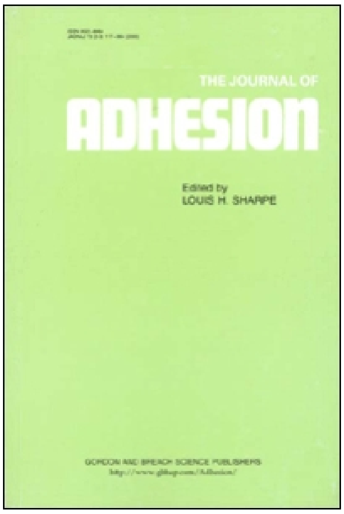

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Preparation and Characterization of Demethylated Lignin-Polyethylenimine Adhesives

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Petrochemical-based adhesives such as urea-formaldehyde and phenol-formaldehyde resins are predominant wood adhesives. In this study, a new wood adhesive from lignin was developed and characterized. The new adhesive consisted of demethylated kraft lignin (DKL), a byproduct in the production of dimethyl sulfoxide from kraft lignin, and a polyethylenimine (PEI). Lap-shear specimens bonded with this new DKL-PEI adhesive system had very high shear strength and were very water-resistant. The effects of the preparation time, the curing conditions, the total solids content of the adhesive, the DKL/PEI weight ratio and the molecular weight of PEI on the shear strength and water-resistance of the resulting lap-shear specimens were studied in detail. Investigation on the curing chemistry of this new adhesive revealed that phenolic hydroxyl groups were oxidized to form quinones that further reacted with PEI. It was proposed that the curing mechanisms of this DKL-PEI adhesive were similar to the quinone-tanning processes in nature.

Keywords: Adhesives; Demethylation; Kraft lignin; Marine adhesive; Mussel protein; Polyethylenimine; Wood composites

INTRODUCTION

The formaldehyde-based wood adhesives such as urea-formaldehyde (UF) and phenol-formaldehyde (PF) resins are major wood adhesives used in the production of wood composites in North America. They account for about 92% of annual adhesive consumption of North America [1]. There are two issues associated with the presently used

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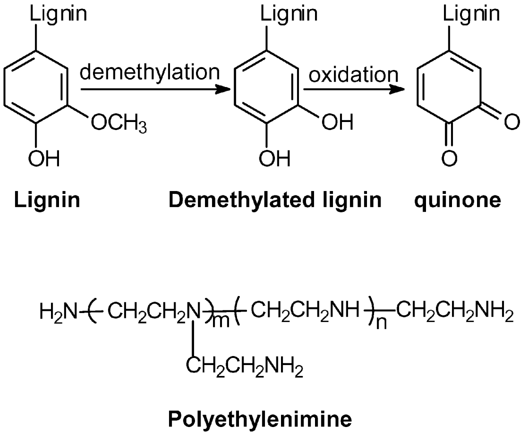
formaldehyde-based wood adhesives. The first issue is related to formaldehyde, one of the key ingredients in currently used wood adhesives. It has been well documented that formaldehyde is emitted from the production and use of wood composites bonded with UF resins [2–5]. That formaldehyde causes skin irritation and respiratory discomfort has been known for a long time [6]. Through extensive studies on the toxicity of formaldehyde, the International Agency for Research on Cancer has recently re-classified formaldehyde as a human carcinogen [7]. The second issue is that phenol and formaldehyde are derived from non-renewable petrochemicals whose prices may keep increasing. The increasing concerns about the emissive formaldehyde on human health and sustainable supply of the raw materials for wood adhesives have generated a need for the development of formaldehyde-free wood adhesives from renewable resources.

To withstand the impact of turbulent tides and waves, mussels stick to rock and other substance in seawater through an adhesive protein, commonly called marine adhesive protein (MAP). MAP is an excellent example of formaldehyde-free and renewable adhesives. Extensive studies reveal that the MAP contains two key functional groups: an amino group and a catechol group. Various reactions between the amino group and the catechol group solidify and crosslink the MAP, thus converting the MAP into a very strong and very water-resistant adhesive [8,9]. Our previous studies reveal that a combination of condensed tannins and polyethylenimine (PEI) and a combination of poly (*N*-acryloyldopamine) and PEI can be used as a strong and



SCHEME 1 Representative structures of lignin, demethylated lignin, quinone, and polyethylenimine.

