Influence of Polyethylene Oxide (PEO) on the Performance of Chinese Lacquer Films

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The Chinese lacquer composite films were prepared by modifying raw lacquer with polyethylene oxide. The film was characterized *via* Fourier-transform infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy. The infrared spectra confirmed the interaction between the polyethylene oxide and urushiol. The heat-resistance of the film was found to have decreased due to the presence of polyethylene oxide *via* thermogravimetric analysis. Additional pores and wrinkles were observed in the scanning electron microscopy image of polyethylene oxide modified lacquer films. The mechanical properties were tested according to the national standard. The results indicated that the gloss and flexibility of the modified film was enhanced by the presence of polyethylene oxide. When the ratio of polyethylene oxide was 3%, the gloss was increased from 59.8 to 81.6 and the flexibility changed from 15 mm to 1 mm. The alkaline-resistance, hardness, and adhesion were also increased *via* the modification of polyethylene oxide.

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INTRODUCTION

Chinese lacquers have been applied for several thousand years as a coating on the surface of different materials, *e.g.*, metal, wood, ceramics leather, cloth, and paper, as both decoration and protection (Kumanotani 1995; Lu *et al.* 2013). Although many synthetic coatings have been prepared and widely applied, Chinese lacquer is still used nowadays due to its remarkable properties, *i.e.*, its high gloss and good durability (Yang *et al.* 2015). The sap from Chinese lacquer trees consists of catechol derivatives (60% to 65%), water (20% to 30%), plant gum (4% to 10%), glycoprotein (3% to 5%), and laccase enzyme (1% to 2%). Urushiol is a mixture of various catechol or phenol derivatives being substituted with C15 and C17 side chains (Vogl 2000; Lee *et al.* 2015). Lacquer sap is dried through the oxidation of urushiol on the long unsaturated aliphatic side chain under a specific temperature and relative humidity (Nimura and Miyakashi 2006; Zhang 2012). The drying process has an effect on the properties of the coating (Xia *et al*. 2010; Wan *et al.* 2016; Gao *et al.* 2019). The lacquer film has excellent properties; however, as a kind of coating, the lacquer has some disadvantages, *e.g.*, poor chemical resistance, which restricts its applications. Therefore, it is necessary to improve its performance in order to widen its application. Tannins were used to treat the Chinese lacquer sap, and the thermal stability and alkali resistance of the film was found to be improved (Zhou *et al.* 2014). Wan *et al.* (2016) used tung-oil to treat the lacquer sap and found that the modified lacquer film showed improved resistance to alkali, salt, acid, and gasoline. Carbon black nanoparticles were also employed to enhance the corrosion resisting ability of the lacquer film (Zhang *et al.* 2007). Deng *et al.* (2019) prepared different degradation inhibitors by mixing lignins, aniline, and 4-fluoroaniline with Chinese lacquer and found that the degradation resistance of the film was improved by the addition of these inhibitors.

However, scientist have not paid much attention on the flexibility of Chinese lacquer. Zhang *et al.* (2020) modified Chinese lacquer with polyamidoamine (PAMAM) and the comprehensive mechanical properties, such as impact resistance, adhesion, and hardness, were significantly improved compared to the unmodified lacquer film. They also found that the flexibility of the film was increased. Xue *et al.* (2020) developed a blend by diallyl trisulfde (TS) and urushiol and found that the presence of flexible segments provided the coating composition with good flexibility but the hardness of coating dropped to 2H. Therefore, blending polymers with Chinese lacquer was believed to be a possible solution for improving the flexibility. Polyethylene oxide (PEO) is an attractive polymer, with amphiprotic characters that contain "hydrophobic ethylene units and the hydrophilic oxygens" (Ali *et al.* 2017). Therefore, PEO is soluble not only in water and but also in organic solvents. Moreover, the polymer consists of C, H, and O atoms linked together into a linear chain; thus, it has a relatively high degree of crystallinity (approximately 50%) (Chang *et al.* 2020). In addition, PEO has been applied in various fields due to its good biocompatibility and low toxicity. Polyethylene oxide was also reported to be a suitable candidate as a flexibilizer for Chinese lacquer due to its high flexibility of the chain (Migliardo *et al.* 2013). In the present work, different amount of PEO were used to modify Chinese lacquer sap to make a film, and the morphology, thermal properties, and mechanical performance of the PEO modified lacquer film were investigated.

