Kun-Tsung Lu* and Lang-Yue Wu

Substitution of phenol in phenol-formaldehyde (PF) resins by wood tar for plywood adhesives

Abstract: Wood tars from *Acacia confusa* Merr. and *Cryptomeria japonica* D. Don. were produced by reduced pressure distillation at 76 mm Hg and 50°C from the bottom layer of crude wood vinegars that had set for over 6 months. The feasibility of using water-soluble, resole-type, wood tar phenol-formaldehyde resins (WT-PF) was investigated. The resins were prepared from phenol (P) and wood tars (WTs) at weight ratios of 100:0, 80:20, 60:40 and 40:60 and F/P molar ratios of 1.5, 1.8 and 2.0 as plywood adhesives. The results demonstrated that WT-PF resins had a higher viscosity, shorter gel times, a higher polydispersity, a lower curing temperature and less heat of curing than conventional PF resins under the same conditions. The shear strength of plywood bonded with WT-PF resins was slightly lower than that of conventional PF resin. However, the WT-PF resin still met the CNS 1349 requirement for the dry test, and phenol substitution levels could be up to 60%, but only 20% for type I and type II plywood. The addition of *A. confusa* bark powder fillers could significantly improve the bonding strength of WT-PF resins, especially for the warm water soaking and soaking in boiling water tests. The required amounts of fillers added were up to 5% for *A. confusa* WT-PF resins and up to 3% for *C. japonica* resins.

Keywords: adhesive, curing behavior, plywood, resole-type phenol-formaldehyde resin, shear strength, wood tar

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*Corresponding author: Kun-Tsung Lu, Department of Forestry, National Chung Hsing University, No. 250, Kuo-Kuang Road, Taichung 402, Taiwan, Fax: +881-4-22873628, e-mail: lukt@nchu.edu.tw
Lang-Yue Wu: Department of Forestry, National Chung Hsing University, Taichung, Taiwan

Introduction

Limited amounts of fossil resources and their increasing costs are the driving forces for the better utilization of biomass either as biofuels or as value-added chemicals (Demirbas 2001; Wang et al. 2009). Slow pyrolysis, i.e., charcoalization, is a process for converting wood to charcoal in a steel kiln (formerly in an earth kiln) with tar, methanol, wood vinegar and gas as by-products. In Taiwan, the manufacture of wood or bamboo charcoal and vinegar products is an emerging industry. The applications of charcoal (mainly as activated carbon) and vinegar (disinfection, sterilization against germs and mold, and insect repelling) are well established but tar utilization is not adequately explored. Wood tar (WT) is the dark brown residue of the precipitate obtained by setting wood vinegar for 6 months or by distilling wood vinegar under reduced pressure. The composition of WT is known (Horne and Williams 1996; Takashi et al. 2008a,b; Li and Suzuki 2009). Pyrolysis oils ("bio crude oils") from rapid pyrolysis of wood are described with even more detail (Azeez 2011; Azeez et al. 2011; Dobele et al. 2011), which are similar to WT. Both contain complex aromatic compounds, phenol derivatives with alkan, alkene, methoxy substitutes and neutral and acidic components. These substance classes arise in the course of the pyrolysis process of charcoalization, via de- and repolymerization of the components of the lignocellulosic biomass. A tar is not stable; it undergoes an aging process by condensation, oxidation and evaporation of its volatile components (Fratini et al. 2006). A large part of the tar is of lignin origin, i.e., the products have a phenolic nature (Bayerbach et al. 2006). Accordingly, tar is a potential source of biophenol, which could be utilized for various purposes.

The utilization of *Eucalyptus* tar pitch, a by-product of charcoal production in Brazil, was explored. For example, Araújo and Pasa (2003) and Melo and Pasa (2004) synthesized polyurethanes derived from this material and evaluated the mechanical and thermal properties of polyurethane elastomers. In this context, polyurethane coatings (Araújo and Pasa 2004) and flexible polyurethane foams (Araújo et al. 2005) were also studied. Prauchner et al. (2002, 2004) have examined the rheology of *Eucalyptus* tar pitches and found that they have potential as carbon fiber precursors. Lu and Hong (2010) investigated polyurethane coatings based on bamboo tar for finishing of exterior wood. Gagnon et al. (2004) tested adhesives made from isocyanates and pyrolysis oils for wood composites.

