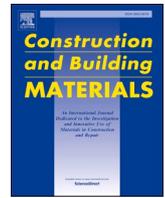




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Optimized condition for eco-friendly wood composites manufactured from castor oil-based polyurethane

Yi-Hua Chen, Cheng-Hao Wu, Yi-Chun Chen*

Department of Forestry, National Chung-Hsing University, Taichung, 402202, Taiwan

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ABSTRACT

Castor oil is used as polyurethane (PU) polyol raw material with three kinds of isocyanate. In this study, polymeric diphenylmethane diisocyanate (PMDI), Desmodur L and Desmodur N were used to compare the structures of aromatic isocyanate oligomers, aromatic isocyanate trimers and aliphatic isocyanate trimers. Water, organosiloxane and dibutyltin dilaurate were used as the bubble agent, surfactant and catalyst to manufacture PU resin with molar ratios of NCO/OH of 1/1, 1.5/1 and 2/1, respectively. The results show that increasing the NCO/OH molar ratio increases the water absorption and hard segment content of PU resins. PMDI-based PU and Desmodur N-based PU resins have high thermal stability. The low-density composites of ca. 450 Kg/m³ were prepared successfully from a mixture of PU resin and China fir (*Cunninghamia lanceolata*) particles. The results demonstrated that increasing the NCO/OH molar ratio and using Desmodur L are optimal and beneficial to improving the composites' dimensional stability and internal bonding strength. The composites prepared with bio-based PU resins have lower thickness swelling rates and higher internal bonding strengths than formaldehyde-based and commercial PU-based resins. Bio-based PU composites can be used as eco-friendly building materials and replace formaldehyde-based manufacturing composites.

1. Introduction

Traditional adhesives include formaldehyde-based adhesives, such as urea–formaldehyde resin, phenol–formaldehyde resin and melamine–urea–formaldehyde resin for manufacturing wood composite materials. Formaldehyde is suspected to be a human carcinogen. Moreover, urea–formaldehyde resin in wood composites for furniture, floor underlayment, home constructions, and other application leads to formaldehyde emissions [1–3]. For improving composite performance, adding nanoparticles and chemicals to adhesive or modified resins/processes can increase the properties. Previous studies use organic [4,5] or inorganic nanofiller [6–8] to enhance the mechanical properties and reduce formaldehyde emission. Using the vacuum-assisted resin transfer molding process can also help manufacture hybrid green composites with enhanced performance [9–11]. In addition, using non-toxic resins such as PU resin to replace formaldehyde resin is very attractive [12,13]. Polyol is the main component of PU resins, and it contains at least two reactive groups, including polyether polyols, polyester polyols, and polycarbonates. Isocyanates are also one of the main raw materials of PU resins and have highly reactive organic functional groups involved in

various chemical reactions [14]. PU resins can be prepared by mixing a diisocyanate with a diol or polyol in a specific NCO/OH ratio. Commercially available organic isocyanates include aliphatic, cycloaliphatic, araliphatic, aromatic, and heterocyclic isocyanates. PU resins offer a high flexibility of formulation and facilitate application technologies to tune the mechanical and adhesion properties. The weather and solvent resistance of PU resin comes from its hard-segment and cross-linking structure [15,16], and thus this resin is widely used in the field of coatings and adhesives [13,17].

Raw materials of PU resin are drawn from sustainable resources. This further promotes the renewable and eco-friendly application of PU resin. Plant oils are the most important renewable raw materials for the chemical industry [18]. Castor oil is an essential bio-based chemical and can easily be extracted from castor seeds with 47–49% oil. Castor oil is renewable, low in cost, eco-friendly and non-edible, which means it is non-competitive with food crops [19]. Castor oil is a triglyceride derived from ricinoleic acid and is mainly chemically composed of 90% fatty acids. Castor oil is used for industrial applications because of its chemical composition, low cost, and stable supply [19,20]. Ricinoleic acid, a monounsaturated 18-carbon fatty acid, has a hydroxyl functional group

* Correspondence author.

E-mail address: chenyc@nchu.edu.tw (Y.-C. Chen).<https://doi.org/10.1016/j.conbuildmat.2021.124789>

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at the 12th carbon. The hydroxyl group can react with the NCO group of isocyanate to form a urethane structure [21]. Castor oil-based PU resin can be used as an adhesive to manufacture composites. Fiorelli et al. [22] reported a method for producing coconut fiber particle board using castor oil-PU adhesive. Fiorelli et al. [23] manufactured bagasse granules-based composite using a castor oil-based PU adhesive. Wechsler et al. [24] prepared castor oil and methylene diphenyl diisocyanate derived resin to make a composite of ground macadamia nut shells. Chen and Tai [25] mixed castor oil and poly (4,4'-methylene diphenyl isocyanate) to prepare PU resin for manufacturing bamboo charcoal composites. Cassales [26] used castor oil, polymeric methyl phenyl diisocyanate, and kraft lignin to prepare lignopolyurethane films. According to previous studies, castor oil-based PU resin has been used to prepare composites and has a high potential to replace traditional PU and urea-formaldehyde resin [27]. However, previous studies have only used one kind of isocyanate for castor oil-based composites. No studies have compared various structures of isocyanates for castor oil-based PU resins and their lignocellulosic composites.