water-resistant wood adhesive, respectively [10,11]. Both condensed tannins and poly (*N*-acryloyldopamine) contain catechol groups. Somehow, condensed tannins are not produced in the U.S. and are thus not readily available. Poly(*N*-acryloyldopamine) is a synthetic polymer, and is expensive and not readily available. Demethylated kraft lignin (DKL), a byproduct in the production of dimethyl sulfoxide from the kraft lignin, also contains a catechol group and is abundant and readily available (Scheme 1) [12]. In this paper, we investigated whether a combination of DKL and PEI was able to serve as a formaldehyde-free wood adhesive.

EXPERIMENTAL

Materials

DKL was donated by Gaylord Chemical Corporation (Bogalusa, LA, USA). Polyethylenimines (PEIs) with molecular weights (M_w) of 10,000 and 70,000 (30 wt% aqueous solution) were purchased from Polysciences Inc (Warrington, PA, USA). PEI with the molecular weight (M_w) of 750,000 (50 wt% aqueous solution) was purchased from Sigma-Aldrich (Milwaukee, WI, USA). All PEIs were used as received. Phenol-formaldehyde (PF) resin for production of laminated veneer lumber was provided by Georgia Pacific Resins, Inc. at Albany, Oregon, USA. Peeled maple veneer was donated by States Industries (Eugene, Oregon, USA). The veneer was conditioned at 20°C and 65% relative humidity for a minimum of one week.

Preparation of DKL-PEI Wood Adhesives

DKL (10.0 g) was suspended in water (40 mL). The pH value of the mixture was adjusted to and maintained at 10 by adding 6N NaOH solution while the mixture was stirred. After the DKL completely dissolved, the solution was freeze-dried for further use. The freeze-dried lignin was called alkaline DKL.

The DKL-PEI lignin was prepared by stirring a mixture of PEI (1.0 g of 50 wt% PEI aqueous solution, *i.e.*, 0.5 g dry PEI, $M_w = 750{,}000$), the alkaline DKL (0.5 g) and water (3.5 mL) for 10 min.

Preparation of Lap-Shear Specimens

Maple veneer with a thickness of 0.6 mm was cut into small boards with the dimension of 7.5 cm × 12 cm. A DKL-PEI wood adhesive (0.25 g) was applied to the area of 1.0 × 12 cm on one side of a veneer board. The spread rate of adhesive solids on the bond area was 4.16 mg/cm^2. Two adhesive coated veneer boards were lapped together and then hot-pressed under conditions specified in each figure caption to form lap-shear specimens. Each lap-shear specimen was cut into 6 test specimens. Each test specimen had a bond area of 2 × 1.0 cm. The drawing of making lap-shear specimens and test specimens can be found in our previous publication [13].

Evaluation of Shear Strength of Lap-Shear Specimens Bonded with DKL-PEI Adhesives

The lap-shear strength of the lap-shear specimens bonded with DKL-PEI adhesives was evaluated on an Instron TTBML universal testing machine (Instron, Canton, MA, USA) at 1 mm/min of the crosshead speed. Grain direction of veneer was parallel to the shear direction. The maximum force at breakage of test specimens was recorded to calculate the shear strength.

Evaluation of Water Resistance of Lap-Shear Specimens

The water resistance of the lap-shear specimens bonded with DKL-PEI adhesives was evaluated in accordance with the U.S. Voluntary Product Standard PS1-95 for Construction and Industrial Plywood (published by the U.S. Department of Commerce through APA-The Engineered Wood Association, Tacoma, WA, USA). The boiling water test (BWT) was performed as follows: 16 test specimens were boiled in water for 4 h, dried for 20 h at 63 ± 3°C, boiled in water again for 4 h and then cooled down with tap water. Eight test specimens were evaluated for shear strength while they were wet. The shear strength evaluated in this manner was called BWT/wet strength. Eight test specimens were further dried at room temperature in a fume hood for 24 h and then evaluated for shear strength. The shear strength evaluated in this manner was called BWT/dry strength.