EXPERIMENTAL

Materials

The Chinese lacquer used in this work was purchased from Sichuang and filtered using nylon cloth of 200 mesh by gravity before use. The polyethylene oxide (PEO) (molecular weight of 1000000) was purchased from BASF Biochemical Reagent Company (Hefei, China). The C_2H_5OH, H_2SO_4, NaOH, and NaCl were bought from Fuchen Chemical Regent (Tianjin, China). All reagents were used as received without any treatment.

Preparation of the Sample

A certain amount of PEO was dissolved into deionized water, and a 0.6% homogeneous PEO solution was obtained after being stirred continuously for 24 h under ambient conditions. The PEO solution was added into filtered Chinese lacquer at different mass ratios (1%, 3%, and 5%). The mixture was stirred for 3 h under ambient conditions. Finally, the modified-lacquer was coated onto the glass slides and tin plates according to GB standard 1727-79 (1979). The samples were placed in the oven at 120 °C. After being heated for 2 h, the film was taken out from the oven temporarily every 10 min to check the drying state of the film *via* touching the edge using a finger. The time was noted as the touch-free drying time (TF time), providing that no mark was observed on the surface of the film.

Characterization of the Sample

The FT-IR spectrum of the film was recorded using a MPIR8400S FI-IR spectrometer (Shimadzu, Japan) *via* the ATR method. A total of 32 scans were carried out with a resolution of 4 cm^{-1}.

The TGA experiments were carried out at a heating rate of 10 °C/min in a temperature range from 30 to 800 °C with a STA449F3 thermal analyzer.

The SEM images were recorded via S3400 field emission SEM (Hitachi, Japan) with an acceleration voltage of 25 kV.

The gloss of the films was measured by a gloss meter (JFL-B60^{o}, Jinfulun, China). The value gives an indication of the ratio of the reflected light on the film to the reflected light on the reference plate.

The scratch hardness of the film was determined using a QHQ-A pencil hardness testing meter (China). The hardness is expressed as 6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H, which is in the order from the softest to the hardest (Gao *et al.* 2019).

The flexibility test was carried out according to the GB/T standard 1731-1993 (1993). The coated tinplate was bent along the cylinder with various diameters. As the bent film was not cracked, the diameter of the cylinder axis is the value of the flexibility of the film (Zhang *et al.* 2020).

The adhesive capacity of the film was tested by a bagel knife. It is expressed by 0B, 1B, 2B, 3B, 4B, and 5B ASTM levels, meaning that the adhesion of the film successively increases.

The chemical resistance of the lacquer to acid, alkali, and salt was characterized by dipping the lacquer film coated glass slides into 10% HCl, 10% NaOH, and 10% NaCl solutions for 14 d under ambient conditions, respectively.

RESULTS AND DISCUSSION

Influence of Polyethylene Oxide (PEO) on Touch-Free Drying Time

The touch-free (TF) drying times of the untreated and treated lacquer film are listed in Table 1. The data in Table 1 showed that the TF drying time was affected by the presence of PEO. The drying time increased when more PEO was used. This was attributed to the fact that the large amount of water present in the PEO solution retarded the drying process of the film and thus increased the TF drying time. The complete drying time of all the films were almost same, it was about 480 min.

Table 1. Influence of Polyethylene Oxide (PEO) on Touch-free (TF) Drying Time of the Films

