

Combination of lignin polyol-tannin adhesives and polyethylenimine for the preparation of green water-resistant adhesives

Abbas Hasan Faris,^{1,2} Afidah Abdul Rahim,¹ Mohamad Nasir Mohamad Ibrahim,¹
Adel Mustafa Alkurdi,³ Irfan Shah¹

¹School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

²Materials Research Directorate, Ministry of Sciences and Technology, Baghdad, Iraq

³Ministry of Foreign Affairs, Baghdad, Iraq

Correspondence to: A. H. Faris (E-mail: abbas_hf@yahoo.com)

ABSTRACT: In this study, a green adhesive from renewable lignin and tannin was developed with polyethylenimine (PEI) with a method to improve the water resistance of the lignin/tannin adhesive. Lignin polyols were prepared through the liquefaction of oil-palm empty fruit bunches. The characteristics of the adhesive samples were compared with those of a commercial phenol-formaldehyde resin. Three plywood specimens bonded with the new adhesive showed a very high tensile strength (63.04 MPa) and were very water resistant. The effect of the solid content of the adhesives on the tensile strength and gel time and various weight ratios of PEI on the tensile strength and water resistance of the plywood specimens were evaluated. Thermal stability tests revealed that the lignin polyol-tannin/PEI adhesives had a high heat resistance (360 °C). © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43437.

KEYWORDS: adhesives; applications; biomaterials

Received 10 May 2015; accepted 15 January 2016

DOI: 10.1002/app.43437

INTRODUCTION

Wood adhesives have a very important function in the industrial production of wood-based panels. Synthetic adhesives based on formaldehyde, such as urea-formaldehyde, phenol-formaldehyde (PF), and melamine-formaldehyde resins, are usually used for wood-composite production. Synthetic resins derived from fossil fuels will be exhausted, and in addition to impacting CO₂ emission, these materials are nonrenewable and toxic. Recent health and environmental concerns include the emission of carcinogenic volatile formaldehyde compounds¹ and the continuous fluctuation of the price of oil and its derivatives. Consequently, several studies have been conducted to develop renewable and inexhaustible natural resources for the reduction or replacement of synthetic adhesives for wood panels; this decreases the emission of formaldehyde.²⁻⁶ Renewable natural resources are considered very promising alternatives for synthetic resins;⁷⁻⁹ they provide appropriate solutions to overcome the drawbacks, such as low moisture resistance.¹⁰ Lignin and tannin are considered renewable natural resources, and they are of particular interest in phenolic resins because of their chemical structure. The latter is similar to the phenol group with comparable interactions between phenol and formaldehyde in the presence of either basic or acidic catalysts. The main features of this type are its ease of handling and its environmentally friendly properties; however,

they do not have the fundamental required bonding strength and water resistance.^{11,12} As reported earlier, marine adhesive protein (MAP), which is secreted by marine mussels, is a good example of a renewable resource and formaldehyde-free adhesive.^{13,14} MAP has the ability to form strong linkages on wet surfaces and, thus, could be used as a strong, water-resistant wood adhesive,^{13,14} although it is costly and not readily available. MAP usually contains two functional groups (catechol and amino groups). The different reactions between catechol and the amino group lead to the crosslinking and solidification of MAP; this, thereby, converts MAP to a strong and water-resistant adhesive.^{13,15} Condensed tannins and lignin are one of the few natural polymers containing a catechol moiety.^{16,17} Previous studies have shown the possibility of using a combination of condensed tannins or lignin and polyethylenimine (PEI; Figure 1) to synthesize wood adhesives.¹⁸ This adhesive exhibited a high shear strength and significant water resistance.¹⁷⁻¹⁹ In this study, lignin polyols had a number of activated free aromatic ring positions capable of reacting with glyoxal as a curing reagent and formed a crosslinked reaction in the same way as in the PF condensation reaction. In addition, water-resistant wood adhesive systems consisting of a glyoxalated lignin polyol/tannin and PEI were evaluated for plywood production, and the different effects were compared to plywoods produced with commercial phenol-formaldehyde (CPF) resins.