In this study, castor oil is used as a polyol to increase the biomass content of a composite. PMDI, Desmodur L, and Desmodur N were aromatic isocyanate oligomer, aromatic isocyanate trimer and aliphatic isocyanate trimer that provided NCO groups to prepare bio-based PU resin. The structures of PMDI, Desmodur L, and Desmodur N are polymeric 4,4'-diphenylmethane diisocyanate, an adduct of toluene diisocyanate with trimethylol propane and trimer of hexamethylene diisocyanate. The chemical structures of isocyanates, castors oil, and the PU resins are shown in Scheme 1. The other purpose of this study is to increase the usage rate of domestic thinning wood that is granulated for the preparation of bio-based composite. This study compared the effects of three kinds of isocyanates and three different ratios of NCO/OH, with molar ratios of 1.0, 1.5, and 2.0, on PU resin properties and composites. Reactivity, chemical structure, and thermal stability of PU resins were investigated. PU resin was used as the adhesive to manufacture low-density composites with the target density set as 450 Kg/m³. The water absorption, dimensional stability, and internal bond strength of the composites were measured and discussed.

2. Materials and methods

2.1. Materials

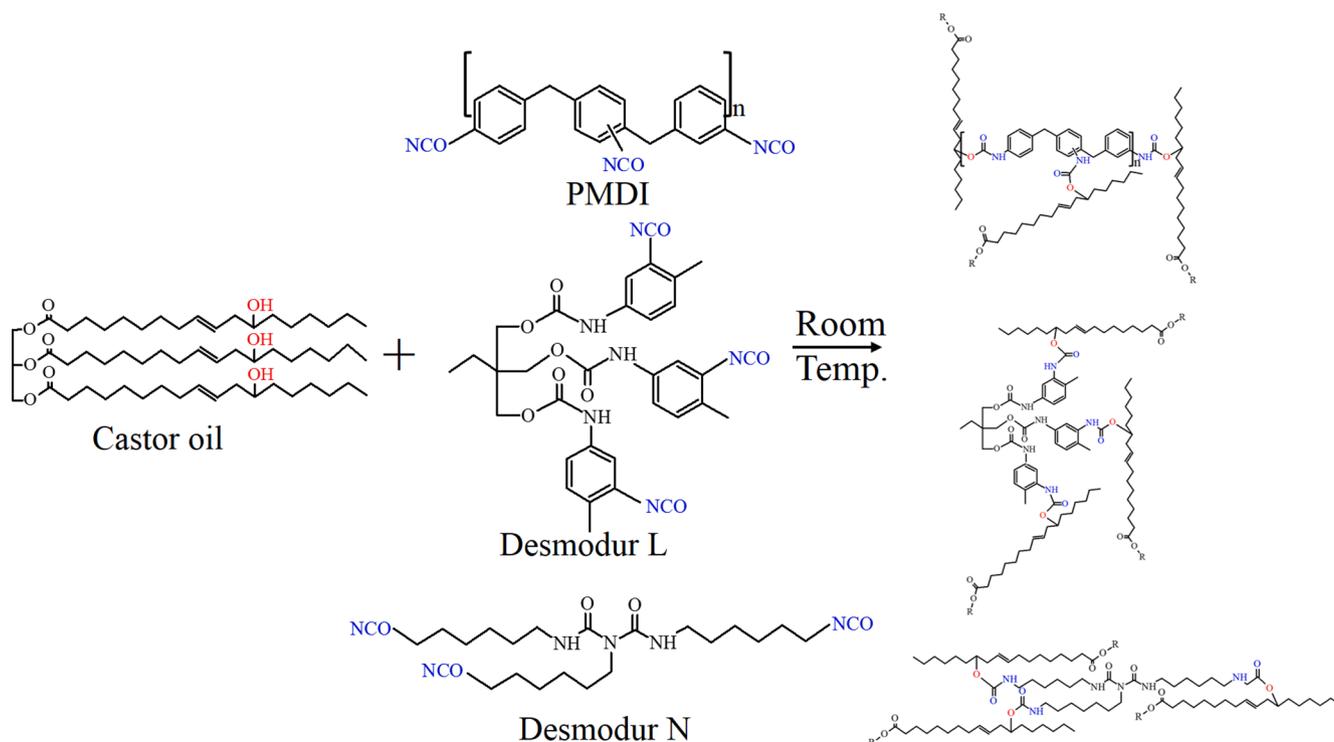
China fir was used in this study and obtained from the Hui-Sun Experimental Forest Station in Nantou, Taiwan. The wood particles were ground to pass through a 2.4-mm screen and dried in an oven at 103 ± 2 °C for 24 h. PMDI, Desmodur L (Aromatic polyisocyanate based on toluene diisocyanate), Desmodur N (Hexamethylene diisocyanate trimer), dibutyl tin dilaurate (DBTDL) and organosiloxane were purchased from An Fong Develop Co., Ltd., Taichung, Taiwan. PMDI, Desmodur L and Desmodur N with NCO contents of 28.9, 12.2 and 21.0 %, were used as isocyanate compounds. The NCO content was 23.07%. Castor oil was purchased from Chung-Hsing Chemical, Taichung, Taiwan. Tetrahydrofuran (THF) and potassium bromide were purchased from Merck. The hydroxyl value of castor oil is 148.83 mg KOH/g. The previous properties of chemicals were determined in the authors' laboratory.