The resole type of PF resin is a common adhesive for wood panel production that is synthesized under alkali

conditions from phenol (P) and formaldehyde (F) at a molar ratio F/P >1. Pyrolytic oils or tars as a P substitute would have high commercial interest as pointed out by Amen-Chen et al. (2002a,b,c), who focused on softwood bark pyrolysis oils for production of PF resols. Charcoal and pyrolytic oils are usually produced from softwoods and hardwoods (Effendi et al. 2008). In Taiwan, *Cryptomeria japonica* and *Acacia confusa* are the potential candidates to this purpose. The total cultivation area of the former is 39 100 ha and of the latter is 21 200 ha (Forestry Bureau 2005). This is the reason why in the present study, the feasibility of replacing commercial phenol with *C. japonica* and *A. confusa* WTs in the manufacture of a PF resin will be examined. In focus are adhesives for plywood production.

Materials and methods

Materials

WT was obtained from the reduced-pressure distillation (70 mm Hg, 50°C) of the bottom sedimentation layer of tar from crude wood vinegar that had set for over 6 months. The wood (20- to 30-year-old *A. confusa* and *C. japonica* wood stems) was obtained from Hui-Sun Forest Station of the Experimental Forest of National Chung Hshing University in Nan-Tou County, Taiwan. The charcoalizaton was performed in a steel kiln at 500°C; heating rate, 100°C h^{-1}; holding time, 1 h. The WT yields were approximately 23% (*A. confusa*) and 36% (*C. japonica*) after sedimentation. Gas chromatography-mass spectrometry (Perkin-Elmer Clarus 600D, Norwalk, CT, USA) analysis of the WT of *A. confusa* resulted in 2,6-dimethoxyphenol (9.1%), phenol (8.1%), and methoxyphenol (5.1%); in WT of *C. japonica* were found phenol (5.2%), 2-methoxy-4-methylphenol (4.9%), and methoxyphenol (4.7%). Phenol, NaOH and HCl are from Union Chemical Co., Xin-zhu, Taiwan, and formaldehyde (37%) from Scharlau Chemie S.A. Spain.

Reactive phenol content in WT

WT (3–5 g), 37% formaldehyde (F, 10 ml) and HCl (5 ml) were added into a 250-ml Erlenmeyer flask with a condenser. The flask was stirred for 1 h at 100°C in a water bath. The mixture was poured into a weighed G3 filter beaker and suction filtered. The residue was washed completely with hot water, dried at 103±2°C and weighed after cooling in a desiccator. The reactive P content (%) was calculated on the basis of the weight of the residue.

Preparation of resole-type PF resins

The PF resins were prepared with P/WT weight ratios of 100:0, 80:20, 60:40 and 40:60 and with F/P molar ratios (including commercial P and reactive P from WT) of 1.5, 1.8 and 2.0. The molar ratio of NaOH/P was 0.6, and the concentration of NaOH was 50%.

The calculated amounts of P, F, and WT were added into a four-necked round-bottomed flask equipped with a stirrer, reflux condenser, thermometer and a dropping funnel for the addition of catalyst. The mixture was initially heated to 60°C, and NaOH solution was added dropwise. Then, the mixture was heated to 90°C and stirred for 45 min. After cooling, the water-soluble resole-type PF resins were ready to use.

Characterization of PF resins

A Suntex sp-701 pH meter (Taichung, Taiwan) with a glass reference electrode (25°C) was used for pH measurements. Viscosity was measured with a Brookfield RV-T viscometer (Piddeboro, MA, USA) at 25°C, and the solid content was estimated in accordance with Chinese National Standards (CNS) 5133. Gel time was measured in a gel meter assembled in our laboratory. A 3-g charge of PF resin was placed into a glass tube with a diameter of 10 mm and length of 180 mm. A spiral end of a longer iron wire was placed inside the glass tube. The glass tube was heated in an oil bath at 135±2°C, and the iron wire was pulled up and down manually. The times at which the gelled resin was pulled up together with the glass tube were noted. An average value of three replicate measurements is reported.