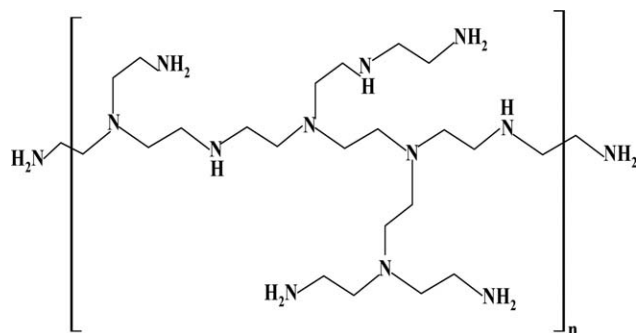


Figure 1. Representative structure of PEI.

EXPERIMENTAL

Materials

Oil-palm empty fruit bunch (OPEFB) long fibers were supplied by Sabutek Sdn. Bhd. (Malaysia) in 2014. Tannin powder form was supplied by Xian Aladdin Bio-Tech Co., Ltd. (China). Polyethelenimine (weight-average molecular weight \approx 25,000, number-average molecular weight \approx 10,000) was purchased from Aldrich (Germany). Poly(ethylene glycol) with a molecular weight of 400 (PEG 400) was obtained from R & M Chemicals (Essex, United Kingdom), and glycerol, which was supplied by HmbG Chemicals, was used as the liquefaction reagent. Dioxane was supplied by HmbG Chemicals, and sulfuric acid was supplied by QREC (Asia), Malaysia. Hexamethylenetetramine (hexamine) was purchased from Acros Organics. Sodium hydroxide (NaOH) was obtained from QREC (Asia), Malaysia.

Preparation of Lignin Polyols through the Liquefaction of OPEFB

Air-dried OPEFB was ground and sieved (20–60 wire mesh) with a Wiley mill. The OPEFB was dried overnight at 105 °C in a laboratory oven before the liquefaction process. The mass ratio between the dried OPEFB and the solvent was 1:10. The 3 wt % of sulfuric acid (on the basis of the solvent content) was added to the mixture. An amount of 30 g of dried OPEFB was then placed in a round-bottom flask equipped with a mechanical stirrer, condenser, and thermocouple. An amount of 9 g of 95% w/v aqueous sulfuric acid was added as catalyst together with 300 g of PEG 400 and glycerol. The flask was immersed in a silicone oil bath preheated at 160 °C for 4 h, after which it was quenched to room temperature in an ice–water bath. Then, 600 mL of 80% w/v dioxane aqueous solution was added to the reaction mixture. The resulting mixture was filtered through a filter paper to remove the insoluble parts of the wood. The mixture of dioxane and water was evaporated under reduced pressure after filtration. The liquefied wood was obtained and contained PEG 400 and glycerol. The residual mixture was transferred to a three-necked flask equipped with a mechanical stirrer, a condenser, and a thermocouple. The flask was heated at 140 °C for 2.5 h. The reaction flask was cooled to room temperature, and then, the solution was mixed with 2 L of distilled water with continuous stirring for 30 min. The viscous lignin polyols were then collected by centrifugation at 3500 rpm for 15 min and then freeze-dried.

Preparation of the Glyoxalated Lignin Polyol Resin

The glyoxalation of lignin polyols was adapted from El Mansouri *et al.*²⁰ Lignin polyols (29.5 g) were added to 38.4 mL of water, whereas the NaOH solution (30%) was added periodically to maintain the pH of the solution between 12 and 12.5 for a better dissolution of the lignin polyols, which was also facilitated by vigorous stirring with an overhead stirrer. The mixture was placed in a 250-mL, flat-bottomed flask equipped with a condenser, a thermometer, and a magnetic stirring bar and heated to 60 °C. A quantity of 17.5 g of glyoxal (40 wt % in water) was added, and the lignin polyol solution was maintained at pH 12–12.5 with a magnetic stirrer on a hot plate for 8 h.

Preparation of the Tannin Adhesives

An aqueous tannin solution was prepared at a 45% w/v concentration, and its pH was adjusted to 10 with a 33% w/v NaOH solution. A concentration of 6% w/v hexamine (on the basis of tannin) was added to form a 33% w/v solution as a hardener.

Blending Adhesive Lignin Polyols and Tannin

The adhesive (final resin) was formulated by the blending of a tannin solution with glyoxalated lignin polyols [tannin/glyoxalated lignin polyol (TGLP)] in a 60:40 w/w solid proportion.