Characterization of DKL-PEI Adhesives with Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transform Infrared (FTIR) spectra of DKL and a DKL-PEI adhesive (the weight ratio of DKL to PEI was 1:1, M_w of PEI was 750,000) were acquired on a Thermo Nicolet Nexus^{TM} 470 FTIR spectrometer (Thermo Electron Corp., Waltham, MA, USA) with a

Golden Gate Heatable Diamond ATR (attenuated total reflectance) accessory at 20°C and 120°C for 3 min. DKL and PEI were dried under high vacuum for 24 h and ground to fine powder before they were used for acquiring FTIR spectra. The number of scans for each sample was 32.

Statistical Analysis of Results

All data were analyzed with a standard two-sample t-test using S-plus statistical software (Insightful Corp., Seattle, WA, USA). All comparisons in the Results and Discussion section were based on a 95% confidence level.

RESULTS AND DISCUSSION

Effects of Mixing Time on Shear Strength of Lap-Shear Specimens Bonded with DKL-PEI Adhesives

The DKL-PEI adhesives were prepared by mixing an aqueous solution of DKL with an aqueous solution of PEI at pH 10. The mixing time at the range of 2 min to 2 h had little effect on the shear strength of

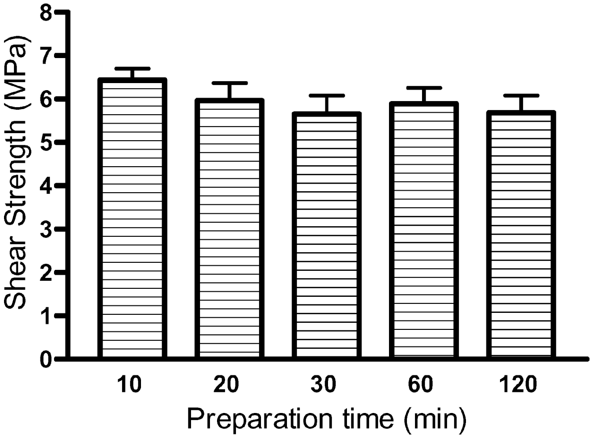


FIGURE 1 Effects of mixing time on shear strength and water resistance of lap-shear specimens bonded with DKL-PEI adhesives. M_w of PEI was 750,000; hot-press conditions: 10 kg/cm^2, 120°C and 5 min; the DKL/PEI weight ratio was 1:1. Data are the mean of six replicates and the error bars represent one standard error of the mean.

lap-shear specimens bonded with DKL-PEI adhesives (Figure 1). This implies that the DKL-PEI adhesives are easy to prepare.

Effects of Total Solids Content on Shear Strength and Water Resistance of Lap-Shear Specimens Bonded with DKL-PEI Adhesives

The viscosity of the DKL-PEI adhesives increased with increasing total solids content. When the total solids content was higher than 25 wt%, the DKL-PEI was too viscous to be uniformly applied to veneer. When the total solids content was increased from 14 wt% to 17 wt%, all three shear strengths (dry, BWT/dry, and BWT/wet) did not significantly increase (Figure 2). When the total solids content was further increased from 17 wt% to 20 wt%, the dry shear strength significantly increased while BWT/dry and BWT/wet shear strengths remained statistically the same (Figure 2). All three shear strengths did not significantly change when the total solids content was increased from 20 wt% to 25 wt%. The DKL-PEI adhesives at 20 wt% total solids content were readily applied to veneer- and, therefore, were used in further experiments.

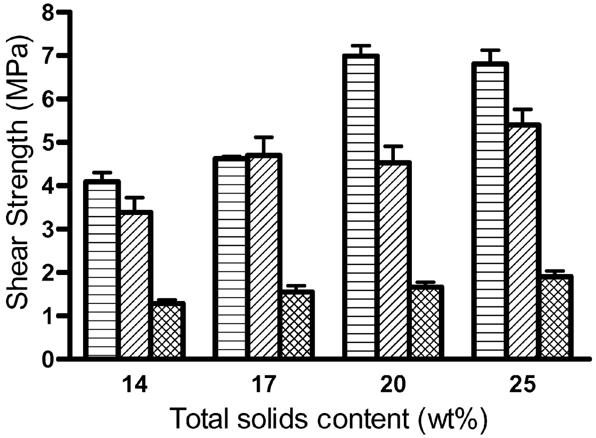


FIGURE 2 Effects of total solids content on shear strength and water resistance of lap-shear specimens bonded with DKL-PEI adhesives. M_w of PEI was 750,000; hot-press conditions: 10 kg/cm^2, 120°C and 5 min; the DKL/PEI weight ratio was 1:1. Dry (▤); BWT/dry (▨); BWT/wet (▩). Data are the mean of six replicates and the error bars represent one standard error of the mean.

