

Preparation and Application of Polyurethane Adhesives Made from Polyhydric Alcohol Liquefied Taiwan Acacia and China Fir

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ABSTRACT: Taiwan acacia (*Acacia confusa*) and China fir (*Cunninghamia lanceolata*) were liquefied in polyethylene glycol (PEG)–glycerol cosolvent, with sulfuric acid (H_2SO_4) as a catalyst. The liquefied woods were blended with three kinds of isocyanate, such as poly-4,4'-diphenylmethane diisocyanate (PMDI), Desmodur L (adduct of toluene diisocyanate with trimethylol propane), and Desmodur N (trimer of hexamethylene diisocyanate), to prepare polyurethane (PU) resins. From the results, China fir had better liquefaction effect than Taiwan acacia. Those PU resins prepared from liquefied wood blending with isocyanate could cure at room temperature. Their gel property was influenced by the type of isocyanate, the molar ratio of the functional group of isocyanate to liquefied wood [$NCO/(OH+COOH)$], and the rate of catalyst added. PU resins prepared from Desmodur L had an appropriate gel time

for processing. But those prepared from PMDI had too short gel time to process. Contrary, the PU resins prepared from Desmodur N would take a longer time to gel. However, addition of catalyst could shorten the gel time significantly. FT-IR analysis showed that a urethane bond had formed between the liquefied wood and isocyanate. When these PU resins were used as wood adhesives, liquefied wood blended with Desmodur L had better dry and wet bonding strength than others. Increasing the molar ratio of $NCO/(OH+COOH)$ could increase the bonding strength. On comparing liquefied Taiwan acacia and China fir, the former had better bonding strength than the latter. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 23–31, 2008

Key words: adhesion; biomaterials; liquefied wood; polyhydric alcohol; polyurethane

INTRODUCTION

Wood is the most plentiful renewable bioresource on earth, but its solid characteristics restrict its utilization. If we can convert wood from solid to liquid, the applications of wood will be expanded substantially. Solvent liquefaction is one of the effective method to liquefy wood. Using this method, the polymeric structure component of wood will be broken down, and then the solvent used for liquefaction will react with these broken-up fragments and form a derivative and dissolve in the free solvent.

Phenol and polyhydric alcohol are two major solvents commonly used in the liquefaction of biomass. The biomass liquefied with phenol can be used to prepare phenolic resins. Alma et al.^{1–4} had liquefied the wood in phenol, with hydrochloric acid and oxalic acid as catalysts, and used these phenolated woods to prepare thermoplastic novolak-type PF resin and thermosetting resol-type PF resins. In our previous studies,^{5–7} wood of Taiwan acacia and China fir were liquefied in phenol, with hydrochloric acid and sulfuric acid as catalysts, and the liquefied

products were used in the preparation of resol-type PF resins and used in the manufacture of plywood and particleboard.

Polyurethane (PU) resin that has the urethane linkage in its molecular structure is one of the most important synthetic resin used nowadays. It is composed of two major components—one is the compound containing active hydrogen and the other is the isocyanate containing the NCO group. The polyols such as polyester and polyether are the extensively used active, hydrogen-containing compounds. They have the hydroxide group in their molecular structure, which can react with the NCO group in isocyanate to form the urethane linkage. It is well known that the properties of PU resins depend on the characteristic of polyol and isocyanate used. In the polyhydric alcohol liquefied biomass, the wood fragment, the solvent and the wood derivatives have the hydroxide group, so that it can react with isocyanate to prepare PU resins. However, most of the researches about the polyhydric alcohol liquefied biomass were focussed on finding the suitable liquefaction condition and their utilization as PU foams and films. Yao et al.⁸ used polyethylene glycol (PEG)-liquefied wood and starch to prepare the rigid PU foams, and they pointed that the mechanical properties of these PU forms were the same as com-

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mercial products. Kurimoto et al.^{9–11} prepared the PU films from polyhydric alcohol-liquefied wood of various species and investigated their mechanical properties. In our previous studies,^{12–14} we had liquefied the wood of Taiwan acacia and China fir in PEG and glycerol cosolvent, and the liquefied wood had been used in manufacturing PU foams. But the report using PU resins that is prepared from liquefied wood as wood adhesive are still few, especially on the subject of comparing the influence of the kind of isocyanate on the gluing properties. Tohmura et al.¹⁵ prepared the PU adhesive from polyhydric alcohol-liquefied wood blending with poly-4,4'-diphenylmethane diisocyanate (PMDI) and used in the manufacturing of plywood with hot-pressing. In this study, polyhydric alcohol-liquefied Taiwan acacia and China fir were used to blend with various kinds of isocyanate to understand the potential of which one to be used as the cold-setting PU adhesive. Three kinds of isocyanate—PMDI (aromatic isocyanate polymer), Desmodur L (aromatic isocyanate monomer), and Desmodur N (aliphatic isocyanate monomer)—were used to compare the influence of molecular structure of isocyanate on the gluing properties of PU resins.