Modification of the Lignin Polyol/Tannin Adhesives by PEI

Modification of the lignin polyol/tannin adhesive was carried out through mixing with different percentages of PEI (10, 12, 14, 16, 18, and 20%) after we dissolved it in very small amounts of water with soft heating (40 °C). The blending of lignin polyol/tannin adhesive with PEI was done for 30 min at room temperature with stirring.

Preparation of Plywood Samples

A three-ply veneer with each veneer having dimensions of 150 × 150 × 2 mm³ was manufactured with the spread level for a single glue line of 250 g/m². Then, it was pressed with a cold-press machine under a 2500-psi pressure; it was then pressed by a hot press operating at 140 °C with a 2500-psi pressure. The total pressing time was maintained at 7 min both in the cold and hot presses. When all of the laminated veneer lumber panels were produced, the panels were cut off with a band saw machine to a size of 135 ± 0.2 mm long (in the direction of the face grain) and 25 ± 0.1 mm wide according to a British standard (part 8, 1985).²¹

Gel Time

Gelation is defined as the point at which the resin ceases to be a viscous liquid and becomes a soft, elastic, rubbery solid.²² An amount of 5 g of each mixture was put into a glass test tube and then placed in a water bath at 100 °C. A wooden rod was manually moved upward and downward rapidly. A stopwatch was used to calculate the time of gelation.

Mechanical Properties

We measured the tensile strength of each sample with an Instron universal machine (model 4301) by controlling the rate of the separation of the straining heads, which was fixed at 5 mm/min. The distance between the clamps was 50 mm with the sample being mounted at the center. These tests were performed for dry, tap-water-soaked (for 24 h), and boiling-water-soaked

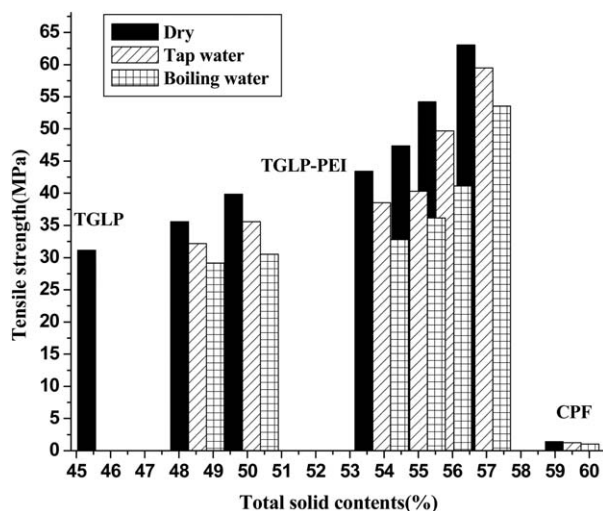


Figure 2. Effect of the total solid content of the TGLP–PEI adhesives on the tensile strength (dry, tap-water soaked for 24 h, and boiling-water soaked for 2 h): comparison with TGLP and CPF.

(for 2 h) bonding samples to determine their strength. The water soaking and drying (WSAD) test was implemented according to the following procedure: the test specimens were soaked in tap water at room temperature for 24 h and then dried in a fume hood at room temperature for 24 h, after which their tensile strengths were determined.

For the boiling water test (BWT), specimens were first soaked in boiling water for $2 \text{ h} \pm 15 \text{ min}$; after that, the specimens were dried for 20 h at $60 \pm 3^\circ\text{C}$. After drying, the specimens were soaked again in boiling water for $2 \text{ h} \pm 15 \text{ min}$ and finally placed in tap water until they cooled down; this was followed by the tensile strength measurements. The plywood specimens were air-dried in a fume hood at room temperature for 24 h and their tensile strength was determined. This tensile strength was identified as BWT strength/dry strength. The wood failure of the testing specimens was evaluated by the naked eye from the glue line of the destroyed specimens. Five samples were tested for each condition.

