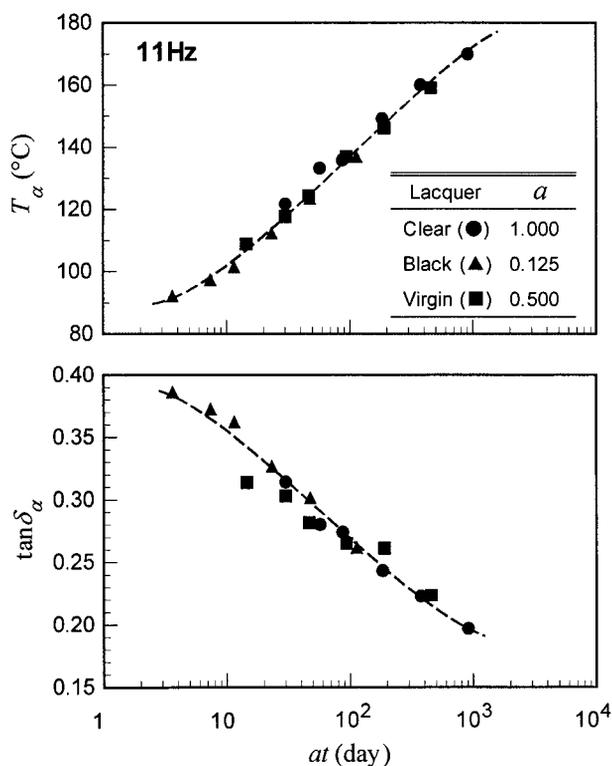


Figure 4 The T_α and $\tan\delta_\alpha$ of the oriental lacquer films plotted against the reduced aging duration (at). For keys, see Fig. 2.

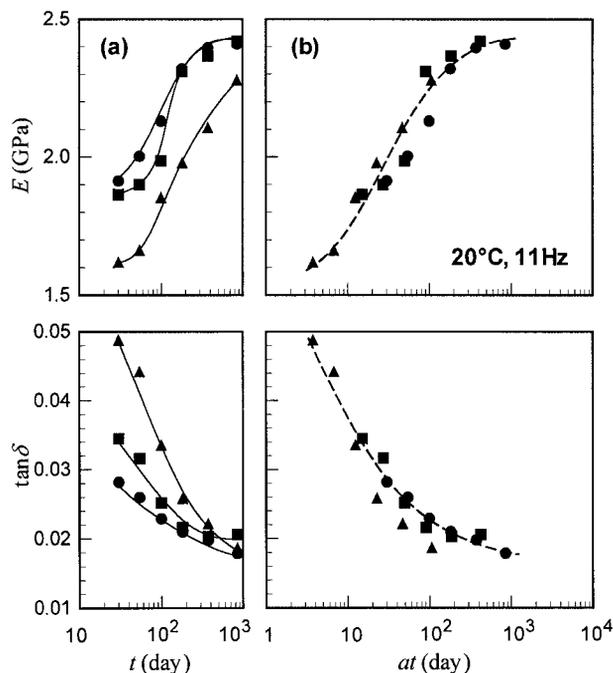


Figure 5 The dynamic Young's modulus (E) and loss tangent ($\tan\delta$) at 20°C and 11 Hz for the oriental lacquer films plotted against the aging duration (t) and the reduced aging duration (at). For keys, see Fig. 2. The a values are listed in Fig. 4.

2.4 GPa and 0.016 were evaluated as the critical values of E and $\tan\delta$ for the lacquer films.

Effects of Pre-cure on the Viscoelastic Properties of Lacquer Films

The pre-cure is a useful method to improve the transparency of the C lacquer film.⁶ It is also effective to prevent contact dermatitis due to the unpolymerized urushiol.⁷ However, few reports have dealt with the effects of pre-cure on the viscoelastic properties of the lacquer film. Figure 6 represents the viscoelastic profiles of the C lacquer film previously cured at 100°C for 12 h. By the pre-curing, the temperature location of the α loss peak shifted to higher temperature and its peak value decreased. These changes were similar to those due to the prolonged aging. The T_α and $\tan\delta_\alpha$ of the pre-cured lacquer films are plotted against t and at in Figure 7, and their E and $\tan\delta$ values at 20°C are plotted against the t and at in Figure 8. As shown in Figure 7, the pre-cured films showed higher T_α and lower $\tan\delta_\alpha$ as compared with the corresponding master curves of the uncured films. Consequently, the pre-cured films seemed more stable during aging than that