EXPERIMENTAL

Materials

Taiwan acacia (*Acacia confusa*) and China fir (*Cunninghamia lanceolata*) were used in this study. The wood particles were ground to pass through a 2-mm screen and dried in an oven at 105°C for 12 h before liquefaction. PEG (PEG-400) and glycerol were used as cosolvents. H₂SO₄ was used as the catalyst. The PMDI, Desmodur L, and Desmodur N with the NCO content of 28.19%, 20.59%, and 12.15%, respectively, were used as isocyanate compounds. As for the PU resin preparation, organosiloxane and dibutyltin dilaurate were used as surfactant and catalyst, respectively. The wood of Lauan (*Shorea* spp.) was used for the bonding test.

Preparation of liquefied wood

The liquefaction reaction of wood was conducted in a 1000-mL separable glass flask equipped with the stirrer, thermometer, and reflux condenser. The PEG-400 and glycerol with a weight ratio of 9 : 1 and sulfuric acid were premixed thoroughly in the reaction flask, and then about a third of wood powder was added. The mixture was stirred and heated to 130°C by a electric heating mantle. Then, the remnant woods were added gradually to the reaction flask. After all of the wood was added, the temperature of the mixture rose to 150°C, and was main-

tained for 90 min to undergo the liquefaction reaction. In the reaction of liquefaction, the weight ratio of poly(hydric alcohol)/wood/sulfuric acid was set at 3/1/0.09.

Characterization of liquefied wood

Residue content

About 1 g of liquefied wood was weighed and diluted with 50 mL of dioxane, and then the dilution was filtered through a G3 glass filter in vacuum. The residue was washed with excess dioxane until it became colorless, and dried to a constant weight in an oven at 105°C. The residue content was calculated.

Viscosity

The viscosity of liquefied wood was measured with a Brookfield rotary viscometer at 25°C ± 2°C.

Acid value

About 8 g of liquefied wood was diluted with 80 mL of dioxane and 20 mL of water, and then titrated with a 1N potassium hydroxide solution. The change in pH was monitored with a pH meter. The neutralization volume of the sample was gained from the neutralization curve. And the acid value was calculated according to the following equation: Acid value = $[(A - B) \times N \times 56.1]/W$; where *A* and *B* were the consuming volume (mL) of the potassium hydroxide at the neutralization point for the sample test and blank test, respectively, and *N* was the equivalent concentration of potassium hydroxide solution, and *W* was the weight of liquefied wood.

Hydroxyl value

About 1–2 g of liquefied wood was charged into a 250-mL Erlenmeyer flask, followed by adding 10 mL of pyridine-acetic anhydride mixture (7/3; v/v) and heating gradually to the reflux temperature. It was boiled slightly for 20 min and then cooled to room temperature. After this, 25 mL of toluene and 50 mL of water were added, and then the mixture was titrated with 1N potassium hydroxide solution. The change in the pH was monitored with a pH meter. The neutralization volume of the sample was gained from the neutralization curve. The hydroxyl value was calculated according to the following equation: hydroxyl value = $[(B - A) \times N \times 56.1]/W + \text{acid value}$; where *A* and *B* were the consuming volume (mL) of potassium hydroxide at the neutralization point for sample test and blank test, respectively, and *N* was the equivalent concentration of potas-

TABLE I
Formulary of the PU Resins

Polyols	Isocyanate	NCO/(OH+COOH) (molar ratio)	Surfactant (%)	Catalyst (%)
Liquefied wood	PMDI, Desmodur L, Desmodur N	1.0, 1.5, 2.0	0, 2	0, 1, 2, 3

The surfactant and catalyst added is based on the weight of liquefied wood.

sium hydroxide solution, and W was the weight of liquefied wood.

FT-IR analysis

The liquefied wood was diluted with dioxane and filtered through a G3 glass filter. The filtrate was concentrated by rotary vacuum evaporator at 135°C followed by oven drying, to remove the dioxane and unreacted polyhydric alcohol. The residue solid ingredient was ground and mixed with KBr powder at a weight ratio of 1 : 100. The FT-IR spectra were gained with a Fourier transform infrared spectrometer (Mattson Genesis II) using a diffuse reflectance accessory, with a deuterated triglycine sulfate detector. The scanning wave number of infrared was 4000–400 cm^{-1} at a resolution of 4 cm^{-1} .