PEO Content(%)	0	1	3	5
TF Drying Time (min)	140	220	270	300

Fourier-transform Infrared (FTIR) Spectra Analysis

Fourier-transform infrared spectroscopy is well known as a good method to determine the composition of a sample. The comparison between the characteristic peaks of the untreated lacquer and the PEO treated films is shown in Fig. 1. The absorption peaks at 3200 cm^{-1} to 3500 cm^{-1}, 1363 cm^{-1}, and 1277 cm^{-1} were attributed to the O-H stretching vibration, βO-H stretching vibration, and γO-H stretching vibration, respectively (Reddy *et al.* 2006; Yang *et al.* 2018). The absorption peaks at 2925 and 2850 cm^{-1} (as shown in Fig. 1) corresponded to the aliphatic -CH_3 and -CH_2 stretching, respectively. The peak at 1150 cm^{-1} was caused by the C-O stretching vibration of the C-O-H group of urushiol (Gao *et al.* 2019). The intensities of the peak at 1055 cm^{-1} increased with the increase of PEO content, as it was derived from the vibration of the C-O-C group (Lu *et al.* 2004). The peak positions of the PEO modified lacquer film were almost the same as those of the pure original lacquer, which indicated that there was no crosslinking between the PEO and lacquer. However, the existence of PEO may have an influence on the thermal and mechanical behavior of the lacquer film, which is discussed in the following sections.

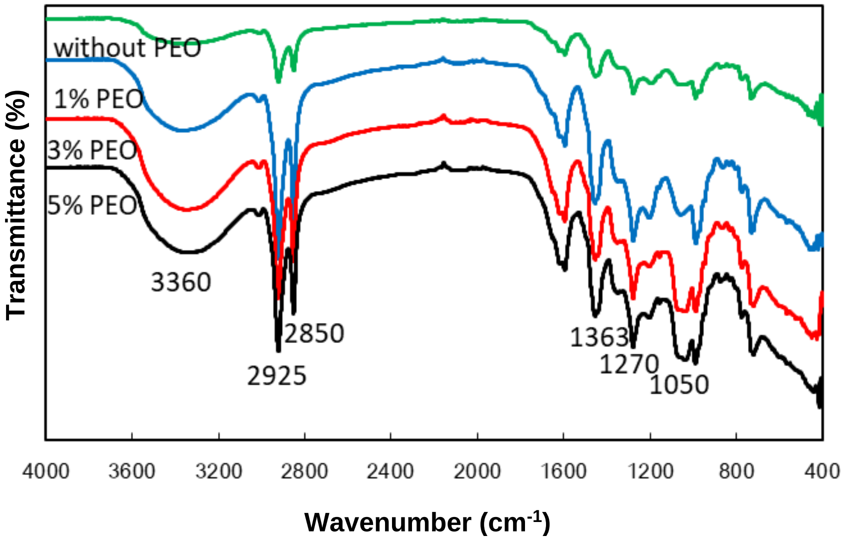

Fig. 1. FT-IR spectra of the untreated and PEO modified lacquer films

Thermal Properties of the Lacquer Film

Raw lacquer films typically show excellent thermal stability. The thermal stability of the untreated Chinese lacquer film and PEO modified film was investigated *via* thermogravimetric analysis. The TGA curves of the untreated and PEO modified films are presented in Fig. 2. It could be observed, according to the TGA curves, that there were three different degradation stages. At the first stage, at a temperature of 30 to 250 °C, the weight losses of the four samples were almost same (approximately 5%), which was attributed to the degradation of the residual urushiol oligomers and water in the lacquer film (Gao *et al.* 2019). At the second stage of 250 to 400 °C, the weight loss was due to the fact that the glycoproteins and polysaccharides decomposed. The weight loss of the raw lacquer film and the film treated with 1.0%, 3%, and 5.0% PEO were 26.2%, 27.9%, 26.5%, and 31.1%, respectively. At the third stage of 400 to 480 °C, the rapid degradation of the urushiol polymer contributed to the weight loss. The degradation rate of original lacquer film and the films modified with 1.0%, 3.0%, and 5.0% PEO were 67.5%, 71.8%, 70.9%, and 76.5%, respectively. In addition, their residuals were 18.7%, 19.7%, 17.7%, and 11.5%, respectively. Based on the results above, it might be summarized that the lacquer film treated by 1.0% and 3.0% PEO had similar thermal stability compared to the untreated lacquer film. However, when 5% PEO was added to the lacquer, the thermal stability of the film became worse. Therefore, too much PEO will deteriorate the thermal stability of the film, which also provides the evidence that there is no strong chemical bond formed between the PEO and urushiol.