of the uncured films in respect to the α process. By contrast, the pre-cure did not remarkably affect the E and $\tan\delta$ values at 20°C. In fact, the pre-cured results fell on the master curves of the uncured films as shown in Figure 8. These facts indicated that the effects of pre-cure on the viscoelastic properties of the lacquer films were different from those of the prolonged aging at room temperature. It was considered that the pre-cure did not accelerate the polymerization of urushiol involving the changes of E and $\tan\delta$ in a glassy state, while it accelerated the formation of crosslinking to shift the T_α and reduce the $\tan\delta_\alpha$. At least the mechanical properties of lacquer films were not degraded remarkably by the pre-curing. Similar result has been reported for the effects of pre-cure on the static mechanical properties of the oriental lacquer films.⁸ Thus, the pre-cure might be a useful method to improve the practical quality of lacquer coatings without serious degradation of their mechanical properties.

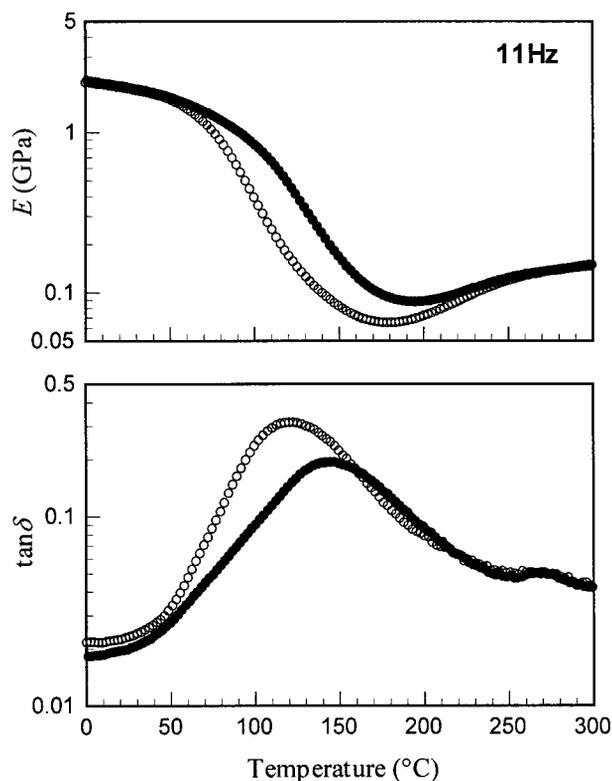


Figure 6 Temperature variations of storage modulus (E) and loss tangent ($\tan\delta$) at 11 Hz for the oriental lacquer films aged for 30 days. \circ , uncured; \bullet , pre-cured at 100°C for 12 h.

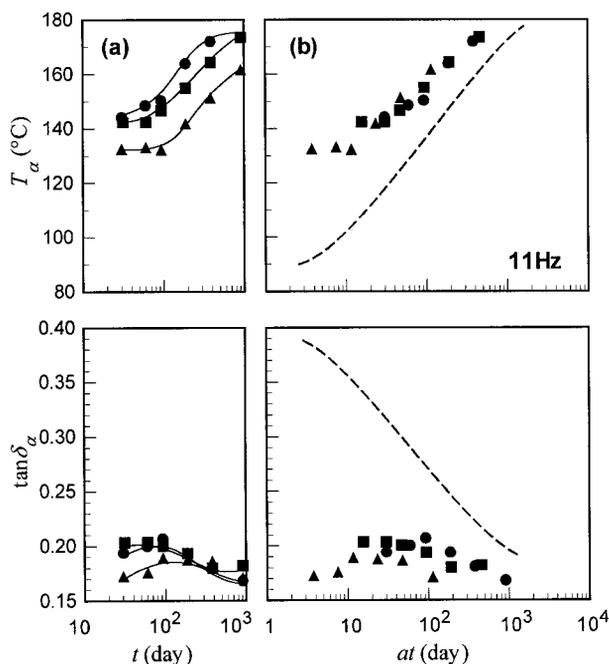


Figure 7 The T_α and $\tan\delta_\alpha$ of the pre-cured oriental lacquer films plotted against the aging duration (t) and the reduced aging duration (at). Broken line exhibits the trend in the uncured films. For keys, see Fig. 2. The a values are listed in Fig. 4.