2.2. Preparation of PU resins

The method of PU resin preparation followed the approach proposed in previous studies [13,25]. Briefly, castor oil, surfactant, bubble agent and catalyst were weighted, and stirred at 200 rpm for 1 min. The PU resins were prepared by blending the mixture with isocyanate PMDI, Desmodur L, and Desmodur N and also stirred at 200 rpm for 1 min. The molar ratios of NCO/OH were set as 1.0, 1.5, and 2.0 and the formulation of PU resins are shown in Table 1. According to a previous study [28], the foaming properties were recorded. Before the tests, the PU resin was kept at room temperature for one week. Powder of PU resin was ground to pass through a 0.074-mm screen for the followed experiments.

2.3. Characterization of PU resins

PU resin was cut into $2 \times 2 \times 2$ cm³ specimens. The apparent density



Scheme 1. The synthesized route of PU resin with PMDI, Desmodur L, and Desmodur N.

Table 1
The formulation of PU resin (Weight by parts).

Code	PMDI	Desmodur L	Desmodur N	Castor oil	Surfactant	Bubble agent	Catalyst
P-1.0	51	–	–	100	4	2	2
P-1.5	76	–	–	100	4	2	2
P-2.0	101	–	–	100	4	2	2
L-1.0	–	120	–	100	4	2	2
L-1.5	–	180	–	100	4	2	2
L-2.0	–	241	–	100	4	2	2
N-1.0	–	–	70	100	4	2	2
N-1.5	–	–	105	100	4	2	2
N-2.0	–	–	140	100	4	2	2

and water immersion testing was measured using an approach outline in a previous study [29]. The weight and size of specimens were measured, and then the samples were immersed in distilled water at room temperature. After immersing for one week, the specimens were dried in an oven at 103 ± 2 °C and then weighed. The density, water absorption, and weight retention were calculated using the followed equations.

$$\text{Density (Kg/m}^3\text{)} = \frac{W_0}{V_0} \quad (1)$$

$$\text{Water absorption(\%)} = \frac{W_1 - W_0}{W_0} \times 100 \quad (2)$$

$$\text{Weight retention (\%)} = \frac{W_2}{W_0} \times 100 \quad (3)$$

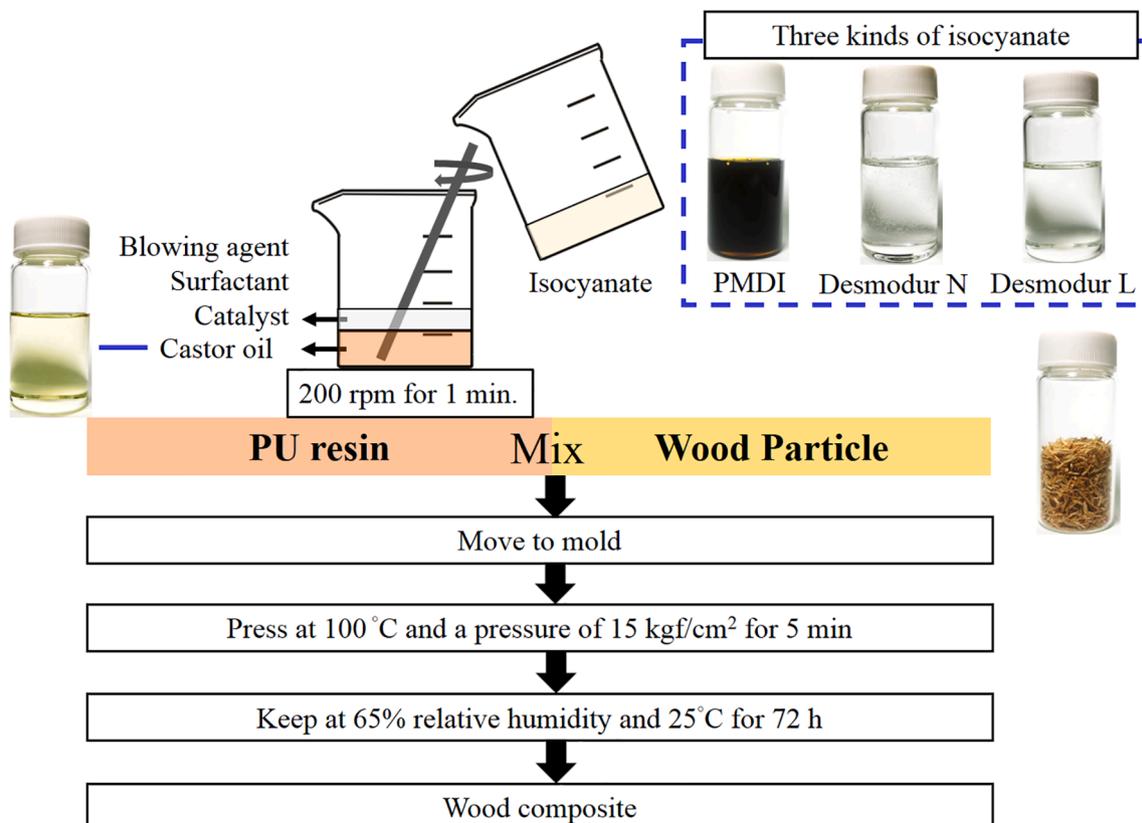
W_0 and V_0 are the weight and volume of the specimen before immersing (dry weight basis), W_1 is the weight of the specimen after immersing for one week, and W_2 is the dry weight after immersing. Three specimens were used in this experiment.