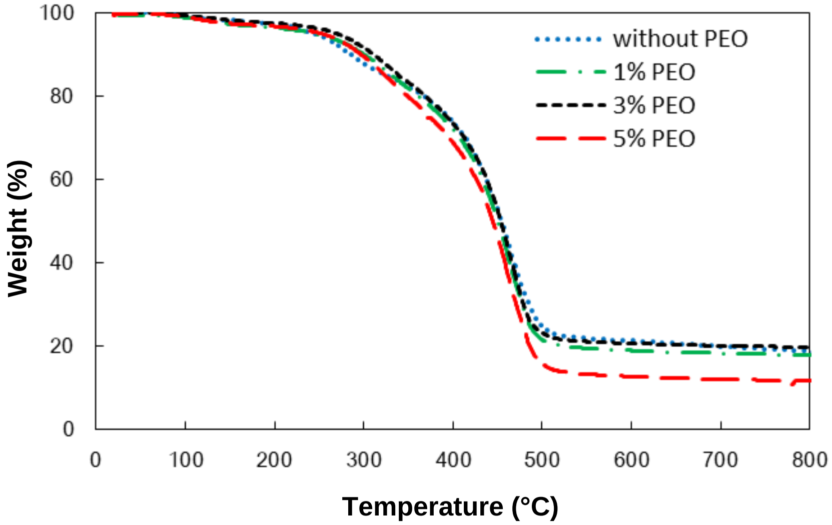

Fig. 2. TGA curves of the original and PEO modified films

Scanning Electron Microscopy (SEM) Analysis

Figure 3 shows the SEM images of the cross-sectional morphologies of the original films and the films modified with PEO.

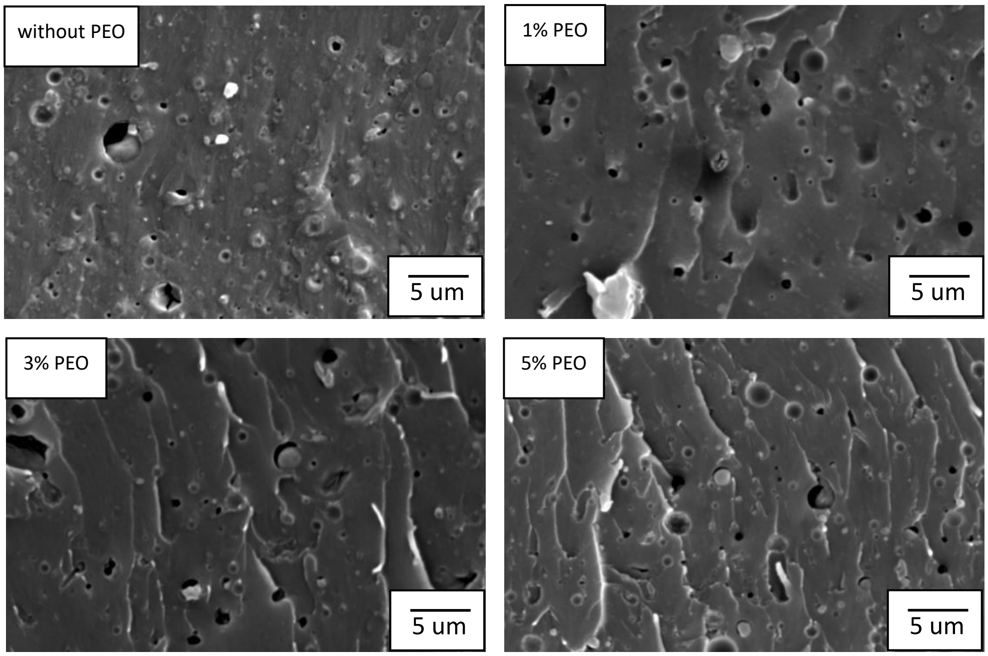

Fig. 3. SEM images of the cross-section of the unmodified and PEO modified lacquer films

It can be seen from the SEM images that the lacquer films were fully cured (Nijenhuis *et al.* 1996). With the addition of PEO, the sectional structure of the PEO modified films showed additional and bigger voids, which was due to the loss of water. The amount of lost water affected the number of voids in the film, therefore having a major impact on the morphology and the mechanical performance (Ali *et al.* 2017). The more PEO added, the more the water was lost, thus the greater the void. In addition, as additional PEO was added (3% and 5%), the wrinkling phenomenon was more easily observed. It was attributed to the fact that the viscosity was increased, which cause the wrinkles when it was dried due to the addition of viscous PEO.