Thermal Stability

The thermal behaviors of the adhesives samples were studied by thermogravimetric analysis with a PerkinElmer TGA 7 thermogravimetric analyzer. About 10 mg of resin was put into a platinum sample pan. Scans were recorded from room temperature to 900°C at a heating rate of $20^\circ\text{C}/\text{min}$ under a nitrogen atmosphere with a flow rate of 20 mL/min. The curves of weight loss [thermogravimetry (TG)] and derivative weight loss [derivative thermogravimetry (DTG)] were plotted.

RESULTS AND DISCUSSION

Effect of the Solid Content of the TGLP–PEI Adhesives on the Tensile Strength

We observed that an increase in the total solid content of the TGLP–PEI adhesives led to an increase in the viscosity. Moreover, when the total solid content in the adhesives reached 55%, the TGLP–PEI adhesives became too viscous.¹⁸ The total solid content increased from 48.54 to 56.92% when the ratio of PEI

was changed from 10 to 20% in the TGLP resin. The tensile strengths (dry, WSAD, and BWT/dry) of wood composites bonded with the adhesives revealed dramatic increases⁸ in its values (63.04, 59.48, and 53.53 MPa), respectively, and a linear relationship among all of the values. The TGLP–PEI adhesives with a total solid content of 56.92% were applied to plywood and used in subsequent experiments.

The production of wood composites does not favor the use of wood adhesives with low solid content because of the higher energy consumption and the comparatively longer time of water evaporation through the hot press. In this study, a significant total solid content of adhesives (56.92%) was obtained during the modification of lignin polyol–tannin resins with PEI. There were substantial differences in the solid contents of the modified (56.92%), unmodified (45.82%), and CPF adhesive (59.50%) under the same experimental conditions. The solid content of the TGLP resin (45.82%) was lower than the solid content of the commercial PF resin (59.50%). However, the solid content of the TGLP–PEI resins was almost comparable to that of the commercial PF resin; in particular, there was a 20 wt % content in the TGLP–PEI resin (Figure 2). It was reported that commercial PF resins contain a large amount of urea, and for this reason, their solid content is very high.²³

Effect of the Solid Content of the TGLP–PEI Resin on the Gel Time

The total solid content of the TGLP–PEI adhesives was shown to have a strong influence on the gelation time. As shown in Figure 3, the gelation time of the TGLP–PEI adhesives decreased with increasing weight ratio of PEI. With an increase in the total solid content in the system as a result of the increase in the PEI ratio, a proportional decrease in the water quantity present in the adhesive system was observed. This led to an increase in the crosslinking reaction, whereby these water molecules did not serve as an energy barrier during the curing process. Thus, the curing rate increased, and this led to a shorter gel time. It was, therefore, essential to control the moisture

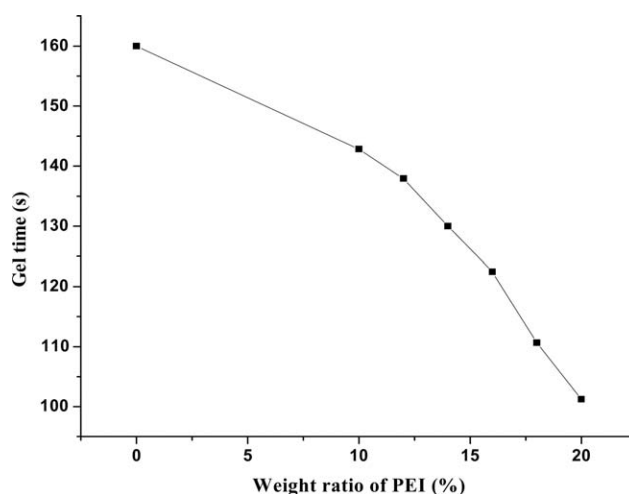


Figure 3. Effect of the solid content ratio on the gel time of the TGLP–PEI resin.

