Viscoelastic Properties of Japanese Lacquer Film

EIICHI OBATAYA,¹ KENJI UMEMURA,² MISATO NORIMOTO,² YOSHITAKA OHNO³

¹ Institute of Agricultural and Forest Engineering, Tsukuba University, Tsukuba 305-8572, Japan

² Wood Research Institute, Kyoto University, Kyoto 611-0011, Japan

³ Oita Industrial Research Institute, Hita Industrial Art Research Division, Hita 877-0061, Japan

Received 14 September 1998; accepted 12 December 1998

ABSTRACT: The storage modulus (E') and loss modulus (E'') of Japanese lacquer films were measured over a temperature range of -150 to 400° C. Three relaxation processes labeled α , β , and γ were detected at 80, -60, and -140° C, and their apparent activation energies (ΔE) were 63–91, 13, and 9 kcal/mol, respectively. These were attributed to the micro-Brownian motions of polymerized urushiol, the molecular motion related to the absorbed water, and the motions of methylene groups in the side chains, respectively. With aging at room temperature, the location of the α peak shifted to higher temperature and its ΔE value decreased. This result was ascribed to the autoxidative polymerization of urushiol. The E' of lacquer films increased with heat treatments at 100°C or above. When treated at temperatures below 200°C, the location of the α peak shifted to higher temperature, with a reduction in the ΔE value. Heat treatments at 200°C or above resulted in remarkable shrinkage and weight loss of films owing to the pyrolysis of lacquer constituents. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1727–1732, 1999

Key words: Japanese lacquer; urushiol; viscoelastic properties; relaxation process; heat treatment

INTRODUCTION

The sap of Japanese lacquer tree (*Rhus vernicifela*) has been widely used for the coating of tableware and artistic works in the Orient. A lot of ancient wooden artifacts have been protected by the indoor durability of the Japanese lacquer over thousands of years. For its beautiful luster and high resistance to water and chemicals, the lacquer is still widely preferred today as it symbolizes traditional Japanese beauty.¹ The major component of the lacquer is urushiol. The chemical structure of urushiol and the mechanisms of its polymerization have already been clarified.²⁻⁴

Journal of Applied Polymer Science, Vol. 73, 1727–1732 (1999)

© 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/091727-06

Urushiol, a mixture of 3-substituted pyrocatechol derivatives, is usually hardened with the laccasecatalyzed polymerization system. To date, few studies have focused on the viscoelastic properties of dried lacquer films. In the present study, the viscoelastic properties of Japanese lacquer films were measured over a wide temperature range, and the mechanical relaxation processes detected were assigned in relation to the structure of urushiol.

It is said that insufficiently hardened Japanese lacquer works sometimes poison the users because of unpolymerized toxic urushiol. If it is possible to accelerate the hardening of lacquer with minimal degradation, the production time could be shortened with assured safety in utilization. In this respect, the effect of heat treatment on the viscoelastic properties of lacquer film was also investigated.

Correspondence to: E. Obataya.



Figure 1 Temperature dependence of storage modulus (E') and loss modulus (E'') at 11 Hz for the air-dried Japanese lacquer films aged for 2 months at room temperature.

EXPERIMENTAL

Materials

Three commercially available Japanese lacquers, virgin (V), clear (C), and black (B), produced from the sap of R. vernicifela harvested at Iwate (Japan) were used. The V lacquer, a neat filtered sap, has a naturally high moisture content (MC) of over 20% and low degree of polymerization (DP). The **C** and **B** lacquers have lower MC of about 3% and higher DP during the initial stirring and heating at below $45^{\circ}C^{1,5}$. The **B** lacquer is specially colored with 1% (w/w) of iron powder. These lacquers were applied 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 0.23mm. The films were cut into strips of 70 by 5 mm, and aged at room temperature and 90% RH for 0.5, 2, 4, 6, and 12 months prior to the measurement.