Effects of Hot-Press Time on Shear Strength and Water Resistance of Lap-Shear Specimens Bonded with DKL-PEI Adhesives

When the hot-press time was increased from 3 min to 5 min, the dry shear strength increased significantly while the BWT/dry and BWT/wet shear strengths basically remained the same (Figure 3). When the hot-press time was further increased from 5 min to 7 min, the shear strengths did not change significantly. These results implied that the DKL-PEI adhesives were not fully cured after 3 min hot-press. Therefore, the hot-press time of 5 min was used for further investigation.

Effects of Hot-Press Temperature on Shear Strength and Water Resistance of Lap-Shear Specimens Bonded with DKL-PEI Adhesives

When the hot-press temperature was increased from 100°C to 120°C, the BWT/dry shear strength greatly increased, whereas both dry and BWT/wet shear strengths only increased slightly (Figure 4). When the hot-press temperature was increased from 120°C to 140°C, all three shear strengths (dry, BWT/dry, and BWT/wet) did not

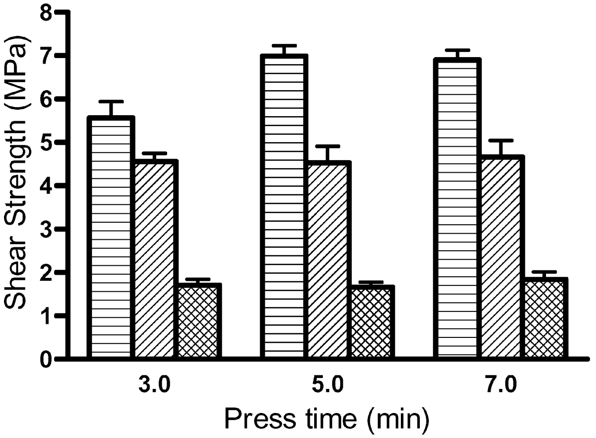


FIGURE 3 Effects of the hot-press time on shear strength and water resistance of lap-shear specimens bonded with DKL-PEI adhesives. M_w of PEI was 750,000; hot-press conditions: 10 kg/cm^2 and 120°C; the DKL/PEI weight ratio was 1:1. Dry (▤); BWT/dry (▨); BWT/wet (▩). Data are the mean of six replicates and the error bars represent one standard error of the mean.

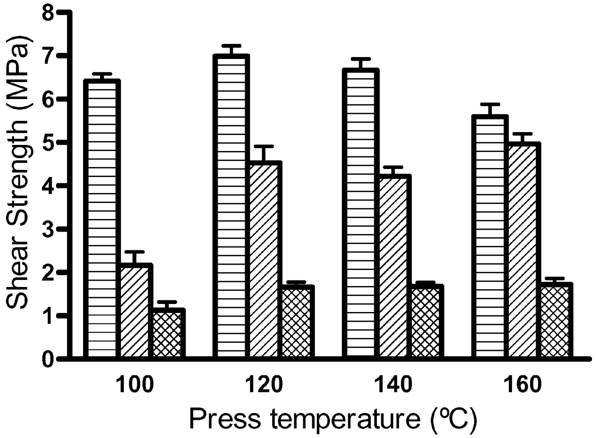


FIGURE 4 Effects of hot-press temperature on shear strength and water resistance of lap-shear specimens bonded with DKL-PEI adhesives. M_w of PEI was 750,000; the DKL/PEI weight ratio was 1:1; hot-press conditions: 10 kg/cm^2 and 5 min. Dry (▤); BWT/dry (▨); BWT/wet (▩). Data are the mean of six replicates and the error bars represent one standard deviation.

change significantly (Figure 4). Further increasing the hot-press temperature from 140°C to 160°C significantly decreased the dry shear strength, but did not significantly change both BWT/dry and BWT/wet strengths. These results indicated that 120°C was the optimal hot-press temperature for curing DKL-PEI adhesives.