Preparation of PU resins and measurement of gel properties

As the PU resins prepared, the molar ratios of the functional group of NCO for isocyanate to (COOH+OH) for liquefied wood were set as 1.0, 1.5, and 2.0. The organosiloxane was added as the surfactant and dibutyltin dilaurate was added as the catalyst, and the formulation was shown as Table I. The liquefied wood with surfactant and catalyst were mixed thoroughly first, and then the isocyanate was added and kept stirring. The time when the isocyanate was added until it could not flow was identified as the gel time.

FT-IR analysis of cured resins

The cured PU resins were ground to powder and dried in a vacuum oven at 60°C. The dried resin powder would be mixed with KBr, and the FT-IR spectra were measured as described in the previous section.

Bonding strength of PU resins

The counted amount of liquefied wood, surfactant, and catalyst were mixed and stirred first, and then the isocyanate was added and stirred thoroughly again. The strips of Lauan with the dimensions of 26 × 2.5 × 1.0 cm^3 were used as the adherend. The

resin would be applied on the surface of wood strips after it became sticky. The resin spread for each glue line was 200 g/m^2 . The glued specimens were cured at room temperature under 15 kgf/cm^2 pressure for 24 h. After de-pressing, the glued specimens were conditioned at 20°C and at 60% of relative humidity for 1 week. The bonding strength was measured with the compression shear test according to CNS 5809 standards, with the universal testing machine (Shimadzu UEH-10) under the loading rate of 1 min/mm . The shear bonding area of the testing specimens was 2.5 $\text{cm} \times 2.5 \text{ cm}$. The strength measured included both the dry and wet bonding strength. For the wet bonding strength, specimens were immersed in water under two different conditions before testing. One was immersion of the specimens in 60°C water for 3 h; and the other was immersion of the specimens in boiling water for 4 h, and then drying in an oven (60°C) for 20 h, and immersing in boiling water for 4 h again. After water-immersion treatment, the specimens were cooled in water (about 20°C) and then underwent the shear bonding strength testing. For all of the tested specimens, the wood failure was estimated by naked eye to the nearest 5% of shear area. Eight specimens were tested for each condition.

RESULTS AND DISCUSSION

Properties of liquefied wood

In this study, Taiwan acacia and China fir were liquefied in PEG/glycerol cosolvent, with sulfuric acid as a catalyst at 150°C, for 90 min. At the period of liquefaction procedure, wood components such as cellulose, hemicellulose, and lignin would be degraded or decomposed to lower molecular weight fragment under high temperature and acid condition. And then the hydroxide group, both in the decomposed wood fragment and polyhydric alcohol, would react with each other to form a derivative with an ether bond and then dissolve in the remaining free polyhydric alcohol. As shown in Table II, China fir had less undissolved wood residue than Taiwan acacia. This showed that the former had better liquefaction effect than the latter. Kurimoto et al.⁹ had pointed out that lignin was the component most easy to be liquefied, followed by hemicellulose and

TABLE II
Properties of Liquefied Wood

Wood species	Residue (%)		Viscosity (cP)	Acid value	Hydroxyl value
	By weight of liquefied wood	By weight of wood powder			
Taiwan acacia	4.8	19.4	5900	25.6	310
China fir	1.6	6.5	1370	38.0	287

noncrystalline cellulose, but crystallized cellulose was more hard compared to the liquefied one. Because Taiwan acacia had more cellulose than China fir,¹⁶ this may cause a higher residue in liquefied Taiwan acacia. If the polysaccharide was reacted with alcohol under suitable conditions, the alcohol-D-glycosides could be formed by glycolysis reaction. Kurimoto et al.⁹ had indicated that this reaction might occur at the liquefaction of wood within PEG. The hydroxyl value for China fir was lower than Taiwan acacia in Table II. This might be caused by the better effect of liquefaction for China fir and much more of the glycolysis reaction taking place between the polyhydric alcohol and wood component resulting in a lower hydroxyl value.