Influence of Polyethylene Oxide (PEO) on the Gloss of the Lacquer Film

The surface of the film has a major influence on the gloss of the film (Gao *et al.* 2019). As shown in Table 2, the gloss of the film was improved due to the presence of PEO. The gloss of the lacquer film increased as the amount of PEO increased. When the PEO content was 3%, the gloss of the film reached its maximum. This was attributed to the fact that the surface of the film was smoothest when 3% PEO was added. When more than 3% PEO was added, the surface of the film was not smooth any more due to the high viscosity, which resulted in the low gloss.

Table 2. Influence of Polyethylene Oxide (PEO) on the Gloss of the Films

PEO Content (%)	0	1	3	5
Gloss	59.8±1.2	73.9±1.5	81.6±0.8	76.2±1.0

Influence of Polyethylene Oxide (PEO) on the Scratch Hardness of the Film

The scratch hardness of the original and PEO modified films are listed in Table 3. The hardness of the original lacquer film was 4H; when PEO was added, the hardness of the film increased. As the ratio of PEO was increased, the scratch hardness of the film changed from 5H to 6H, which was attributed to hydrogen bonding between the PEO and urushiol. Therefore, the structure of the film became denser; thus, the hardness was improved.

Table 3. Influence of Polyethylene Oxide (PEO) on the Hardness of the Films

PEO Content (%)	0	1	3	5
Hardness	4H	5H	6H	6H

Influence of Polyethylene Oxide (PEO) on the Flexibility of the Lacquer Film

The flexibility of the film was examined by bending the coated tinplate along the cylinder axis with various diameters (15, 10, 5, 4, 3, 2, and 1 mm). The flexibility value in the table is the minimum diameter of the cylinder axis when no cracking appears. It can be observed from Table 4 that the flexibility of the unmodified lacquer film was 15 mm; however, the flexibility of the lacquer film modified with PEO was 1 mm and it did not change whatever the PEO content. As such, it could be bent at almost 180° without any cracks. The data indicated that the flexibility of the film was enhanced dramatically due to the addition of PEO, which is consistent with the previous report by Chang *et al.* (2020).

Table 4. Influence of Polyethylene Oxide (PEO) on the Flexibility of the Films

PEO Content (%)	0	1	3	5
Flexibility(mm)	15	1	1	1

Influence of Polyethylene Oxide (PEO) on the Adhesion of the Film

The adhesion of the lacquer films was determined by using a bagel knife. The adhesion of the original and PEO modified films are listed in Table 5. The film with flat grid scratches and no peeling at the edges was rated as Grade 5B. The grade 5B in the table corresponds to the highest adhesion. It can be observed that the adhesion of the film increased from 4B to 5B due to the addition of PEO, which indicated that the presence of PEO considerably ameliorated the adhesion. The hydrogen bond between the PEO and urushiol contributed to the drying process and had a positive effect on the adhesion of the film.

Table 5. Influence of Polyethylene Oxide (PEO) on the Touch-free (TF) Drying Time of the Films

PEO content (%)	0	1	3	5
Adhesion	4B	5B	5B	5B

Effect of Polyethylene Oxide (PEO) on the Chemical Resistance of the Film

During curing, the Chinese lacquer formed a network structure due to cross-linking. Generally, the untreated lacquer film has high acid resistance, but it has low alkali resistance. In this work, the raw lacquer film and PEO modified films were immersed in a 10% HCl solution, 10% NaOH, and 10% NaCl solutions for 14 d under ambient conditions, respectively. Then the film was removed from the solution to observe the surface of the film. The untreated lacquer film and PEO modified film showed good resistance in 10% HCl and 10% NaCl solutions, as no wrinkling, discoloration, or peeling occurred. However, the untreated film showed obvious peeling after being immersed in the 10% NaOH solution. However, only slight bubbling was observed on the PEO modified lacquer films. Therefore, the presence of PEO had a positive effect on the alkali resistance of the lacquer film. This could be due to the PEO molecules forming hydrogen bonds with urushiol to form a condensed structure, which improved the alkali resistance of the lacquer film.