2.4. FTIR analysis

Water was removed from the powder of PU resin by in a vacuum oven set at 40 °C overnight. Each sample was characterized by Fourier transform infrared spectroscopy (FTIR) with attenuated total reflectance mode (ATR). Castor oil and isocyanates were diluted with THF deposited on the potassium bromide tablet for FTIR analysis. The samples were analyzed by transmittance, in the region between 4000 and 650 cm^{-1} with a resolution of 4 cm^{-1} and 16 scans were carried out.

2.5. Thermal stability

The thermal stability of PU resin was measured using Perkin-Elmer Pyris 1. For thermogravimetric analysis (TGA), 3–5 mg of PU resin powder was put into a platinum sample pan and heated from 50 to 650 °C at a heating rate of 10 °C /min under a nitrogen atmosphere. The powder PU can help the heat evenly in small platinum plate. TGA repeated twice to check the precision and accuracy. The weight losses at various temperatures were also recorded. Curves of weight losses and their derivatives were plotted. The temperatures were determined at 10% (T_{10}) weight.



Scheme 2. Flow chart for the manufacture of wood composite.

2.6. Preparation of wood composites

The target density of the composites was 450 kg/m^3 at the size of $15 \times 15 \times 1.2 \text{ cm}^3$. Weight ratios of wood particles/PU resin were 1/1, 1.5/1, and 2/1. Scheme 2 shows the flow chart for the preparation of wood composites and the appearance of the raw materials. In the beginning, surfactant, catalyst, distilled water, and castor oil were weighed and stirred at 200 rpm for 1 min. The previous mixture was well mixed with wood particles and isocyanates. Immediately, the composites were pressed at a platen temperature of $100 \text{ }^\circ\text{C}$ and a pressure of 15 kgf/cm^2 for 5 min. The composites were kept at 65% relative humidity (RH), and $25 \text{ }^\circ\text{C}$ for 72 h. $5 \times 5 \times 1.2 \text{ cm}^3$ pieces were used to determine internal bond strength, density, moisture content, and water resistance.

2.7. Characterizations of wood composites

2.7.1. Density

The particle board density tests were conducted according to CNS (National Standards of the Republic of China) 2215. The density was calculated by equation (1).

2.7.2. Equilibrium moisture content

The specimen were kept at 65% RH and $25 \text{ }^\circ\text{C}$ until reaching constant weight. Then they were placed in an oven set at $103 \pm 2 \text{ }^\circ\text{C}$ for 24 h. After 24 h, we measured the oven-dry weight of specimens. Moisture content was calculated using Eq. (4). Three specimens were measured in this experiment.

$$\text{Moisture content}(\%) = \frac{M_3 - M_4}{M_3} \times 100 \quad (4)$$

M_3 and M_4 are the air- and oven-dry weight of the specimen.

2.7.3. Internal bond strength

The tensile load was applied vertically to each specimen with 2 mm/min load speed, measuring the maximum load (P') at the time of fracture of the internal composite. The internal bond can be calculated by Eq. (5). Three specimens have used in this experiment.

$$\text{Internal bond (N/mm}^2\text{)} = \frac{P'}{b \times L} \quad (5)$$

P' is the maximum load (N), b the width of the specimen (mm), and L is the length (mm) of the specimen.

2.7.4. Water resistance

The specimens were horizontally placed 3 cm under the surface of the water. The water absorption and thickness swelling of specimens were calculated before and after immersing in water for 24 h. The percentages of the water absorption and thickness swelling were calculated by Eq. (6) and (7), respectively. Three specimens were used for this experiment.

$$\text{Water absorption}(\%) = \frac{W_5 - W_3}{W_3} \times 100 \quad (6)$$

W_5 is the final weight after immersing for 24 h, and W_3 is the air-dry weight.

$$\text{Thickness swelling rate}(\%) = \frac{T_1 - T_0}{T_0} \times 100 \quad (7)$$

T_1 is the final thickness after soaking for 24 h, and T_0 is the initial thickness.