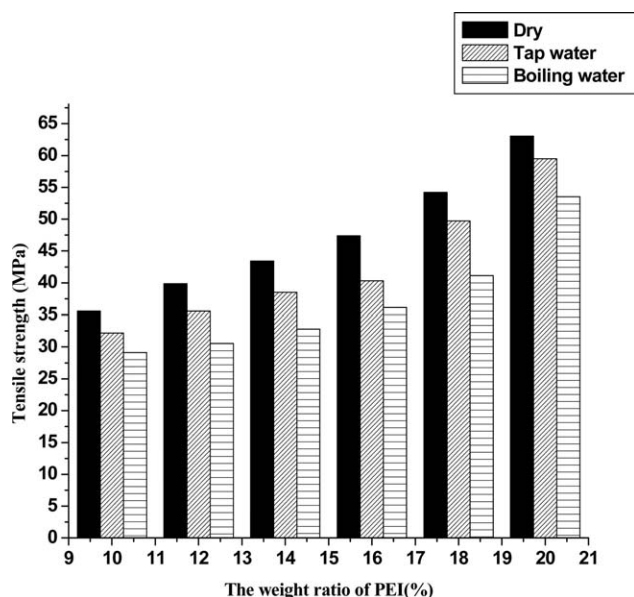


Figure 4. Effect of the weight ratio of PEI on the tensile strength of the TGLP-PEI resin (dry, tap-water soaked for 24 h, and boiling-water soaked for 2 h).

contents of the material during the manufacturing of the wood-composite products.

Effects of the PEI Weight Ratios on the Tensile Strength and Water Resistance of the Wood Composites Bonded with the TGLP-PEI Adhesives

Some earlier researches have proven that the TGLP adhesives are more effective in bonding to plywood.^{24,25} However, these findings revealed that the combination of TGLP and PEI possessed an even stronger bonding capacity toward plywood. The weight ratio of the PEI had significant impacts on the tensile strength and water resistance of the wood composites that were bonded with the TGLP-PEI adhesives (Figure 4). The TGLP adhesive had a dry tensile strength of 31.1 MPa but delaminated during the WSAD test and BWT/dry treatment. At a 10% weight ratio of PEI in TGLP, the dry tensile strength of the resulting plywood samples was relatively higher (35.57 MPa) than that of the TGLP. At this percentage of PEI, the delamination of the resulting plywood samples did not occur when it underwent the WSAD test and BWT/dry treatment, and the plywood samples retained with a high tensile strength. All three tensile strengths (dry, WSAD, and BWT/dry) significantly increased when the weight ratio of PEI in TGLP increased from 10 to 20% as compared to the TGLP and CPF resins. We inferred that the modification of TGLP with PEI significantly increased the tensile strength and water resistance of the resulting of plywood samples. One possible explanation was that this increase was due to further reactions between the amino groups of PEI with catechol moieties present in both lignin and tannin, and this increased the amount of crosslinking in the resin and ultimately increased the tensile strength and water resistance.

Some Possible Reactions between Lignin and PEI

To date, the reactions between lignin, tannin, and PEI are not fully understood. Some of the proposed potential reactions are

given in Figure 5. The nature of the TGLP-PEI resin curing mechanism was comparable to the quinone-tanning methods reported elsewhere.²⁶ Moreover, the reaction mechanisms between lignin and PEI were mostly similar to the possible reactions between tannin and PEI.⁸ At elevated temperatures, the catechol moiety (structure 2) in the demethylated lignin was highly vulnerable to oxidation; this led to the formation of quinones (structure 3). This occurred at higher temperatures (140 °C) in a hot press during the formation of the wood composites. The quinones (structure 3) possibly reacted with the amino groups present in the PEI structure and, thus, formed Schiff bases (structures 4 and 5). Some other possible reactions between the quinones and amino groups of PEI (e.g., Michael addition reaction) may have also occurred to form (structure 6) further Schiff bases (structures 7 and 8). A similar kind of reaction occurred during the oxidation process to form phenolic hydroxide in the lignin structure (during hot pressing); this further resulted in the formation of quinone. The latter further supported an increase in the reactions with amino groups of PEI to form Schiff bases. It is well known that wood contains lignin, which has phenolic hydroxyl groups. These groups could be oxidized to quinone at 140 °C; hence, they could not be excluded from the covalent-bond formation between the TGLP-PEI adhesive and wood. In addition to the reaction of the quinone, catechol moieties could react with the amino groups of PEI and form strong hydrogen bonds. Strong hydrogen bonds could also be formed with the hydroxyl groups in the wood components (structures 9 and 10 in Figure 5). We inferred from these reactions that the curing reactions through the hot-press process led to the formation of highly crosslinked TGLP-PEI network polymers and water-resistant adhesives. These results