Effects of DKL/PEI Weight Ratios on Shear Strengths and Water Resistance of Lap-Shear Specimens Bonded with DKL-PEI Adhesives

The lap-shear specimens bonded with DKL alone, *i.e.*, DKL/PEI weight ratio = 1:0, had very low dry shear strength and delaminated during the BWT (Figure 5). When the weight ratio of DKL to PEI in DKL-PEI adhesives was 4:1, the dry shear strength of the resulting lap-shear specimens was significantly higher than that with DKL alone. The resulting lap-shear specimens did not delaminate during the BWT. All three shear strengths (dry, BWT/dry, and BWT/wet) significantly increased when the DKL/PEI weight ratio was changed from 4:1 to 2:1. When the DKL/PEI weight ratio was changed from 2:1 to 1:1, the dry shear strength of the resulting lap-shear specimens further increased, but their BWT/dry and BWT/wet shear strengths did not change significantly (Figure 5). When the DKL/PEI weight

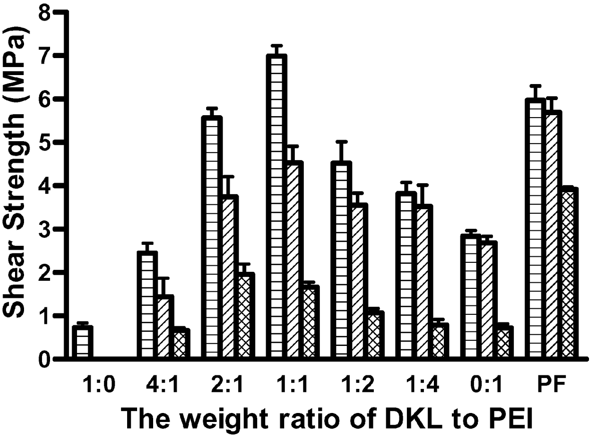


FIGURE 5 Effects of the DKL/PEI weight ratio on shear strength and water resistance of lap-shear specimens bonded with DKL-PEI. M_w of PEI was 750,000; hot-press conditions: 10 kg/cm^2, 120°C and 5 min. Dry (▤); BWT/dry dry (▨); BWT/wet (▩). PF represents a commercial phenol-formaldehyde resin. Data are the mean of six replicates and the error bars represent one standard deviation.

ratio was changed from 1:1 to 1:2, all three shear strengths significantly decreased. When the DKL/PEI weight ratio was changed from 1:2 to 1:4, the shear strengths were statistically unchanged. The optimal DKL/PEI weight ratio of DKL-PEI adhesives in terms of enhancing the shear strength and water resistance of the resulting lap-shear specimens appears to be 1:1. At the 1:1 DKL/PEI weight ratio, the DKL-PEI had higher dry shear strength than PF, but had lower BWT/dry and BWT/wet strengths than PF (Figure 5).

Effects of Molecular Weight (M_w) of PEIs on Shear Strength and Water Resistance of Lap-Shear Specimens Bonded with DKL-PEI Adhesives

PEIs with three different molecular weights (M_w = 10,000, 70,000 and 750,000) were investigated. The results are shown in Figure 6. When the M_w of PEI was 10,000, the lap-shear specimens bonded with DKL-PEI adhesives had moderate dry shear strength and water resistance. The resulting lap-shear specimens did not delaminate during the BWT. When the M_w of PEI was increased from 10,000 to 70,000, all three shear strengths (dry, BWT/dry, and BWT/wet) significantly increased. However, further increase in the M_w of PEI from 70,000

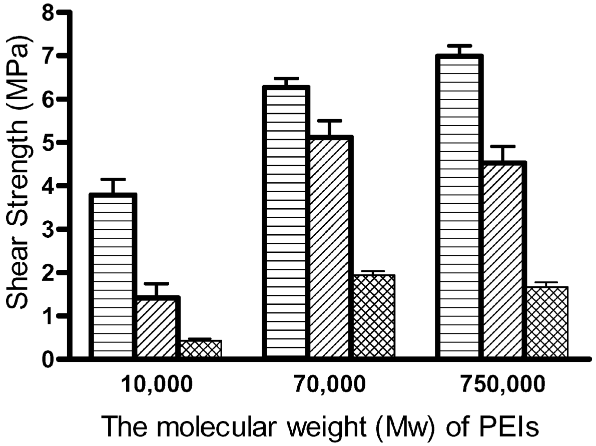


FIGURE 6 Effects of the molecular weight (M_w) of PEI on shear strength and water resistance of lap-shear specimens bonded with DKL-PEI adhesives. The DKL/PEI weight ratio was 1:1; hot-press conditions: 10 kg/cm^2, 120°C, and 5 min. Dry (▤); BWT/dry (▨); BWT/wet (▩). Data are the mean of six replicates and the error bars represent one standard deviation.

to 750,000 did not result in statistically significant changes of the shear strengths.