Measurements

The storage modulus (E') and loss modulus (E'') of lacquer films were measured in the range of -150

to 400°C at frequencies of 1, 3.5, 11, and 35 Hz, while heated at a programmed heating rate of 3°C/min by using a viscoelastometer, Orientec, DDV-25FP. The IR spectra of the C lacquer films were observed at 20°C by the KBr method using an IR spectrometer, Nihon-Bunko, FT-IR 7000. Thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis for the C lacquer films were carried out under atmospheric condition, from 30 to 300°C at a heating rate of 10°C/ min using the TA instruments, TGA2050 and DSC2910. Further, the E' at 1 Hz of the C lacquer films aged for two weeks was measured at 30, 50, 100, 150, 200, and 250°C for 12 h, respectively. The IR spectra and the temperature dependence of E' and E'' for the heat-treated **C** lacquer films were measured after a month of aging at room temperature.

RESULTS AND DISCUSSION

Mechanical Relaxation Processes of Lacquer Films

Figure 1 shows the temperature dependence of E'and E'' at 11 Hz for the air-dried lacquer films aged for 2 months. With increasing temperature, a remarkable fall and rise of E' were recognized in the range 50–250°C. The increment in E' at above 150°C indicated the effect of postcuring by heat. With respect to E'', three peaks were detected in all of the films at about 80, -60, and -140°C, labeled as α , β , and γ , respectively. An additional E'' peak, α' , was detected in the **V** lacquer film at around 20°C. Figure 2 shows the plots of logarithmic frequencies (log f) against the reciprocals of the absolute temperatures at the E''



Figure 2 Plots of logarithmic frequencies (log f) against the reciprocals of absolute temperature at E'' maxima (1/T) for the α , α' , β , and γ processes detected in the air-dried films: (O) clear lacquer, (\bullet) black lacquer, and (\triangle) virgin lacquer.



Figure 3 Temperature dependence of storage modulus (E') and loss modulus (E'') at 11 Hz for the absolutely dried Japanese lacquer films aged for 2 months at room temperature.

maxima (1/*T*). The apparent activation energies (ΔE) of α , α' , β , and γ given by the plots of log f versus 1/*T* were 63–91, 48, 13, and 9 kcal/mol, respectively.

The MC of the air-dried **C**, **B**, and **V** lacquer films were 0.7–1.2, 2.5–2.7, and 2.3–2.9%, respectively. These values were independent of the aging time. Figure 3 shows the temperature dependence of E' and E'' at 11Hz for the absolutely dried lacquer films aged for 2 months. Both the α' and β processes disappeared after the removal of adsorbed water.

In the temperature region of the γ process, it is known that a relaxation process occurs due to the presence of three units of methylene groups, and its ΔE value ranges from 8 to 9 kcal/mol.⁶ As illustrated in Figure 4, the side chains of urushiol include at least 7 units of methylene groups, and the ΔE values of the γ process were 9 kcal/mol irrespective of lacquers and aging time. Therefore, the γ process was attributed to the motion of methylene groups in the side chains of urushiol.

The β process disappeared when the adsorbed water was removed. Its temperature location and ΔE value were independent of lacquers and aging

time. A similar process has been detected in a lot of hydrophilic polymers, and is attributed to the molecular motion related to the adsorbed water.⁷⁻¹² Thus the β process seemed to be due to the motion related to the adsorbed water.

In the temperature region of the α process, the E' decreased remarkably with increasing temperature, the E'' had a relatively large peak, and the maximum values of the loss tangent (E''/E')ranged from 0.3 to 0.5. In addition, the relatively large values of ΔE suggested that the α process was responsible for the principal dispersion of polymerized urushiol.