2.8. Statistical analyses

Statistical analysis was performed using SPSS software version 20 (SPSS Inc., Chicago, IL, USA). Tukey's multiple range test was used to determine the statistical significance ($P \leq 0.05$) between pairs. Statistical

results are showed as English alphabet in Table 3 and Fig. 4; different letters reveal statistical differences significantly. The statistical difference of data uses "significantly" to describe the results and discussion.

3. Results and discussion

3.1. Foaming behavior and appearance of PU resins

Table 2 shows the foaming properties of the castor oil mixed with three kinds of isocyanate: PMDI, Desmodur L, and Desmodur N. The result shows isocyanate type affects its foaming properties. The reaction time of the foaming reaction is Desmodur L > Desmodur N > PMDI. This result may be attributed to different chemical structures of isocyanates. Reactivity of linear chain isocyanates (PMDI) to OH groups was greater than those of trimers with side chains (Desmodur L and Desmodur N). Desmodur L has low reactivity because the NCO groups exist at the *ortho*-position of the methyl group in the benzene ring. It is possible to achieve stereochemical hindrance of the hydroxyl group and the -NCO group [30]. The results also indicate that varying NCO/OH ratios do not influence on foaming reactions. After reaction, Fig. 1A shows that the colors of PMDI, Desmodur L, and Desmodur N-based PU resin are brown, pale yellow, and yellow, respectively. As the ratio of isocyanate increases, the colors of PMDI- and Desmodur N-based PU resins become darkening. The results also indicated PU resins have a uniform appearance.

3.2. Characterization of PU resins

Table 3 shows the density, water absorption, and weight retention of the PU resins. Increasing NCO/OH ratio reduces the density of the PU resin and increases the water absorption, which is similar to the findings of a previous investigation [13]. The weight retention of PU resin is higher than 96.7%, revealing excellent water resistance. The results also indicate that using Desmodur L decreases the weight retention of PU resin significantly, which may be due to the stereochemical hindrance of functional groups. Water absorption and retention of bio-based PU resin are related to the pore structure and cross-link density, respectively [31]. The results demonstrated that PU resins with high NCO/OH ratios have lower relative density and absorb more water with larger pores. Lee et al. [32] indicated that weight retention after solvent immersion could be a positive index of the degree of cross-linking of PU resin. Therefore, Desmodur L-based PU resin had slightly less cross-link density than PMDI-based and Desmodur N-based PU resins.

3.3. FTIR analysis

The FT-IR spectra of castor oil and isocyanates are shown in Fig. 2A. The pattern of castor oil shows characteristic peaks at 3450 cm^{-1} and 3008 cm^{-1} , indicating O-H stretching vibration and C-H stretching of aliphatic CH = CH. The bands at 2926 and 2885 cm^{-1} are assigned to the stretching vibration of -CH₃ and -CH₂ groups, respectively. The bands at around 1743 cm^{-1} correspond to C = O stretching vibration. Two peaks appearing at 1161 and 722 cm^{-1} are attributed to C-O-C stretching

Table 2
Foaming properties of the PU resins.

Code	Cream time (s)	End of rise time (s)	Tack-free time (s)
P-1.0	5	78	192
P-1.5	2	58	58
P-2.0	2	64	64
L-1.0	10	<900	<900
L-1.5	20	<900	<900
L-2.0	17	<900	<900
N-1.0	17	290	290
N-1.5	28	387	387
N-2.0	16	249	249