Effects of Moisture on the Viscoelastic Properties of Lacquer Films

Figure 9 shows the water sorption isotherms of the C and V lacquer films aged over a thousand days. The equilibrium moisture content (MC) of the V lacquer film was higher than that of the C lacquer film over the RH range. Because the chemical components of these lacquers were identical, morphological difference in the lacquer films should be taken into consideration. Figure 10 illustrates the structure of C and V lacquer films.^{1,2} As described above, a fine and homogeneous "core-shell" structure is formed in the C lacquer film as a result of the kurome treatment [Fig. 10(a)]. By contrast, the water-soluble polysaccharides in the V lacquer can aggregate during drying because of its naturally high MC, to form large irregular islands [Fig. 10(b)]. Actually, we could find a considerable number of irregular grains on the surface of V lacquer film, by means of electron microscopy, whereas such grains were fewer and smaller in the C lacquer film. Those grains were probably formed during drying with the aggregation of polysaccharides. The hygroscopicity of polysaccharides is higher than that of

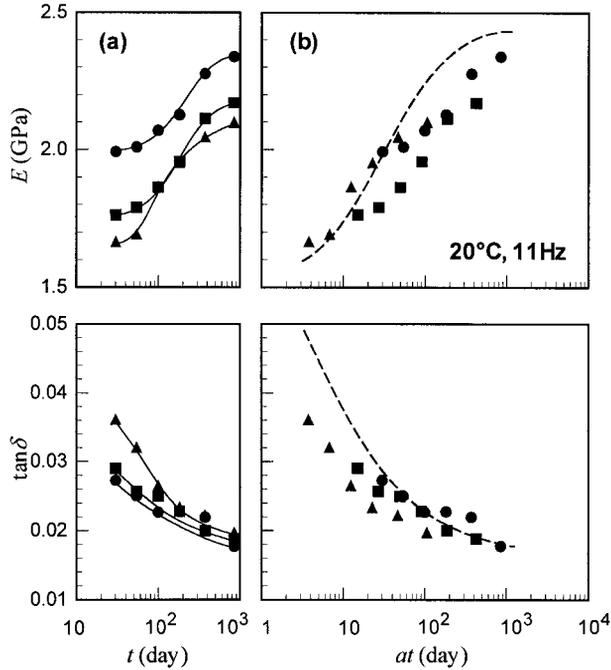


Figure 8 The E and $\tan\delta$ at 20°C and 11 Hz for the pre-cured oriental lacquer films plotted against the aging duration (t) and the reduced aging duration (at). Broken line exhibits the trend in the uncured films. For keys, see Fig. 2. The a values are listed in Fig. 4.

the polymerized urushiol. Furthermore, the hygroscopicity of polysaccharides in the V lacquer film must be higher than that in the C lacquer

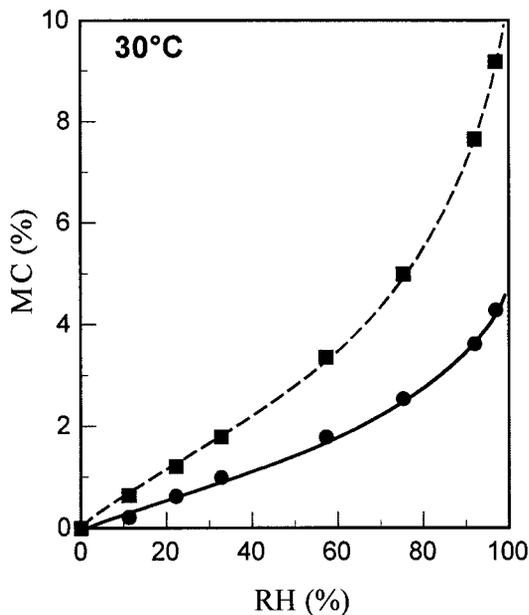


Figure 9 Equilibrium moisture contents (MC) of the clear (●) and virgin (■) oriental lacquer films aged over 1000 days plotted against the relative humidity (RH).

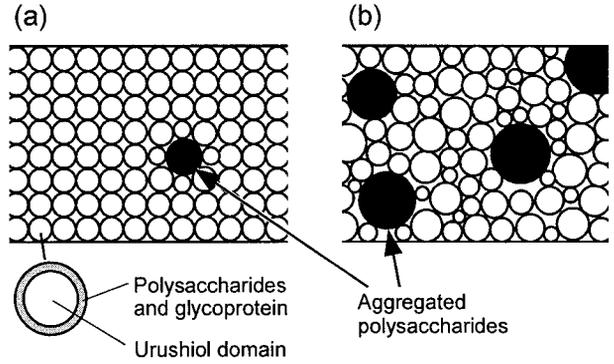


Figure 10 Schematic illustration of the structure of kurume-treated lacquer film (a) and that of sap film (b).^{1,2}

film because the former is held more loosely among the urushiol domains. Thus, the higher moisture content of the V lacquer film is attributable to the hygroscopicity of polysaccharides aggregated during drying.