The M_w and polydispersity (M_w/M_n) of the PF resins were measured with a gel permeation chromatograph (Hitachi 6200A, Tokyo, Japan) equipped with a Shodex KF-802 column and a UV index detector (L-4000). Tetrahydrofuran (THF) was the mobile phase (1 ml min^{-1}). Samples (0.01 g) were diluted in 10 ml of THF and filtered over 0.45-μm molecular sieves. Differential scanning calorimetry (DSC) was done with a Perkin-Elmer DSC-7 instrument (Norwalk, CT, USA). Temperature program was 10°C min^{-1} from 30 to 225°C in N_2 atmosphere, and the onset, peak temperatures and reactive heat were noted.

Bonding shear strength of PF resins

These data of plywood specimens were measured by tension loading in accordance with CNS 1349 (2008). The 3-ply plywood specimens (1-mm top veneers, 2-mm middle veneer) were made of lauan (*Shorea* spp.) veneer (30 cm×30 cm, 12% moisture content). The PF resins (50% solid content) were applied on both sides of the interface (170 g m^{-2} for each layer). Pressing was done with a compression molding machine at 150°C and 10 kg cm^{-2} for 10 min. After conditioning at room temperature (r.t.) for 48 h, the plywoods were cut into 25-mm×80-mm specimens. Testing of the normal (dry), warm water soaked, and boiling water treated specimens was done with a Universal Testing Machine (Shimadzu UEH-10, Kyoto, Japan) at a crosshead speed of 1 mm min^{-1}, and wood failure was noted. The warm water soaking test involved soaking the specimens in 60±3°C water for 3 h and then placing them in cold water until r.t. was reached. The bonding performance test was conducted while the specimens were still wet. Experiments with boiling water were done as follows: specimens were treated in boiling water for 4 h, followed by drying at 60±3°C for 20 h. Then, a second boiling water treatment followed for another 4 h, and the specimens were cooled down to r.t. in cold water. The bonding performance test was conducted while the specimens were still wet. In additional tests, a filler of a 200-mesh *A. confusa* bark powder was added to the PF resins at weight ratios of 3%, 5%, and 10% to improve the bonding strength of the specimens.

Results and discussion

Fundamental properties of the PF resins

The intention was to examine also P/WT weight ratios of 20:80 and 0:100, but the experiments failed because of gelation of the mixtures during preparation. The fundamental properties of the other PF resins are listed in Table 1. As demonstrated, the pH values for all PF resins were approximately 11.50. For the *A. confusa* WT-PF resins, the viscosity of specimens with the same P/WT ratios of 80:20 and 60:40 decreased as a function of F/P ratio increment. The opposite is true for the 40:60 ratio because the WT with a higher M_w reacted with F, but the resin with an F/P of 2.0 gelled. In addition, at a constant F/P ratio, viscosity elevates with increasing WT content. The results are similar for the *C. japonica* WT-PF resins. Furthermore, the WT-PF resins from *A. confusa* have the highest viscosity, followed by the WT-PF *C. japonica* resins; the standard PF resins have the lowest viscosity at the same F/P ratio level. The WT-PF *A. confusa* resin has the highest viscosity due to the higher viscosity of the *A. confusa* WT itself (717 mPa.s vs. 106 mPa.s of *C. japonica* WT).

The solid content of all the PF resins decreased with increasing F/P ratio at a constant P/WT ratio because of the additional F and water added. For the WT-P-*A. confusa* resins, the solid content increases if the WT content is higher. This trend is not visible for WT-P-*C. japonica* resins. At the same F/P and P/WT levels, the solid content of the WT-PF *A. confusa* resins is higher than that of the corresponding *C. japonica* resin because the WT of the former contains 67% less reactive phenol and requires the addition of more WT during synthesis. WT *C. japonica* contains 85% reactive P (not shown). Compared with the commercial PF resin, the WT-PF resins have shorter gel times, which are inversely proportional to the WT contents.