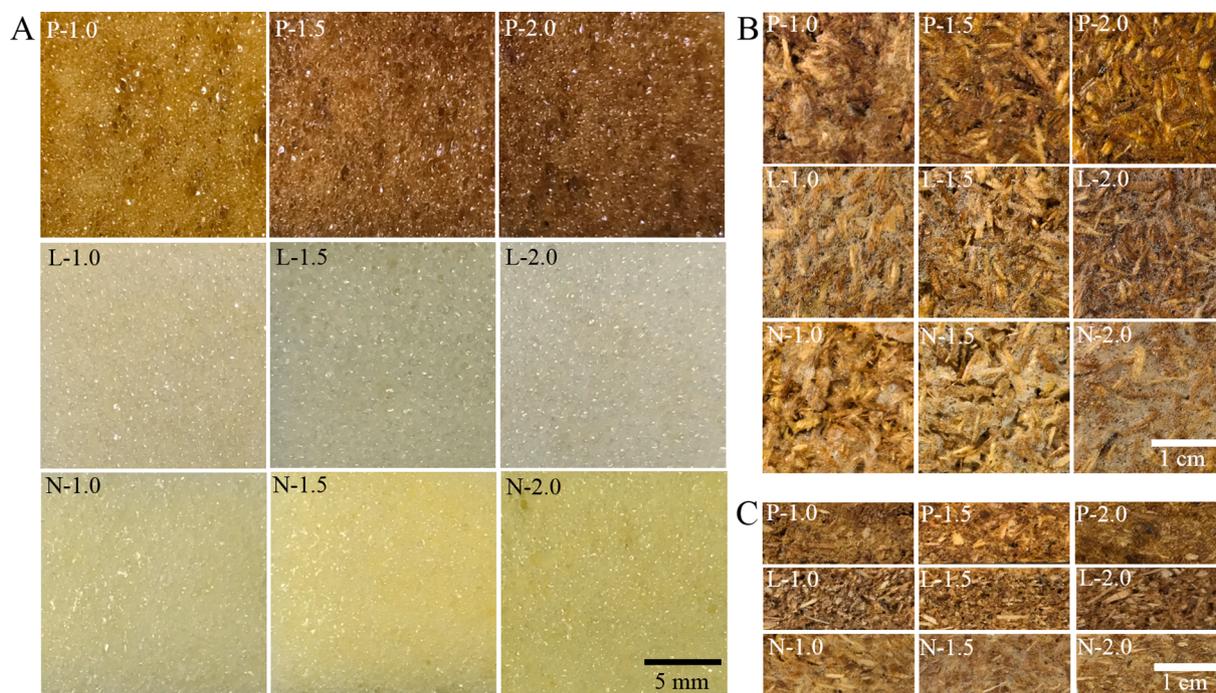


Fig. 1. Appearance of PU resins (A). Front view (B) and side view (C) of wood composites.

Table 3
Characterization of PU resins.

Code	Density (kg/m ³)	Water absorption (%)	Weight retention (%)
P-1.0	190 ± 10 ^b	61.5 ± 19.5 ^{ab}	98.8 ± 0.2 ^c
P-1.5	140 ± 10 ^a	72.5 ± 2.3 ^b	99.2 ± 0.03 ^d
P-2.0	110 ± 10 ^a	114.6 ± 27.7 ^c	99.2 ± 0.06 ^d
L-1.0	260 ± 10 ^c	32.4 ± 5.6 ^a	99.3 ± 0.09 ^d
L-1.5	200 ± 10 ^b	38.3 ± 11.9 ^{ab}	98.0 ± 0.1 ^b
L-2.0	120 ± 10 ^a	46.2 ± 3.6 ^{ab}	96.7 ± 0.04 ^a
N-1.0	540 ± 10 ^e	26.3 ± 5.9 ^a	99.2 ± 0.03 ^d
N-1.5	400 ± 10 ^d	28.2 ± 11.4 ^a	99.3 ± 0.1 ^d
N-2.0	400 ± 10 ^d	35.5 ± 1.2 ^a	99.1 ± 0.1 ^d

vibration and C–H being out of plane deformation, respectively. The peaks at around 2250–2270 cm⁻¹ of PMDI, Desmodur L and Desmodur N are attributed to the –NCO group [13,26]. Fig. 2B shows the PU foams prepared from PMDI, Desmodur L, and Desmodur N. The spectra of P-2.0 displayed that the peak at 3427 cm⁻¹ can be attributed to O–H

stretching and N–H stretching vibrations. The peaks at 2922 and 2854 cm⁻¹ are also due to the stretching vibration of the –CH₃ and –CH₂ group. The absorption peaks at 1720 and 1611 are attributed to C = O carbonyl bonds in urethane groups, and conjugated double bonds of aromatic rings in hard segments. The peaks at around 1411, 1311, and 1216 cm⁻¹ can be attributed to the isocyanate trimerization products, the peak of C–H in plane bending of ring and C–N in urethane linkage, respectively. Vibrations of C–O–C ether and ester groups appeared at 1170–1050 cm⁻¹ [33,34]. A band at around 960–643 cm⁻¹ can be attributed to the C–H of the benzene ring of isocyanate. The pattern of L-2.0 is similar to that of P-2.0. The spectrum of N-2.0 is the same as that found in a previous study [13]. The FTIR results demonstrated that the reaction between castor oil and isocyanates results incomplete conversion.

3.4. Thermal analysis of castor oil and PU resin

Fig. 3 shows the TG and DTG curves of castor oil and PU resin. The

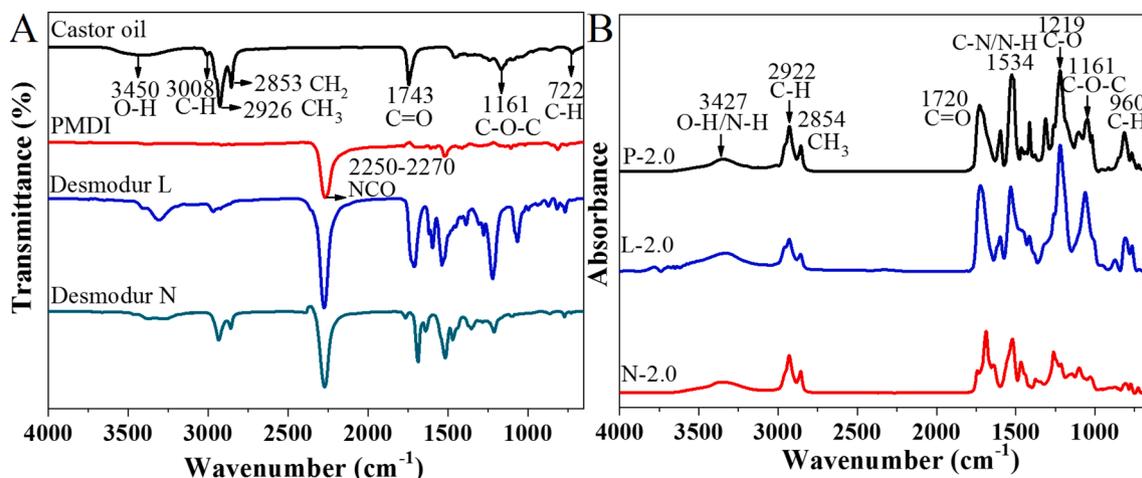


Fig. 2. FTIR spectra of raw materials (A) and PU resin (B).