FT-IR analysis of liquefied wood

Figure 1 shows the FT-IR spectra of the wood and liquefied wood of Taiwan acacia and China fir in the range from 400 to 4000 cm^{-1} . The untreated Taiwan acacia and China fir had a strong and broad absorption band at 3000–3500 cm^{-1} . This was attributed to the hydroxide group in the wood components. After liquefaction, this absorption decreased significantly. This showed that the hydroxide group in wood components would react with polyhydric alcohol in the processing of liquefaction. The absorption band of 2908 cm^{-1} and 2907 cm^{-1} for Taiwan acacia and China fir, respectively, were attributed to the C—H and CH_2 vibration of aliphatic hydrocarbon. Both of them increased significantly after liquefaction, suggesting that PEG had induced into the structure of liquefied wood. The absorption at 1743 cm^{-1} and 1736 cm^{-1} for untreated Taiwan acacia and China fir were the stretching vibration of carbonyl group that belongs to the acetyl group or carboxyl groups. After liquefaction, the intensity of this absorption became stronger, and it indicated that some of the cellulose, hemicellulose, and lignin were oxidated and form a new aldehyde group or carboxyl group in their structure.¹⁰

The untreated China fir had the absorption band which was attributed to the C—O—C symmetrical stretching vibration of the β -O-4'-ether linkage between the phenyl propane of lignin, and the

absorption band at 1151 cm^{-1} which was attributed to the unsymmetrical C—O—C stretching vibration of the ether linkage between the aliphatic components such as cellulose. After liquefaction, these two absorption peaks disappeared, but a significant new ether bond absorption band appeared at 1097 cm^{-1} . This indicated that the wood component would be degraded and reacted with PEG by a new ether linkage to form a derivative. This phenomenon had occurred for liquefied Taiwan acacia too. The 1057 and 1108 cm^{-1} absorption bands in the untreated wood would disappear after liquefaction, and a new absorption had formed at 1100 cm^{-1} .

Gel properties of PU resins

In this study, PU resins were prepared by blending the liquefied wood with three kinds of isocyanate: PMDI, Desmodur L, and Desmodur N. Among which, both PMDI and Desmodur L belong to the aromatic isocyanate, but Desmodur N is an aliphatic isocyanate. Table III is the gel time of PU resins prepared from liquefied woods blending with Desmodur L with the molar ratio of $\text{NCO}/(\text{OH}+\text{COOH})$ as 1.0, 1.5, and 2.0. It showed that addition the surfactant could shorten the gel time. This might be

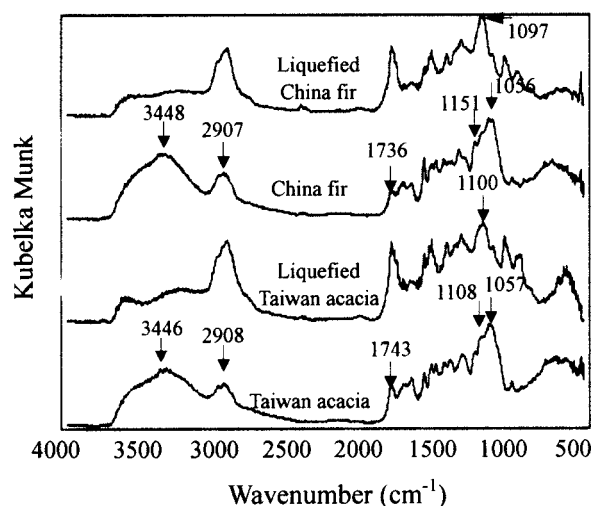


Figure 1 FT-IR spectra of wood and liquefied wood.

TABLE III
Gel Time of PU Resins Prepared from Liquefied Wood Blending with Desmodur L

Liquefied wood	NCO/(OH+COOH) (molar ratio)	Surfactant (%)	
		0	2
Taiwan acacia	1.0	108	101
	1.5	129	126
	2.0	161	157
China fir	1.0	119	114
	1.5	146	125
	2.0	160	151

The unit of gel time is min; the surfactant added is based on the weight of liquefied wood and no catalyst was added.

because the compatibility between the hydrophilic liquefied wood and hydrophobic isocyanate was improved, and hence promote the reactivity between liquefied wood and isocyanate.¹⁷ For PU resins, the isocyanate acts as a crosslinking agent to link the molecule of polyols in the period of curing. In theory, by increasing the rate of isocyanate in the system, the opportunity of reaction between the liquefied wood and isocyanate will be increased. But as shown in Table III, the gel time prolonged as the molar ratio of NCO/(OH+COOH) increased. Since Desmodur L is an adduct compound from three molecules of toluene diisocyanate with one molecule of trimethylol propane. The NCO group in the benzene ring exists at the ortho-position of the methyl group, and the stereochemical hindrance might restrict the reaction between Desmodur L and liquefied wood. So, some of the isocyanate might not react with liquefied wood at a short time if too much Desmodur L was added. This would let it display a sticky appearance, and prolong the gel time. Besides, at the period of curing for PU resins, isocyanate may react with polyol and water existing in the liquefied wood to form a urethane and urea link,

respectively. Although both of them can react with the overdosed isocyanate to form an allophanate and a biuret structure,¹¹ these are secondary reactions with a lower reaction rate. It might be the other reason that causes the prolonged gel time under a higher molar ratio of NCO/(OH+COOH).