The α' process was detected only in the **V** lacquer film. This process was considered to be due to hydrophilic constituents in the lacquer because it disappeared after drying absolutely. Japanese lacquer contains some polysaccharides.^{13,14} In both the **C** and **B** lacquers, these polysaccharides disperse and reorient around the polymerized urushiol, and some of them react with the urushiol during the initial stirring and heating.⁵ Therefore, the polysaccharides in the C or B film might be tightly embedded in the polymerized urushiol. Meanwhile, the polysaccharides in the V lacquer are kept in a swollen state with aggregated water in the early stage. Upon drying, these polysaccharides shrink but remain mobile. Some mobile polysaccharides thus formed might induce the α' process when they are plasticized with moisture.

Effects of Aging on the Viscoelastic Properties of Lacquer Films

Figure 5 represents the temperature dependence of E' and E'' at 11 Hz for the absolutely dried **C**



Figure 4 Urushiol, the major constituent of Japanese lacquer.



Figure 5 Temperature dependence of storage modulus (E') and loss modulus (E'') at 11 Hz for the absolutely dried Japanese lacquer films aged for indicated durations at room temperature.



Figure 6 Temperature locations of E'' peak at 11 Hz (T) and apparent activation energies (ΔE) for the α process of Japanese lacquer films plotted against the aging time.



Figure 7 Changes of storage modulus (E') at 1 Hz for the Japanese lacquer films at indicated temperatures with respect to the treating time.

lacquer films aged for 0.5–12 months. The temperature location of the α process apparently shifted in the early stage. This seems to reflect the autooxidative polymerization of urushiol molecules. The temperature locations of E'' peaks at 11 Hz (T) and the ΔE values for the α process are plotted against the aging time in Figure 6. In the case of **C** and **V** lacquer films, T increased and ΔE decreased with aging. The decrease of ΔE was interpreted as a decrease of molecular unit due to the crosslinking formation of urushiol molecules. However, the ΔE of the **V** lacquer increased in the first 4 months, then decreased. The rate of poly-



Figure 8 TG and DSC curves of the Japanese lacquer film.



Figure 9 Temperature dependence of storage modulus (E') at 11 Hz for the Japanese lacquer films treated at indicated temperatures for 12 h.

merization of the V lacquer is slower in the early stage because it has naturally low DP and high MC. Therefore, it was speculated that the increase of ΔE in the first 4 months was due to the retardation of polymerization of urushiol owing to its own characteristics.

Kumanotani⁵ suggested that the excellent durability of Japanese lacquer film arises from an antioxidation structure, in which the polymerized urushiol is wrapped by a thin layer of polysaccharides. This structure is formed during the initial stirring and heating process, called "Kurome" in Japanese. He also suggested that the V lacquer (sap) film is more rigid and its viscoelastic profile is less stable than other films, because no antioxidation structure is formed.⁴ However, our findings indicated that the E' of the V lacquer film was rather low compared to the others, and its viscoelastic profile was identical to those of other films after a year of aging. It was speculated that the process of oxidation in the multilayered thick films used in our experiments took place rather slowly even though no antioxidation structure was formed.

Effects of Heat Treatment on the Viscoelastic Properties of Lacquer Films

Figure 7 shows the changes of E' at 1 Hz for the C lacquer films at the temperatures 30, 50, 100, 150, 200, and 250°C. The increase of E' above 100°C reflected the thermal hardening of urushiol molecules. Above 150°C, the films shrunk with treatment duration and the degree of shrinkage increased with increasing temperature. Figure 8 shows the TG and DSC curves of the C lacquer film aged for 2 months. The slight endothermic peak at around 70°C detected in the DSC curve corresponds to the α process. The remarkable exothermic peak detected in the range of 100–200°C was due to the oxidative polymerization of urushiol. This consideration was supported by the decreases of IR peaks at 1655 and 992 cm^{-1} , due to the quinoid carbonyl and the conjugated triene in the side chains, respectively. In the same temperature region, a slight weight loss was recognized, and an IR peak was observed at 1719 cm⁻¹ indicating the formation of the carbonyl groups at higher temperature. These results suggest that some degradation of lacquer constituents has occurred. Above 200°C, remarkable weight loss and



Figure 10 Temperature dependence of loss modulus (E'') at 11 Hz for the Japanese lacquer films treated at indicated temperatures for 12 h.