result indicates castor oil degrades in a weight loss peak with the maximum degradation rate at 355 °C, which is slightly higher than that shown in a previous study [35]. In contrast, DTG curves of PU resins show that the three decomposition steps occurred. Characteristic data of TG analysis are summarized in Table 4. The results show that the NCO/OH ratio and kinds of isocyanate affect thermal degradation behaviors. In the first stage, the onset temperatures of PMDI, Desmodur L, and Desmodur N are 264–275 °C, 238–241 °C, and 221–227 °C, respectively. Low NCO/OH ratio and using aromatic isocyanates can increase the onset temperature. PU resin with high NCO/OH contains excess amounts of isocyanate, which react with the amine and urea to form easily dissociated allophanates and biuret structures [36]. The onset temperatures of PMDI, Desmodur L, and Desmodur N are 338–339 °C, 332–345 °C, and 298–303 °C in the second stage, respectively, which affected by the structure of isocyanates. The previous investigation indicates that the first and second stages of the thermal degrading process occur due to the hard segment and soft segments of castor oil, respectively [13,37]. The hard segment is composed of urea, biuret, and urethane structures. In the third stage, the onset temperatures of PMDI, Desmodur L, and Desmodur N are 460–475 °C, 425–428 °C, and 420–437 °C, respectively. The third stage is attributed to thermal decomposition of isocyanurate rings and carbodiimide linkages, which leads to the production of CO₂ and the formation of char in the solid state [38]. Thermal stability is one of the important properties of building materials [39]. T₁₀ of castor oil, P-1.0, P-1.5, P-2.0, L-1.0, L-1.5, L-2.0 N-1.0, N-1.5 and N-2.0 are exhibited at 364, 302, 300, 304, 264, 264, 260, 310, 308 and 304 °C, respectively. The materials of the thermal stability are as follows: Castor oil > PMDI-based based PU ≈ Desmodur N-based PU > Desmodur L-based PU. The thermal stability of castor oil is much higher than that of PU resins. Thermal degradation of PU resin depends on chemical structure, such as urethane bonding, polyol, dangling chains, and unreacted isocyanate [40]. The soft segments of castor oil can offer high stability in PU foams. On the other hands, Desmodur L has aromatic rings with 2,4 or 2,6-isocyanate groups, which form asymmetric rigid chains. The inferior thermal stability of Desmodur L-based PU foams may be attributed to the low castor oil

ratio, high hard segment content, and the steric hindrance of the isocyanate groups. The high thermal stability of PMDI-based PU and Desmodur N-based PU resin is due to its symmetrical nature, which enhances intermolecular interactions [41]. The results indicated that the thermal stability of the PU resins is mainly effected by the structure of isocyanates and the proportion of castor oil. The NCO/OH ratio is the main effect on thermal stability. T₁₀ of plant oil-based PU resins were between 250 and 267 °C in previous studies [42,43]. The results demonstrated that bio-based PU resin has high thermal stability and can be used for building materials.

3.5. Appearance and densities of wood composites

The adhesive is used to bond woody materials for efficient utilization. In general, formaldehyde-based resins are used as adhesives to manufacture wood composites. However, formaldehyde exposure increases the risk of acute poisoning and long-term exposure can lead to chronic toxicity, and cause nasopharyngeal cancer, nasal and paranasal cancer, and leukemia [44,45]. This investigation used formaldehyde-free adhesive to avoid risk to humans and the environment [46]. The bio-based PU resins prepared from PMDI, Desmodur L, and Desmodur N can be used to manufacture wood composites successfully, as shown in Fig. 1 BC. The results can be observed that wood particles were homogeneously distributed in the PU composites. Densities of wood composites made from P-1.0, P-1.5, P-2.0, L-1.0, L-1.5, L-2.0 N-1.0, N-1.5 and N-2.0 were exhibited at 458.6 ± 15.4 Kg/m³, 458.7 ± 22.1 Kg/m³, 468.0 ± 13.5 Kg/m³, 444.9 ± 13.6 Kg/m³, 444.3 ± 5.0 Kg/m³, 431.3 ± 11.3 Kg/m³, 472.6 ± 17.4 Kg/m³, 468.6 ± 17.7 Kg/m³, and 470.8 ± 11.9 Kg/m³, respectively, which indicates all the composites were near the target density of 450 Kg/m³. According to ANSI A208, a density of a composite lower than 640 Kg/m³ can be classified as low-density. Such composites can be categorized as low-density boards.