The Investigation of Curing Mechanism of DKL-PEI Adhesives

The FTIR spectrum of "DKL at 20°C" showed that the absorbance of C=O groups at 1702 cm^{-1} was weak (Figure 7), which implied that the C=O content of DKL at room temperature was low. However, the peak intensity at 1702 cm^{-1} significantly increased when the DKL was heated at 120°C for 3 min (see "DKL at 120°C" in Figure 7). It implied that the heating of the DKL at 120°C significantly increased the C=O content (Figure 7). The increased C=O groups are speculated to be mainly from the oxidation of phenolic hydroxyl groups (Scheme 1).

The FTIR spectra of the DKL-PEI mixtures (the DKL/PEI weight ratio was 1:1) are shown in Figure 8. When DKL and PEI were mixed at 20°C, the shoulder of C=O groups at 1702 cm^{-1} could still be seen. After the DKL-PEI mixture was heated at 120°C for 3 min, the shoulder disappeared, which indicated that the C=O groups in DKL disappeared.

Based on these results, we propose that the curing mechanisms of DKL-PEI adhesives are similar to the quinone-tanning processes in

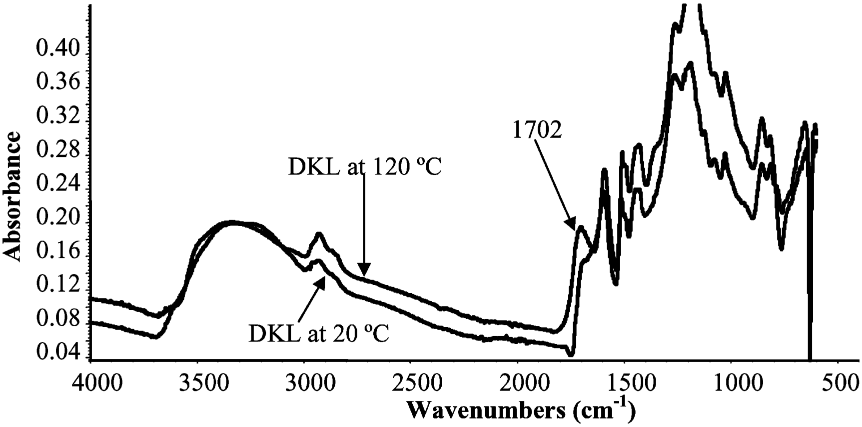


FIGURE 7 FTIR spectra of DKL samples. "DKL at 20°C" is the FTIR spectrum acquired at 20°C. "DKL at 120°C" is the FTIR spectrum acquired after a DKL sample was heated at 120°C for 3 min.

nature [14]. The possible reactions between DKL and PEI are proposed to be very similar to those between condensed tannins and PEI, and the possible reactions between condensed tannins and PEI