Figure 11 Temperature locations of E'' peak at 11 Hz (*T*) and apparent activation energies (ΔE) for the α process of Japanese lacquer films treated at various temperatures for 12 h plotted against the treating temperature.

exothermic reaction were observed. These were ascribed to the marked pyrolysis of lacquer constituents.

Figure 9 shows the temperature dependence of E' at 11Hz for the C lacquer films treated at 30, 50, 100, 150, 200, 250, and 300°C for 12 h. Postcuring was not observed in the films treated at 150°C and above. The films treated at above 200°C were too weak to be tested as they broke during the measurements. Figure 10 shows the temperature dependence of E'' at 11 Hz for the C lacquer films treated at various temperatures. The α process changed remarkably with the heat treatments while the γ process remained almost unchanged. Figure 11 represents the temperature locations of E'' peak at 11 Hz (T) and the ΔE values for the α process plotted against the treating temperature. Below 200°C, the T increased and the ΔE decreased as the temperature increased. Above 200°C, reversed trends were observed for both T and ΔE . These are probably caused by the scissoring of main chains by the pyrolysis process. In addition, treatments at 200°C or above seemed to damage the characteristic deep black, beautiful luster, and flexibility of the films. From these results, it is advisable to treat the lacquer film at around 100°C in order to accelerate the hardening of lacquer with minimal degradation.

CONCLUSIONS

Three relaxation processes were detected at 80 (α), -60 (β), and -140°C (γ) in three different kinds of Japanese lacquer film. These were assigned to the micro-Brownian motion of lacquer molecules, the molecular motion related to the adsorbed water, and the motion of methylene groups in the side chains of urushiol, respectively. With aging at room temperature, the temperature location of the α process shifted to higher temperatures and its apparent activation energy decreased. These were ascribed to the oxidative polymerization of urushiol. Meanwhile, the lacquer films were hardened at a temperature of 100°C or higher with advanced oxidative polymerization of urushiol. With heat treatment at above 200°C, the pyrolysis of lacquer constituents induced remarkable shrinkage and weight loss of films.

REFERENCES

- 1. Taneda, K. Mokuzai Kogyo (in Japanese) 1985, 40, 10.
- Symes, W. F.; Dawson, C. R. J Chem Soc Am 1954, 76, 2959.
- Sunthankar, S. V.; Dawson, C. R. J Chem Soc Am 1954, 76, 5070–5074.
- 4. Kumanotani, J. Makromol Chem 1978, 179, 47.
- 5. Kumanotani, J. Kagaku To Kogyo (in Japanese) 1983, 36, 189.
- 6. Willbourn, A. H. Trans Farad Soc 1958, 54, 717.
- 7. Schmieder, K.; Wolf, K. Kolloid Zeit 1953, 134, 149.
- 8. Illers, K. H. Makromol Chem 1960, 38, 168.
- Gall, W. G.; McCrum, N. G. J Polym Sci 1961, 50, 489.
- Bernier, G. A.; Kline, D. E. J Appl Polym Sci 1968, 12, 593.
- 11. Kimura, M.; Nakano, J. J Polym Sci Polym Lett Ed 1976, 14, 741.
- 12. Obataya, E.; Yokoyama, M.; Norimoto, M. Mokuzai Gakkaishi (in Japanese) 1996, 42, 243.
- Oda, Y.; Ishida, T.; Honda, K. Nippon Nogei Kagaku Kaishi (in Japanese) 1962, 36, 527.
- Oda, Y.; Kanbe, T.; Honda, K. Nippon Nogei Kagaku Kaishi (in Japanese) 1963,37, 132.