Table IV shows the gel time of PU resins prepared from liquefied wood blending with Desmodur N. As compared with Table III, the gel time in Table IV used Desmodur N, as the raw material was triple longer than Desmodur L if no catalyst was added. But the phenomenon that increasing the molar ratio of NCO/(OH+COOH) would prolong the gel time was the same as Desmodur L. This result might be caused by the difference in molecular structure between Desmodur L and Desmodur. Desmodur N is an aliphatic isocyanate. But Desmodur L is an aromatic isocyanate, which has an aromatic benzene ring with resonance structure. This would let the electrons transfer more easily, promote reactivity, and shorten the gel time needed for curing than Desmodur N.

Because the gel reaction of PU resins prepared from Desmodur N without catalyst was too slow, adding the catalyst was needed to shorten their gel time. As shown in Table IV, the gel time could be shortened substantially with the addition of only 1% of the catalyst. By increasing the amount of catalyst, the gel time would be shortened further. Comparing the gel time between the liquefied China fir and Taiwan acacia, the former was shorter than the latter when 1% of catalyst was added. This might be caused the lower viscosity of liquefied China fir as shown in Table II, which could let molecular motion more easier and increasing the chance to react with isocyanate.

Table V shows the gel time of PU resins prepared from liquefied wood blending with PMDI. They were cured within 13 min, and this time was too short for the gluing operation. Also, PMDI had high foaming capacity. If the PU resins were prepared from PMDI and applied on the wood surface, the

TABLE IV
Gel Time of PU Resins Prepared from Liquefied Wood Blending with Desmodur N

Surfactant ^a (%)	NCO/(OH+COOH) (molar ratio)	Catalyst (%)				
		Liquefied Taiwan acacia				Liquefied China fir
		0	1	2	3	1
0	1.0	326	124	79	53	26
	1.5	447	138	68	54	50
	2.0	504	191	100	68	45
2	1.0	326	111	73	49	53
	1.5	417	77	73	59	52
	2.0	462	157	82	64	53

The unit of gel time is min; the catalyst added is based on the weight of liquefied wood.

TABLE V
Gel Time of PU Resins Prepared from Liquefied Wood Blending with PMDI

Liquefied wood	NCO/(OH+COOH) (molar ratio)	Surfactant (%)	
		0	2
Taiwan acacia	1.0	13	11
	1.5	13	13

The unit of gel time is min; the surfactant added is based on the weight of liquefied wood and no catalyst added.

bubbles would exist in the glue-line, and a good adhesive performance could not be expected. So, in follow-up studies, only Desmodur L and Desmodur N would be used to prepare the PU resins for wood gluing.

FTIR analysis of cured PU resins

Figure 2 shows the FTIR spectra of liquefied Taiwan acacia and cured PU resin made from liquefied Taiwan acacia blending with Desmolur L with various molar ratios of NCO/(OH+COOH). The characteristic absorption band of the NCO group at 2250–2270 cm^{-1} had not been found, which suggested that the NCO groups in isocyanate were completely consumed to form urethane or urea linkages. However, new absorption bands appearing at 1720, 1702, 1529, 1216, and 1070 cm^{-1} had been found. This was credited to the urethane linkage formed by the reac-

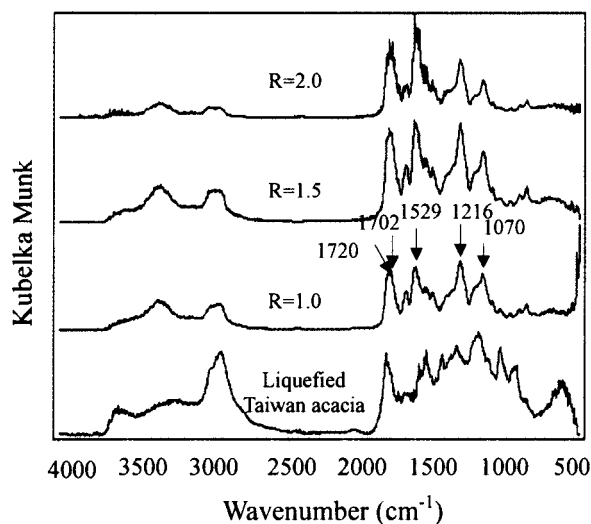


Figure 2 FTIR spectra of cured PU resins prepared from liquefied Taiwan acacia blending with Desmodur L at various molar ratios of NCO/(OH+COOH) (2% of surfactant added based on the weight of liquefied wood and no catalyst added).