Table 6. Influence of Polyethylene Oxide (PEO) on the Acid, Alkali, and Salt Resistance of the Films

PEO Content (%)	0	1	3	5
10% HCl	no change	no change	no change	no change
10% NaOH	obvious peel	few bubbles	few bubbles	few bubbles
10% NaCl	no change	no change	no change	no change

CONCLUSIONS

1. When the poly(ethyleneoxide) (PEO) concentration is higher than 1%, the modified lacquer is not suitable for making the film, due to the agglomeration of PEO. Therefore, a 0.6% PEO solution was employed to make the uniform film.
2. If the ratio of PEO to lacquer was greater than 5%, the film was uneven because of the high viscosity. Thus, a PEO to lacquer ratio of 1%, 3%, and 5% were set to make the films and their properties were systematically investigated. The results showed when the PEO to lacquer ratio was 3%, the film exhibited the best comprehensive performance.
3. The film was reddish brown in color and the touch-free drying time was 270 min. The gloss of the modified film was increased to 81.6, and the flexibility increased from 15 mm to 1 mm. The alkaline resistance, hardness, and adhesion were also improved. This was attributed to the formation of hydrogen bonds between the PEO and urushiol.
4. The flexibility was significantly increased from 15 to 1 mm, and the film could be double folded without cracking. This demonstrates that the prepared lacquer film had good flexibility. It is expected to be applied to a flexible substrate for the real-time monitoring sensor.

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REFERENCES CITED

Ali, N., Chipara, D., Lozano, K., Hinthorne, J., and Chipara, M. (2017). "Polyethylene oxide-fullerene nanocomposites," *Applied Surface Science* 421(Part A), 220-227. DOI: 10.1016/j.apsusc.2016.11.166

Chang, L., Zhou, Y., Ning, Y., and Zou, J. (2020). "Toughening effect of physically blended polyethylene oxide on polyglycolic acid," *Journal of Polymers and the Environment* 28, 2125-2136. DOI: 10.1007/s10924-020-01752-5

Deng, Y., Chen, J., Zhang, X., Wei, F., Zhang, J., Lin, J., and Xu. Y. (2019). "Preparation of water-dispersible corrosion inhibitors for composite lacquer coatings with excellent properties," *Progress in Organic Coatings* 127, 276-285. DOI: 10.1016/j.porgcoat.2018.10.030

Gao, R., Wang, L., and Lin, Q. (2019). "Effect of hexamethylenetetramine on the property of Chinese lacquer film," *Progress in Organic Coatings* 133, 169-173. DOI: 10.1016/j.porgcoat.2019.04.031

GB 1727-1979 (1979). "General preparation of paint film," Standardization Administration of China, Beijing, China.

GB/T 1731-1993 (1993). “Determination of flexibility of films,” Standardization Administration of China, Beijing, China.

Kumanotani, J. (1995). “Urushi (oriental lacquer) - A natural aesthetic durable and future-promising coating,” *Progress in Organic Coating* 26(2-4), 163-195. DOI: 10.1016/0300-9440(95)00559-5

Lee, J., Kim, M., and Kim, M. (2015). “Characterization of traditional Korean lacquers using surface analytical techniques,” *Surface and Interface Analysis* 47(13), 1180-1186. DOI: 10.1002/sia.5876

Lu, R., Harigaya, S., Ishimura, T., Nagase, K., and Miyakoshi, T. (2004). “Development of a fast drying lacquer based on raw lacquer sap,” *Progress in Organic Coatings* 51(3), 238-243. DOI: 10.1016/j.porgcoat.2004.08.006