The PF-WT resins (40:60) of *A. confusa* gelled at F/P ratios of 2.0, but the *C. japonica* resin gelled at a ratio of 1.5, probably because the former reacted slowly with F due to its higher viscosity. When the F content increased and reacted with phenolic compounds, the WTs with more methylol phenols have more opportunity for cross-linking and gelling. Obviously, this may occur at F/P ratios of 2.0 and 1.5, respectively. However, at F/P ratios between 1.8 and 2.0, dimethylene ether linkage may be formed, and this prepolymer is less reactive than the methylene linkage type prepolymer and does not gel rapidly.

The M_w and polydispersity indices M_w/M_n are listed in Table 1 as a function of the various parameters. *A. confusa* WT shows M_n of 320, M_w of 2621, and M_w/M_n of 8.2, whereas

Composition of the resins							Data by GPC			Data by DSC		
WT	P/WT ratio by wt.	F/P molar ratio	pH	Viscosity (mPa.s)	Solid content (%)	Gel time at 135°C (min)	M_w	M_n	M_w/M_n	Onset temp. (°C)	Peak temp. (°C)	Heat curing (J g^{-1})
	100:0	1.5	11.88	76±1	49.1±0.3	9.0±0.2	1010	347	2.91	120	151	174.1
		1.8	11.86	119±0	48.6±0.2	8.2±0.1	641	166	3.87	115	151	1340.4
		2.0	11.78	83±1	46.9±0.1	8.1±0.5	1196	237	5.05	113	150	1183.0
A. confusa	80:20	1.5	11.65	259±5	50.3±0.2	8.3±0.5	724	302	2.40	103	149	99.2
		1.8	11.65	200 ± 1	47.8±0.3	7.8±0.3	734	179	4.09	118	150	753.1
		2.0	11.64	142±2	47.1±0.1	7.3±0.3	1130	207	5.46	115	149	680.2
	60:40	1.5	11.56	922±21	51.9±0.1	7.2±0.3	763	305	2.50	117	146	37.8
		1.8	11.45	719±28	49.6±0.2	6.1±0.6	671	161	4.16	105	143	470.0
		2.0	11.30	405±14	48.3±0.1	6.9±0.3	2043	234	8.74	117	147	308.5
	40:60	1.5	11.31	2972±100	52.9±0.2	5.6±0.3	910	334	2.73	117	141	35.6
		1.8	11.22	5563±146	51.6±0.3	4.8±0.4	413	142	2.91	104	146	308.2
		2.0	Gelled	Gelled	Gelled	Gelled	Gelled	Gelled	Gelled	Gelled	Gelled	Gelled
C. japonica	80:20	1.5	11.98	156±2	47.4±0.3	8.3±0.4	869	323	2.70	109	149	167.5
		1.8	11.68	127±1	47.3±0.0	7.3±0.7	591	166	3.56	118	152	898.6
		2.0	11.81	125±2	44.7±0.0	7.5±0.2	1033	197	5.23	113	149	787.7
	60:40	1.5	11.85	377±2	48.0±0.1	5.9±0.5	903	329	2.74	103	146	43.1
		1.8	11.83	131 ± 1	44.9±0.2	7.5±0.2	862	165	5.23	104	147	462.4
		2.0	11.68	125±4	44.3±0.0	7.6±0.2	1017	190	5.34	116	147	481.7
	40:60	1.5	Gelled	Gelled	Gelled	Gelled	Gelled	Gelled	Gelled	Gelled	Gelled	Gelled
		1.8	11.43	160±0	45.6±0.1	6.6±0.6	527	162	3.26	120	147	261.6
		2.0	11.35	541±9	45.1±0.1	5.9±0.3	2017	195	10.35	109	146	108.7
A. confusa	0:100						2621	320	8.18			
C. japonica	0:100						2922	311	9.40			

Table 1 Properties of PF resins with different F/P molar ratios and WT contents.

the corresponding data for *C. japonica* WT are 311, 2922, and 9.4, respectively. The higher M_w/M_n of the latter can be interpreted by the presence of more components with low M_w, such as guaiacols, catechols and levoglucosan (Takashi et al. 2008b). At an F/P ratio level of 1.5, the M_w of each WT-PF resin is lower than that of a commercial PF resin, whereas at the F/P ratio level of 2.0, the opposite was true. The polydispersity index (M_w/M_n) of all PF resins increased with increasing F/P and P/WT ratios.