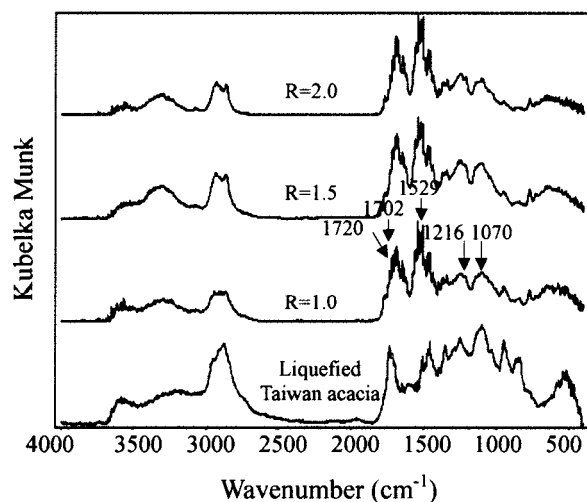


Figure 3 FTIR spectra of cured PU resins prepared from liquefied Taiwan acacia blending with Desmodur N at various molar ratios of NCO/(OH+COOH) (2% of surfactant and; 1% of catalyst added based on the weight of liquefied wood).

tion between liquefied wood and Desmodur L. The absorption band at 1702 cm^{-1} was attributed to the stretching vibration of hydrogen-bonded carbonyl group between the N—H and C=O groups of urethane structure, and the absorption band at 1720 cm^{-1} was attributed to the stretching vibration of the free carbonyl group. The absorption band at 1529 cm^{-1} could be credited to the bending vibration of NH bond, and the 1216 cm^{-1} was the stretching vibration of the C—N bond in the urethane linkage structure.^{10,18} The 1070 cm^{-1} was attributed to the stretching vibration of —COO— in urethane structure. As the molar ratio of NCO/(OH+COOH)

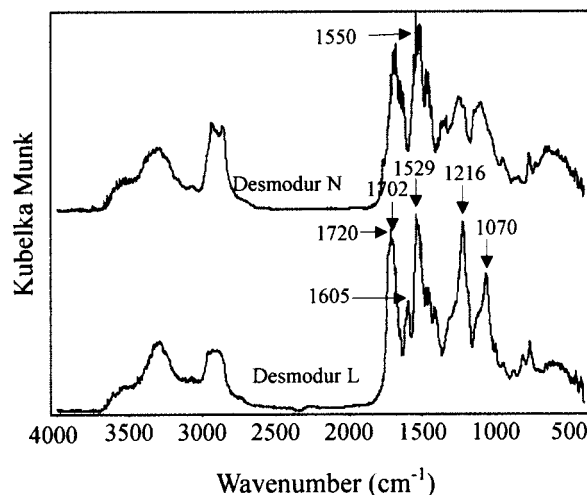


Figure 4 FTIR spectra of cured PU resins prepared from different isocyanate ($R = 1.5$ with 2% of surfactant; no catalyst added for Desmodur L and 1% of catalyst added for Desmodur N).

TABLE VI
Dry Bonding Strength of Wood Specimens Bonded with PU Adhesives

Isocyanate	Liquefied wood	Surfactant (%)	NCO/(OH+COOH) (molar ratio)		
			1.0	1.5	2.0
Desmodur L	Taiwan acacia	0	9.1 ± 1.3 (84)	9.2 ± 1.4 (99)	10.6 ± 1.2 (88)
		2	8.6 ± 1.1 (78)	8.8 ± 1.0 (86)	8.6 ± 1.2 (97)
	China fir	0	8.5 ± 1.6 (83)	9.2 ± 1.1 (86)	9.4 ± 1.2 (94)
		2	8.0 ± 1.9 (61)	9.0 ± 1.2 (99)	8.9 ± 1.4 (99)
Desmodur N	Taiwan acacia	0	3.5 ± 1.9 (2)	3.4 ± 1.0 (0)	6.2 ± 1.3 (19)
		2	2.0 ± 1.4 (0)	4.1 ± 1.0 (0)	5.5 ± 0.7 (0)
	China fir	0	1.2 ± 0.7 (0)	3.2 ± 0.8 (3)	3.3 ± 1.2 (0)
		2	1.8 ± 1.4 (0)	2.6 ± 0.6 (0)	2.7 ± 0.9 (0)

The unit of bonding strength is MPa; values in parentheses indicate wood failure (%); no catalyst added for Desmodur L, and 1% of catalyst added for Desmodur N.