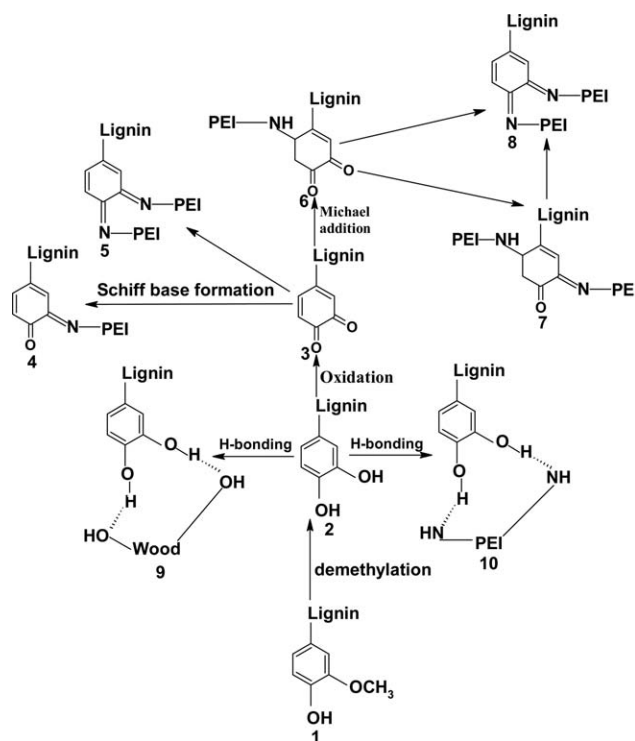


Figure 5. Some possible reactions between lignin and PEI.

were in close agreement with those of the mechanical tests and were proven through the soaking of plywood samples bonded with TGLP–PEI adhesives in tap water and boiling water.

Thermal Stability

The thermal stability of the thermoset polymers heavily depended on the structure of the polymer and on the crosslinking density.^{27,28} The latter is an important feature describing the durability of a polymer. The thermal degradation (TG and DTG) curves of TGLP and TGLP–PEI are presented in Figure 6(a,b), respectively. We found that the thermal features of the PF resin with lignin was similar to those reported in the literature.^{29,30} The maximum degradation temperatures of the TGLP and TGLP–PEI resins were quite similar to the thermal degradation temperature of CPF; this followed an auto-oxidization process and mainly involved three stages. During the first stage, when the temperature rose from room temperature to 200 °C, the weight loss of the resins was mainly due to the loss of water through the dehydration of aldehyde and the degradation of

Table I. Thermogravimetric Analysis Data for the TGLP and TGLP–PEI Resins

| Resin type | $T_{\max 1}$ (°C) | $T_{\max 2}$ (°C) | $T_{\max 3}$ (°C) |
|------------|-------------------|-------------------|-------------------|
| CPF | 80 | 151 | 380 |
| TGLP | 80 | 125 | 225 |
| TGLP–PEI | 70 | 190 | 360 |

$T_{\max 1}$, maximum degradation temperature 1; $T_{\max 2}$, maximum degradation temperature 2; $T_{\max 3}$, maximum degradation temperature 3.

other volatile products coming from the breaking of the side chains.³¹ Water elimination can lead to the formation of new crosslinks.³² For temperatures above 300 °C, the resins underwent further degradation. The weight loss was due to the release of water; this was produced from the condensation reaction between the methylene groups and phenolic OH groups. During the third stage, when the temperature reached 600 °C, major polymer degradation took place,³² and crosslinking between ethylene and carbon–hydrogen led to hydrogen elimination. In addition, this led to the formation of products such as carbon monoxide and methane because of the reaction of water and hydrogen, which were produced with the methylene group. Furthermore, random chain cleavage and the initial formation of char also took place.³³

The thermal behaviors of TGLP and TGLP–PEI resins differed significantly. The modification of TGLP via the incorporation of PEI affected the TGLP resin structure by increasing the crosslinking density of resin, and thus, it became more heat resistant. As shown in Figure 6(b), two distinct thermal degradation (DTG) peaks in the temperature range 200–370 °C for the TGLP–PEI resin were observed, and the results are shown in Table I. In the TGLP resin, the maximum degradation temperatures was 125 °C, and at this temperature, major polymer decomposition occurred. The major polymer decomposition in TGLP–PEI occurred at 360 °C. These findings were in close agreement with the mechanical properties of TGLP–PEI, especially in boiling water.