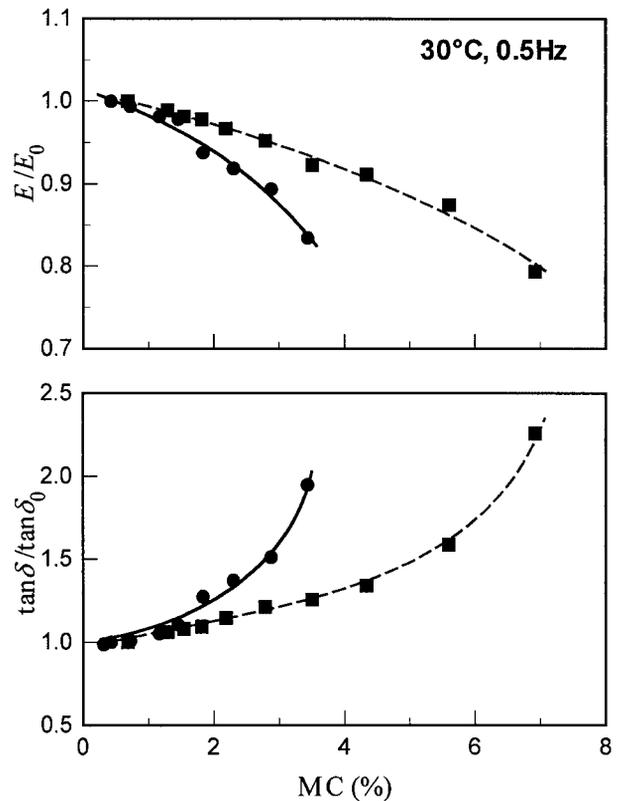


Figure 11 Changes in the E and $\tan\delta$ at 30°C for the clear (●) and virgin (■) oriental lacquer films plotted against the equilibrium moisture content (MC). The E and $\tan\delta$ values were normalized by those at 10% relative humidity (RH), E_0 , and $\tan\delta_0$, respectively.

Figure 11 shows the changes in E and $\tan\delta$ for the C and V lacquer films at 30°C and 0.5 Hz with increasing MC. The changes in the E and $\tan\delta$ of the C lacquer film were larger than those of the V lacquer film. As the hygroscopic polysaccharides are homogeneously dispersed in the C lacquer film, with their softening due to water sorption directly results in the decrease in E and increase in $\tan\delta$. By contrast, a part of polysaccharides in the V lacquer film forms an island as shown in Figure 10(b). Such an isolated region must not affect the E and $\tan\delta$ effectively, while it increases the MC of the lacquer film.

CONCLUSIONS

The dynamic viscoelastic properties of three oriental lacquer films were measured over a period of 1000 days. Furthermore, the effects of pre-cure and moisture were investigated. The conclusions are as follows:

1. With aging at room temperature, the glass-transition temperature of the lacquer films (T_α) shifted to higher temperatures, its loss peak ($\tan\delta_\alpha$) reduced, the storage modulus at 20°C (E) increased, and the loss tangent at 20°C ($\tan\delta$) decreased. These changes were analogous, irrespective of lacquers.
2. When the films were pre-cured at 100°C for 12 h in the early stage of their hardening, the T_α increased and $\tan\delta_\alpha$ decreased as the prolonged aging involved. By contrast, the E values of films remained almost un-

changed by the pre-curing. It was suggested that the pre-cure did not accelerate the polymerization of urushiol involving the enhancement of E in a glassy state, but it affected the T_α , $\tan\delta_\alpha$, and $\tan\delta$ with the acceleration of crosslinking formation.

3. At room temperature, E decreased and $\tan\delta$ increased with increasing moisture content of the lacquer film. Although the hygroscopicity of the virgin lacquer film was larger than that of the clear lacquer film, its E and $\tan\delta$ were more stable against the moisture sorption. It was speculated that the polysaccharides aggregated in the virgin lacquer film did not effectively influence the mechanical properties of the film, while their hygroscopicity led to higher moisture content.

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