Lu, R., Yoshida, T., and Miyakoshi, T. (2013). “Oriental lacquer: A natural polymer,” *Polymer Reviews* 53(2), 153-191. DOI: 10.1080/15583724.2013.776585

Migliardo, F., Magazù, S., and Caccamo, M. T. (2013). “Infrared, Raman and INS studies of poly-ethylene oxide oligomers,” *Journal of Molecular Structure* 1048, 261-266. DOI: 10.1016/j.molstruc.2013.05.060

Nijenhuis, A. J., Colstee, E., Grijpma, D. W., and Pennings, A. J. (1996). “High molecular weight poly(l-lactide) and poly(ethylene oxide) blends: Thermal characterization and physical properties,” *Polymer* 37(26), 5849-5857. DOI: 10.1016/S0032-3861(96)00455-7

Nimura, N., and Miyakashi, T. (2006). “Structural study of oriental lacquer films during the hardening process,” *Talanta* 70(1), 146-152. DOI: 10.1016/j.talanta.2005.12.039

Reddy, M. J., Chu, P. P., and Rao, U. V. S. (2006). “Study of multiple interactions in mesoporous composite PEO electrolytes,” *Journal of Power Sources* 158(1), 614-619. DOI: 10.1016/j.jpowsour.2005.10.008

Vogl, O. (2000). “Oriental lacquer, poison ivy, and drying oils”, *Journal of Polymer Science Part A: Polymer Chemistry* 38(24), 4327-4335. DOI: 10.1002/1099-0518(20001215)38:24<4327::aid-pola10>3.0.co;2-3

Wan, C., Xiao, S., Huang, Q., Kuang, C., and Liao, Y. (2016). “Preparation and properties of modified raw lacquer composite coating,” *China Forest Products Industry* 43(3), 24-28.

Xia, J., Lin, J., Xu, Y., and Chen, Q. (2010). “On the UV-induced polymeric behavior of Chinese lacquer,” *ACS Applied Materials & Interfaces* 3(2), 482-489. DOI: 10.1021/am1010578

Xue, H., Zhang, Y., Li, X., Xia, J., and Lin, Q. (2020). “Degradation urushiol coating composition crosslinked by diallyl trisulfide,” *Journal of Polymers and the Environment* 28, 3192-3200. DOI: 10.1007/s10924-020-01845-1

Yang, J., Deng, J., Zhang, Q., Shen, Q., Li, D., and Li, D. (2015). “Lacquer sap with reactive maleic hemiester surfactant-modified phase interface and its properties,” *Progress in Organic Coatings* 87, 138-145. DOI: 10.1016/j.porgcoat.2015.05.027

Yang, J., Deng, J., Zhu, J., Liu, W., Zhou, M., and Li, D. (2016). “Thermal polymerization of lacquer sap and its effects on the properties of lacquer film,” *Progress in Organics Coatings* 94, 41-48. DOI: 10.1016/j.porgcoat.2016.01.021

Yang, J., Shen, F., Deng, J., Cai, J., Zhang, Q., Liu, W. (2018). “Laccase-catalyzed polymerization drying of Chinese lacquer sap with TiO_2 nanoparticles,” *Journal of Applied Polymer Science* 135(7). DOI: 10.1002/app.45865

Zhang, F. (2012). “Molecular mechanism of lacquer film forming,” *Journal of Chinese Lacquer* 31(1), 13-20. DOI: 10.19334/j.cnki.issn.1000-7067.2012.01.004

Zhang, W., Li, L., Yao, S., and Zheng, G. (2007). “Corrosion protection properties of lacquer coatings on steel modified by carbon black nanoparticles in NaCl solution,” *Corrosion Science* 49(2), 654-661. DOI: 10.1016/j.corsci.2006.06.017

Zhang, D., Xia, J., Xue, H., Zhang, Y., and Lin, Q. (2020). “Improvement on properties of Chinese lacquer by polyamidoamine,” *Polymer Engineering and Science* 60(6), 1177-1185. DOI: 10.1002/pen.25371

Zhou, H., Wang, C., Ye, J., and Chen, H. (2014). “Preparation and properties of tannin modified lacquer composites,” *Journal of Chinese Lacquer* 33(3), 27-30.

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