The weight percent of surfactant and catalyst were based on the weight of liquefied wood.

increased, the intensity of the absorption band of 1720, 1702, and 1529 cm^{-1} became stronger, which signaled that much more of the urethane linkage had formed between the liquefied wood and isocyanate.

Figure 3 shows the FTIR spectra of the cured PU resin made from liquefied Taiwan acacia blending with Desmodur N, with various molar ratios of NCO/(OH+COOH). The absorption bands at 1720, 1702, and 1529 cm^{-1} were obvious, suggesting that urethane linkage had formed between liquefied wood and Desmodur N, but their intensity did not increase as the NCO/(OH+COOH) ratio increased, as shown in Figure 2. Figure 4 compares the FTIR spectra of cured PU resins, those made from Desmodur L and Desmodur N. Both of them had urethane adsorption at 1720, 1702, and 1529 cm^{-1} . The PU resin using Desmodur N as raw materials had an obvious urea absorption band at 1550 cm^{-1} , but less absorption at 1216 cm^{-1} and 1070 cm^{-1} that were attributed to the stretching vibration of C—N and

—COO— bond of urethane, respectively. It could be guessed that using Desmodur N as raw materials led to more urea structure than using Desmodur L in the cured PU resin. Besides, the adsorption band at 1605 cm^{-1} that attributed to the aromatic skeletal ring vibration had formed for aromatic Desmodur L, but not for aliphatic Desmodur N.

Bonding properties of PU resins

Vick et al.¹⁹ used four commercial one-part PU adhesives to bond yellow birch, and they found that these PU adhesives had dry bonding strength stronger than resorcinol adhesive (RF). But after boil-dry-boil treatment, the wet bonding strength of these bonded wood specimens retained was only 36–38% of their dry bonding strength, and the wood failure dropped off to lower than 22%. In our experiment, the dry bonding strength of various PU adhesives prepared from liquefied wood blending with Desmodur L and Desmodur N are shown in Table VI. The

TABLE VII
Wet Bonding Strength of Wood Specimens Bonded with PU Adhesives and Testing After 60°C Water Immersion

Isocyanate	Liquefied wood	Surfactant (%)	NCO/(OH+COOH) (molar ratio)		
			1.0	1.5	2.0
Desmodur L	Taiwan acacia	0	3.3 ± 0.8 (0)	5.9 ± 1.2 (6)	7.8 ± 0.8 (18)
		2	3.3 ± 0.4 (5)	6.5 ± 0.8 (8)	6.7 ± 1.5 (48)
	China fir	0	2.0 ± 0.2 (0)	6.1 ± 1.0 (11)	7.2 ± 0.7 (23)
		2	2.3 ± 0.7 (0)	5.3 ± 1.0 (2)	6.8 ± 1.1 (43)
Desmodur N	Taiwan acacia	0	2.1 ± 1.0 (0)	2.8 ± 1.1 (0)	2.9 ± 0.9 (1)
		2	0.6 ± 0.6 (0)	2.2 ± 1.1 (0)	2.2 ± 0.8 (0)
	China fir	0	1.0 ± 0.4 (0)	1.5 ± 0.4 (0)	2.0 ± 0.5 (0)
		2	0.8 ± 0.2 (0)	1.6 ± 0.9 (0)	1.2 ± 0.4 (0)

Testing after 60°C water immersion.

The unit of bonding strength is MPa; values in parentheses indicate wood failure (%).

No catalyst added for Desmodur L, and 1% catalyst added for Desmodur N.

The weight percent of surfactant and catalyst are based on the weight of liquefied wood.