Curing behavior of the PF resins by DSC

The synthesis of the resole-type PF resin occurs in two steps (Gardziella et al. 1999). The first step is the addition reaction in which the P reacts with F to form a methylol-P, dimethylol-P, or trimethylol-P under alkaline condition. The second stage is the condensation reaction in which the methylol-phenols react with each other through methylene or dimethylene ether linkage to form a prepolymer (PF resin). When applied as an adhesive, the prepolymer is cured with heat to form a 3D network structure. The curing behaviors of the PF resins were examined by DSC analysis, and the DSC curves showed a single exothermic peak (curves not shown). The onset and peak temperatures and the heat of curing as function of the parameters are summarized in Table 1.

For the standard PF resin, the onset temperature decreased with increasing F/P ratios because the higher F content produces more methylol groups and the PF resin is more reactive at low temperatures. The peak temperatures of these PF resins with varying F/P molar ratios are at approximately 151°C. However, the PF resins with F/P ratios of 1.8 and 2.0 have a higher heat of curing than those with an F/P ratio of 1.5. In particular, the resin with F/P of 1.8 had the highest value at 1340.4 J g^{-1}. These results may be attributed to the higher amounts of F and of 2,4-, 2,6- or 2,4,6-substituted methylol-phenols, which lead to the formation of more cross-linked structures and an elevated heat of curing (Chen 1996; Gardziella et al. 1999). Similar results were observed for both woods in focus.

Interestingly, the onset temperatures of both WT-containing PF resins have no relationship with the varying F/P molar ratios or WT contents. However, the peak temperatures and heat of curing of both WT-PF resins were lower than those of the standard PF resin. This is due to the lack of cross-linking sites and the early reaction. Thus, the peak temperature is shifting into a lower temperature range and releases less heat of curing.

Although the peak temperatures of *A. confusa* and *C. japonica* WT-PF resins were similar even under different conditions, the heat of curing of *C. japonica* WT-PF resin was higher than that of *A. confusa* resins especially at the P/WT ratios of 80:20 and 60:40, which results from the greater amount of reactive P in the *C. japonica* WT.

Shear strength of plywood

The results of the shear strength tests of plywood bonded with different types of PF resins are shown in Table 2. According to the CNS 1349, the bonding shear strength of plywood specimens with lauan as core veneer must be ≧0.7 MPa. Moreover, the specimens should pass the warm soaking test for type II plywood and the boiling water test for type I plywood. However, the wood failure values were not specific. The shear strength values of all samples are greater than 0.7 MPa in the dry test, which is in accordance with the CNS 1349 standard. In particular, the commercial PF resins (with F/P of 1.5 and 1.8) had the highest shear strength of 1.21 MPa. The shear strengths of all of the WT-PF resins were lower than those of standard PF resin.

For the *A. confusa* WT-PF resins, the normal shear strength increased with increasing P/WT ratio of 80:20, and the highest wood failure was ca. 90%. The best shear strength of 1.04 MPa could be achieved with an F/P of 2.0. Concerning the WT-PF resins, the resins with 60:40 and 40:60 P/WT ratios (at the F/P level of 1.8) have shear strengths of 1.02 and 0.91 MPa and wood failures of 60% and 40%, respectively. For the *C. japonica* WT-PF resins (at P/WT of 80:20 and 60:40) the best shear strengths of 1.07 and 1.00 MPa were observed, respectively, if the F/P was 1.5. However, with a P/WT ratio of 40:60, the resin at the same F/P level gelled during synthesis. At the F/P level of 1.8, the best shear strength was of 1.10 MPa with a wood failure of 60%. Accordingly, most WT-PF resins have higher wood failure rates than the standard PF resins.

In the warm water soaking test, the shear strength values of all standard PF resins with varying F/P were between 1.09 and 1.16 MPa, which is consistent with the CNS 1349 standard for type II plywood. These data are superior to those of WT-PF resins. For the *A. confusa*, only the resins with a P/WT ratio of 80:20 had shear strengths greater than 0.7 MPa, and the strength was proportional to the F/P ratio increment. The other resins did not conform to the CNS 1349 standard; even the resins with P/WTs of 60:40 at the F/P level of 1.5 had a wood failure of 60%. The WT-PF specimens of *C. japonica* show similar results. Only the resins with a P/WT ratio of 80:20 at the F/P levels of 1.8 and 2.0 have shear strengths above 0.7 MPa and wood failures of 10–15%. The other resins do not fulfill the CNS 1349 requirements for type II plywood.