CONCLUSIONS

In this study, we demonstrated that a combination of TGLP and PEI created an excellent water-resistance adhesive. The results reveal that the increase in the PEI ratio led to the increase in the solid content of the TGLP–PEI adhesives, and thus, the viscosity of the resin increased. However, the TGLP–PEI resin with a total solid content of 56.92% was readily applied to plywood, and the tensile strength increased dramatically. The TGLP adhesives had a poor water resistance compared with the TGLP–PEI adhesive despite a high tensile strength (31.1 MPa), as shown when the plywood specimens soaked in tap water and boiling water were delaminated. However, the addition of 10% PEI with TGLP resin did not lead to the delamination of plywood specimens did not occur after the same treatment. All three tensile strengths (dry, WSAD, and BWT/dry) significantly increased when the weight ratio of the PEI increased from 10 to 20% compared with those of the TGLP and CPF resins. These findings could have been due to further reactions between the amino groups in the PEI with the

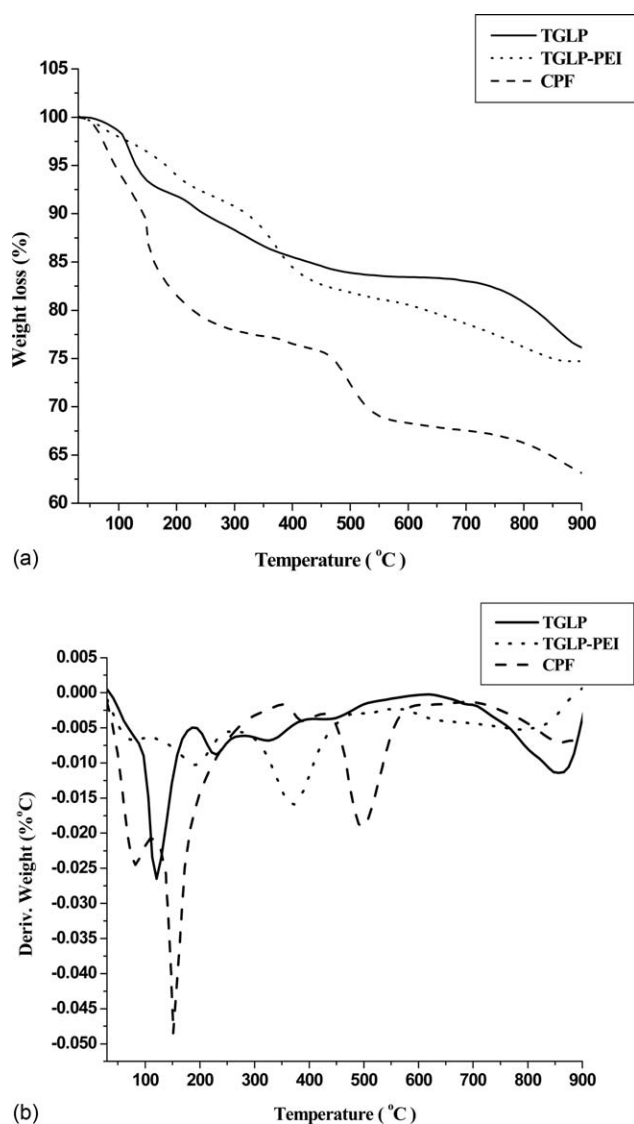


Figure 6. (a) TG and (b) DTG curves of the TGLP and TGLP–PEI resins.

catechol moieties in both lignin and tannin. This resulted in increased crosslinking linkages in the resin, and therefore, the tensile strength and water resistance increased, and the samples showed better heat resistivity (360 °C).

ACKNOWLEDGMENTS

The authors are grateful for the financial support of this research by Universiti Sains Malaysia through Universiti Sains Malaysia Research University Grant 1001/PKIMIA/854002.