TABLE VIII
Wet Bonding Strength of Wood Specimens Bonded with PU Adhesives and Testing
After Repeated Boiling Water Immersion

Isocyanate	Liquefied wood	Surfactant (%)	NCO/(OH+COOH) (molar ratio)		
			1.0	1.5	2.0
Desmodur L	Taiwan acacia	0	1.8 ± 1.1 (0)	4.9 ± 1.9 (10)	3.9 ± 2.3 (15)
		2	1.1 ± 0.7 (0)	3.4 ± 1.1 (0)	4.0 ± 1.6 (14)
Desmodur N	China fir	0	0.9 ± 0.7 (0)	3.2 ± 1.4 (4)	4.8 ± 1.3 (18)
		2	0.6 ± 0.3 (0)	2.1 ± 1.1 (1)	4.0 ± 1.1 (8)
	Taiwan acacia	0	0.1 ± 0.1 (0)	0.4 ± 0.2 (0)	0.7 ± 0.4 (0)
		2	0.1 ± 0.2 (0)	0.2 ± 0.2 (0)	0.3 ± 1.0 (0)
China fir	0	0.2 ± 0.2 (0)	0.1 ± 0.1 (0)	0.1 ± 0.1 (0)	
	2	0.0 ± 0.0 (0)	0.3 ± 0.3 (0)	0.1 ± 0.1 (0)	

Testing after repeated boiling water immersion.

The unit of bonding strength is MPa; values in parentheses indicate wood failure (%).

No catalyst added for Desmodur L, and 1% catalyst added for Desmodur N.

The weight percent of surfactant and catalyst were based on the weight of liquefied wood.

strength was influenced by the kind of isocyanate. Using Desmodur L as the raw material had a bonding strength better than Desmodur N. The PU adhesive prepared from blending liquefied Taiwan acacia with Desmodur L with the molar ratio of NCO/(OH+COOH) of 1.0 and without surfactant added had the bonding strength of 9.1 MPa, but it was only 3.5 MPa for that using Desmodur N as raw material. In addition, the former had 84% of wood failure, but the latter showed adhesive cohesion failure. In general, the bonding strength is a correlative response to both the interfacial strength between adhesive and adherend, and the cohesion strength of adhesive or adherend. Because Desmodur L has the benzene ring in its molecular structure, it can provide the NCO group more reactivity and let the crosslinking reaction more complete. Furthermore, the aromatic structure of Desmodur L may induce the cured PU film more stiffness than aliphatic Desmodur N. All of this may be the reason for Desmodur L having a better bonding strength than Desmodur N.

The dry bonding strength in Table VI obviously depend on the molar ratio of NCO/(OH+COOH). Higher the molar ratio of NCO/(OH+COOH), higher the bonding strength would be. For example, the PU adhesive prepared from liquefied Taiwan acacia blending with Desmodur L at the molar ratio of NCO/(OH+COOH) as 1.0, 1.5, and 2.0 had the dry bonding strength of 9.1, 9.2, and 10.6 MPa, respectively. This trend was displayed for other formulations too. The strength increment might contribute to the higher crosslinking density of the cured glue-line, which was caused by the reaction of the urethane and the urea structure with more isocyanate added to form the allophanates and biuret structure.¹¹

The surfactant could improve the compatibility between liquefied wood and isocyanate and shorten the gel time of PU resins, as described in the previ-

ous section. But it had a negative effect for bonding strength as shown in Table VI. This might be because the surfactant would play as a weak position in the glue-line and reduce the bonding strength.

Tables VII and VIII show the wet bonding strength of various PU adhesives. From these results, using Desmodur L as raw materials had better wet bonding strength than Desmodur N. Increasing the molar ratio of NCO/(OH+COOH) could increase the wet bonding strength as those described in dry bonding strength. For example, as the PU adhesives were prepared with Desmodur L as raw materials, and had the molar ratio of NCO/(OH+COOH) at 1.5 and 2.0, the wet bonding strength could over 5.9 MPa after 60°C water immersed. This strength could fit the requirement of the CNS 11031 standard. But all the bonding strength would decrease significantly after repeated soaking with boiling water.

CONCLUSIONS

In this study, woods of Taiwan acacia and China fir were liquefied in PEG-glycerol cosolvent with the weight ratio of solvent to wood as 3/1, and using H₂SO₄ as the catalyst. The liquefied woods had blended with PMDI, Desmodur L, and Desmodur to prepare PU resins. The result showed that the gel property of PU resins was influenced by the kind of isocyanates, the molar ratio of NCO/(OH+COOH), and the rate of catalyst added. Among those, the PU resins prepared with Desmodur L had a suitable gel time for processing. As these PU resins were used as wood adhesives, blending liquefied Taiwan acacia with Desmodur L had better dry and wet bonding strength than with Desmodur N. The bonding strength of these PU

resins could be increased with a higher molar ratio of NCO/(OH+COOH).

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