WT	P/WT ratio by wt.	F/P molar ratio	Shear strength of plywood (MPa)		
			Normal (dry)	Warm water soaking	Soaking in boiling water
–	100:0	1.5	1.21±0.10 (10)	1.14±0.08 (10)	1.01±0.11 (0)
		1.8	1.21±0.12 (0)	1.16±0.08 (10)	0.97±0.12 (10)
		2.0	1.10±0.11 (10)	1.09±0.12 (10)	0.94±0.11 (10)
A. confusa	80:20	1.5	0.89±0.11 (90)	0.77±0.07 (20)	0.71±0.10 (60)
		1.8	0.92±0.10 (90)	0.79±0.08 (10)	0.74±0.11 (20)
		2.0	1.04±0.12 (100)	0.97±0.10 (50)	0.83±0.12 (50)
	60:40	1.5	0.90±0.04 (70)	0.54±0.14 (60)	0.61±0.08 (40)
		1.8	1.02±0.13 (60)	0.54±0.13 (0)	0.48±0.09 (0)
		2.0	0.86±0.17 (20)	0.65±0.10 (0)	0.34±0.12 (0)
	40:60	1.5	0.73±0.09 (80)	0.48±0.09 (10)	0.42±0.07 (20)
		1.8	0.91±0.147 (40)	0.65±0.08 (10)	0.58±0.17 (20)
		2.0	Gelled	Gelled	Gelled
C. japonica	80:20	1.5	1.07±0.12 (50)	0.59±0.12 (10)	0.64±0.08 (0)
		1.8	0.84±0.08 (30)	0.77±0.16 (10)	0.72±0.12 (0)
		2.0	1.00±0.12 (60)	0.76±0.06 (50)	0.64±0.12 (10)
	60:40	1.5	1.00±0.05 (20)	0.62±0.12 (0)	0.48±0.12 (0)
		1.8	0.90±0.16 (0)	0.64±0.10 (0)	0.60±0.12 (0)
		2.0	0.70±0.07 (0)	0.41±0.12 (0)	0.22±0.05 (0)
	40:60	1.5	Gelled	Gelled	Gelled
		1.8	1.10±0.10 (60)	0.67±0.08 (0)	0.48±0.10 (0)
		2.0	0.80±0.08 (10)	0.36±0.07 (0)	0.24±0.08 (0)

Table 2 Shear strength of plywood bonding by PF with different F/P molar ratios and WT content (data in parentheses: wood failure in %).

In the boiling water test, the results are similar to those from the warm water soaking tests. Only the standard PF resins and the WT-PF resins 80:20 at all F/P levels (*A. confusa*) and at an F/P level of 1.8 (*C. japonica*) met the CNS 1349 requirements for type I plywood. Accordingly, the shear strength of WT-PF adhesives is inferior to those of standard PF resins. WT-PF resins of *C. japonica* were the worst. The interpretation is that the less amount of available positions in WT is an obstacle for an effective cross-linking with F.

Effect of *A. confusa* bark powder as filler

The effect of the addition of bark powder from *A. confusa* (200 mesh) as a filler on the shear strength of plywood was evaluated (Table 3). The viscosity increases with increasing filler content, especially for WT-PF resins in which a higher WT contents elevate the viscosity. For standard PF resins, the filler was only slightly influential on dry shear strength, but the results are worsening at higher filler contents in the warm water soaking and in boiling water tests.

For the WT-PF of *A. confusa*, the results of all three tests could be improved significantly with the filler. When 3–5% filler was added, the shear strength exceeded 0.7

MPa, i.e., it is better than the CNS 1349 requirements. The only exception is the resin with a P/WT of 40:60 with 0.68 MPa. The good bonding strength is in relation to the higher viscosity, and the better workability of WT-PF resins with the filler is an advantage. However, the wood failure decreased significantly in the presence of filler: it was even 0% in warm water soaking and boiling water tests. Thus, the failure occurs in the interface between the PF resin and the wood surface because of the higher viscosity of PF resin with filler.