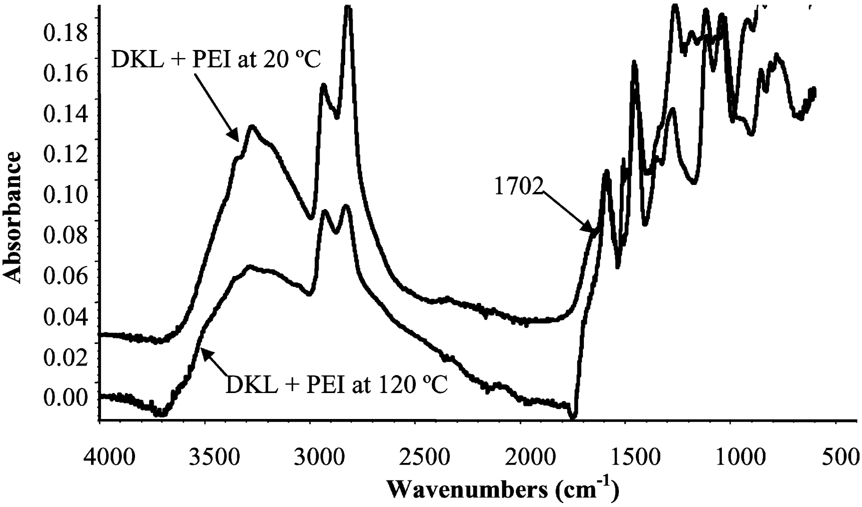


FIGURE 8 FTIR spectra of DKL-PEI samples. The DKL/PEI weight ratio was 1:1; M_w of PEI was 750,000; "DKL + PEI at 20°C" is the FTIR spectrum acquired at 20°C. "DKL + PEI at 120°C" is the FTIR spectrum acquired after a mixture of DKL and PEI was heated at 120°C for 3 min.

have been described in detail in our previous publication [10]. Many reactions can occur between DKL and PEI during hot press. For example, phenolic hydroxyl groups in DKL can be oxidize to form quinones that can further react with amino groups in PEI to form Schiff bases and Michael addition products (Scheme 1). The net results of these curing reactions during the hot-press were to form a water-insoluble, highly cross-linked polymer network. Because lignin in wood also contains phenolic hydroxyl groups that can be oxidized to quinones during the hot-press, the formation of covalent bonds between wood and the DKL-PEI adhesive cannot be ruled out.

The DKL-PEI adhesive had dark-brown color once cured. There was no odor during the preparation, cure and use of this adhesive.

CONCLUSION

The DKL-PEI adhesives were readily prepared and used to bond maple veneer. The 120°C and 5 min appeared to the optimum curing conditions for making the lap-shear specimens. The 1:1 DKL/PEI weight ratio was optimum in terms of enhancing the strength and water resistance of the resulting lap-shear specimens. The molecular weight of PEIs had little effect on the strength and water-resistance of the resulting lap-shear specimens when they were in the range of 70,000 to 750,000. The increased C=O content was observed when DKL was heated at 120°C for 3 min, and the disappearance of the C=O peak was also observed when a mixture of DKL and PEI was heated at 120°C for 3 min.

ACKNOWLEDGEMENT

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REFERENCES

[1] Sellers, T., Jr., *Forest Prod. J.* **51**, 12–22 (2001).

[2] Meyer, B. and Hermans, K., in *ACS Symposium Series 316–Formaldehyde Release From Wood Products*, B. Meyer, B. A. K. Andrews, and R. M. Reinhardt (Eds). (American Chemical Society, Washington, DC, 1986), pp. 1–16.

[3] Marutzky, R., in *Wood Adhesives–Chemistry and Technology*, A. Pizzi (Ed). (Marcel Dekker, Inc., New York, 1989), pp. 307–387.

[4] Henderson, J. T., *TAPPI J.* **62**, 9396 (1979).

[5] Baumann, M. G. D., Lorenz, L. F., Batterman, S. A., and Zhang, G.-Z., *Forest. Prod. J.* **50**, 75–82 (2000).

[6] Liteplo, R. G. and Meek, M. E., *J. Toxicol. Environ. Health, Part B: Crit. Rev.* **6**, 85–114 (2003).

[7] *International Agency for Research on Cancer* **Press release # 153** (2004).

[8] Rzepecki, L. M. and Waite, J. H. in *Bioorganic Marine Chemistry*, P. J. Scheuer (Ed). (Springer-Verlag, Berlin, 1991), pp. 119–148.

[9] Waite, J. H., *Comp. Biochem. Physiol. [B]* **97**, 19–29 (1990).

[10] Li, K., Geng, X., Simonsen, J., and Karchesy, J. J., *Int. J. Adhesion Adhes.* **24**, 327–333 (2004).

[11] Zhang, C., Li, K., and Simonsen, J., *J. Appl. Polym. Sci.* **89**, 1078–1084 (2003).

[12] Glasser, W. G., *Forest Prod. J.* **31**, 24–29 (1981).

[13] Li, K. and Geng, X., *J. Adhesion Sci. Technol.* **18**, 427–439 (2004).

[14] Waite, J. H., *Methods Enzymol.* **258**, 1–20 (1995).