REFERENCES

1. International Agency for Research on Cancer. IARC Classifies Formaldehyde as Carcinogenic to Humans. IARC Press Release No. 153, Lyon, France. World Health Organization: June 2004.
2. Mozaffar, A. K.; Sayed Marghoob, A.; Ved Prakash, M. *Int. J. Adhes. Adhes.* **2004**, *24*, 485.
3. Nihat, S. C.; Nilgül, O. *Int. J. Adhes. Adhes.* **2002**, *22*, 481.
4. Pizzi, A. *Adhes. Age* **1977**, *20*, 27.
5. Thompson, G. E. M.S. Thesis, Colorado State University, **1991**.
6. Yoosup, P.; Dohertyb, W. O. S.; Halleya, P. J. *Ind. Crops Prod.* **2008**, *27*, 163.
7. Li, K.; Geng, X. *Macromol. Rapid Commun.* **2005**, *26*, 529.
8. Li, K.; Geng, X.; Simonsen, J.; Karchesy, J. *Int. J. Adhes. Adhes.* **2004**, *24*, 327.
9. Liu, Y.; Li, K. *Macromol. Rapid Commun.* **2002**, *23*, 739.
10. Liu, Y.; Li, K. *Int. J. Adhes. Adhes.* **2007**, *27*, 59.
11. Charles, R. Handbook of Wood Chemistry and Wood Composites; Taylor and Francis: Boca Raton, **2005**.
12. Pizzi, A.; Mittal, K. L. Handbook of Adhesive Technology, 2nd ed.; Marcel Dekker: New York, **2003**; Chapter 26.
13. Waite, J. H. *Comp. Biochem. Physiol. B* **1990**, *97*, 19.
14. Waite, J. H. *Int. J. Adhes. Adhes.* **1987**, *7*, 9.
15. Rzepecki, L. M.; Waite, J. H. Bioorganic Marine Chemistry; Springer-Verlag: Berlin, **1991**.
16. Glasser, W. G. *Forest Prod. J.* **1981**, *31*, 24.
17. Li, K.; Peshkova, S.; Geng, X. *J. Am. Oil Chem. Soc.* **2004**, *81*, 487.
18. Liu, Y.; Li, K. *J. Adhes.* **2006**, *82*, 593.
19. Geng, X.; Li, K. *J. Adhes. Sci. Technol.* **2006**, *20*, 847.
20. El Mansouri, N. E.; Yuan, Q.; Huang, F. *Bioresources* **2011**, *6*, 4523.
21. Plywood. Specification for Bond Performance of Veneer Plywood; British Standard BS 6566-8:1985; British Standards Institution: London, **1985**; part 8.
22. Navarrete, P.; Pizzi, A.; Tapin-Lingua, S.; Benjelloun-Mlayah, B.; Pasch, H.; Rode, K.; Delmotte, L.; Rigolet, S. *J. Adhes. Sci. Technol.* **2012**, *26*(10–11), 1667.
23. Zhao, Y. Ph.D. Thesis, University of Toronto, **2013**.
24. El Mansouri, H. R.; Navarrete, P.; Pizzi, A.; Tapin-Lingua, S.; Benjelloun-Mlayah, B.; Pasch, H.; Rigolet, S. *Eur. J. Wood Wood Prod.* **2010**, *69*, 221.
25. Taylor, P.; Navarrete, P.; Pizzi, A. *J. Adhes. Sci. Technol.* **2012**, *26*(8–9), 1667.
26. Waite, J. H. *Methods Enzymol.* **1995**, *258*, 1.
27. Erä, V. A.; Mattila, A. *J. Therm. Anal.* **1976**, *10*, 461.
28. Manley, T. R. *Pure Appl. Chem.* **1989**, *61*, 1353.
29. Gabilondo, N. Ph.D. Thesis, University of the Basque Country, **2004**.
30. Tejado, A.; Pena, C.; Labidi, J.; Echeverria, J. M.; Mondragon, I. *Bioresour. Technol.* **2007**, *98*, 1655.
31. Hussin, H. M.; Rahim, A. A.; Ibrahim, M. N. M.; Brosseb, N. *Ind. Crops Prod.* **2013**, *49*, 23.
32. Chen, Y. F.; Chen, Z. B.; Xiao, S. Y.; Liu, H. B. *Thermochim. Acta* **2008**, *47*, 639.
33. Shulman, G. P.; Lochte, H. W. *J. Appl. Polym. Sci.* **1996**, *10*, 619.