The *C. japonica* WT-PF resins show a similar behavior except for the resin with a P/WT of 40:60, which gelled during synthesis. However, the PF resin with only 3% filler added met the CNS 1349 requirement in all three types of shear strength tests.

Conclusions

The WT-PF resins have higher viscosities, shorter gel times, a higher polydispersity, lower curing temperatures and less heat of curing than the standard PF resin under the same conditions. The shear strength of plywood bonded with WT-PF resins was slightly lower than that of standard PF resin, but it still met the CNS 1349

WT	P/WT ratio by wt.	Filler (%)	Viscosity (mPa.s)	Shear strength of plywood (MPa)		
				Normal	Warm water soaking	Soaking in boiling water
–	100:0	0	52±1	1.21±0.10 (10)	1.14±0.08 (10)	1.01±0.10 (0)
		3	77±0	1.31±0.17 (10)	1.06±0.17 (0)	0.94±0.12 (10)
		5	132±1	1.03±0.14 (50)	0.77±0.13 (10)	0.73±0.12 (70)
		10	342±8	1.32±0.12 (0)	0.70±0.08 (0)	0.56±0.10 (0)
A. confusa	80:20	0	154±2	0.89±0.10 (90)	0.77±0.07 (20)	0.71±0.10 (60)
		3	276±2	1.26±0.16 (10)	0.96±0.12 (0)	0.88±0.12 (0)
		5	371±22	1.12±0.13 (30)	1.03±0.14 (0)	0.86±0.10 (0)
		10	1808±80	1.15±0.12 (30)	0.70±0.13 (0)	0.67±0.10 (0)
	60:40	0	494±15	0.90±0.04 (70)	0.54±0.14 (60)	0.61±0.08 (40)
		3	1419±32	1.12±0.10 (0)	0.83±0.06 (0)	0.76±0.07 (0)
		5	1460±7	1.02±0.10 (10)	0.94±0.10 (0)	0.77±0.06 (0)
		10	7300±78	0.95±0.07 (0)	0.58±0.10 (0)	0.50±0.12 (0)
	40:60	0	1522±23	0.73±0.10 (80)	0.48±0.10 (10)	0.42±0.07 (20)
		3	4604±29	1.00±0.14 (0)	0.89±0.12 (0)	0.68±0.10 (0)
		5	6197±100	1.01±0.07 (0)	0.90±0.10 (0)	0.77±0.12 (0)
		10	40 673±897	1.07±0.12 (0)	0.72±0.08 (0)	0.60±0.06 (0)
C. japonica	80:20	0	140±1	1.07±0.12 (50)	0.59±0.13 (10)	0.64±0.08 (0)
		3	263±11	1.08±0.08 (0)	0.82±0.10 (0)	0.74±0.08 (0)
		5	393±21	0.89±0.14 (0)	0.77±0.14 (0)	0.64±0.10 (0)
		10	2302±189	0.80±0.10 (0)	0.38±0.10 (0)	0.73±0.10 (0)
	60:40	0	246±1	1.00±0.05 (20)	0.62±0.12 (0)	0.48±0.13 (0)
		3	1284±23	1.24±0.13 (0)	0.88±0.18 (0)	0.70±0.06 (0)
		5	1421±42	1.00±0.14 (0)	0.70±0.07 (0)	0.58±0.10 (0)
		10	2755±14	1.16±0.12 (40)	0.65±0.10 (10)	0.72±0.10 (0)

Table 3 Shear strength of plywood bonding by PF (F/P=1.5) with different filler contents (filler: 20 mesh *A. confusa* bark powder; data in parentheses: wood failure in %).

requirements, and the phenol substitution level could be up to 60% for both WTs tested by the dry test. However, only 20% P-substitution level could be achieved for type I and type II plywood. Addition of *A. confusa* bark powder fillers improve the bonding strength of WT-PF resins, especially in the warm water soaking and boiling water tests, whereas the requirements of CNS 1349 for type I and II plywood are fulfilled. Up to 5% (*A. confusa*) and 3% (*C. japonica*) fillers are recommendable. In general,

A. confusa WT-PF resins have better bonding properties than those of *C. japonica*.

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