3.6. Moisture content and water absorption of wood composites

A previous study demonstrated the physical and mechanical effects

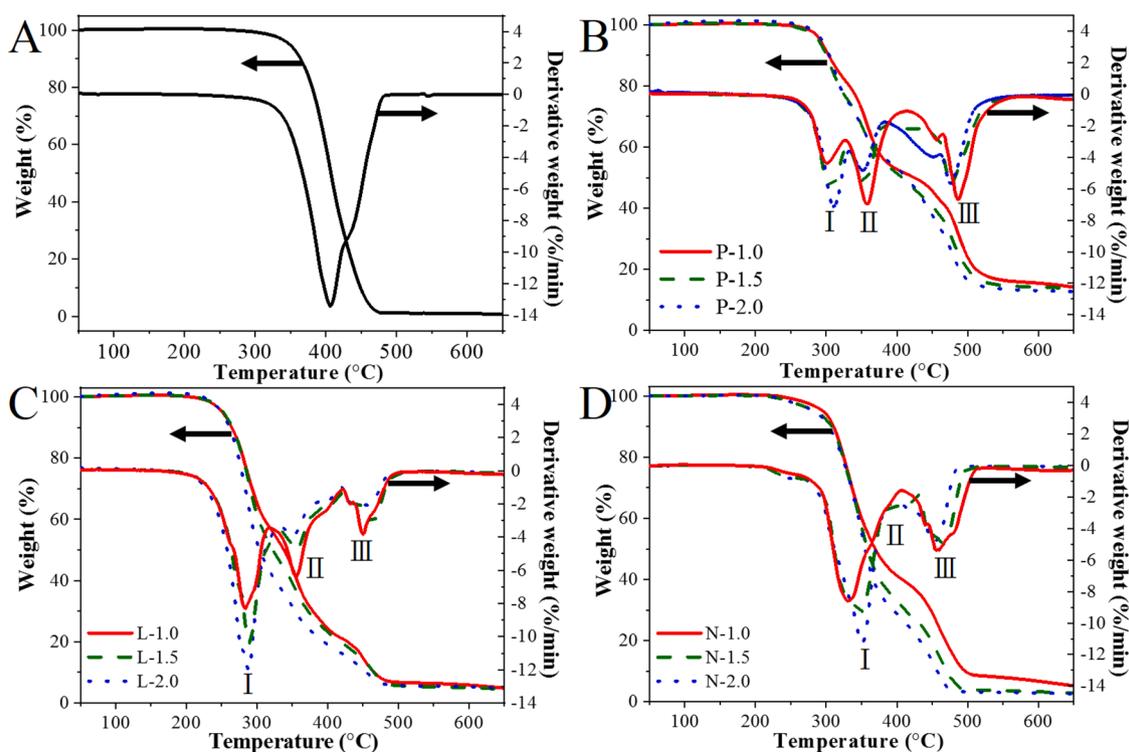


Fig. 3. TG and DTG curves of castor oil and PU resin.

Table 4
Characteristic data of TG analysis for castor oil and PU resins.

Sample	I				II				III				Char yield ^{*4} (%)	
	Onset (°C)	Peak (°C)	WL ^{*1} (%)	PH ^{*2} (%/min)	Onset (°C)	Peak (°C)	WL ^{*1} (%)	PH ^{*2} (%/min)	Onset (°C)	Peak (°C)	WL ^{*1} (%)	PH ^{*2} (%/min)		T ₁₀ ^{*3} (°C)
Castor oil	355	406	97.9	-13.6	-	-	-	-	-	-	-	-	364	0.9
P-1.0	275	301	21.1	-4.4	338	359	39.7	-30.5	475	487	24.7	-6.7	302	14.2
P-1.5	273	306	26.7	-5.9	338	354	36.8	-21.6	466	498	22.3	-5.7	300	13.8
P-2.0	264	310	29.0	-7.2	339	353	37.5	-17.8	460	474	21.6	-5.8	304	12.7
L-1.0	241	283	47.0	-8.3	332	355	32.2	-6.4	428	451	15.3	-3.9	264	4.9
L-1.5	239	289	59.0	-10.4	345	355	22.9	-4.8	428	464	14.1	-3.2	264	4.5
L-2.0	238	288	65.8	-12.1	340	351	19.7	-3.9	425	458	10.9	-2.1	260	4.8
N-1.0	227	261	6.7	-0.6	302	330	57.2	-8.6	430	455	31.2	-5.4	310	5.2
N-1.5	223	271	7.3	-0.8	303	348	68.3	-9.4	437	460	21.7	-4.9	308	2.8
N-2.0	221	266	6.1	-0.8	298	351	70.0	-11.3	420	454	21.4	-4.8	304	2.6

*4 Char yield: The residue at 650 °C
 *1 wt loss
 *2 Peak height
 *3 T₁₀: Temperature at 10% weight loss

of the moisture content of wood composites [47]. The equilibrium moisture contents of composites are shown in Fig. 4A. It was found that the moisture content of PMDI and Desmodur N-based composite decreases as the NCO/OH ratio increases. The equilibrium moisture contents of PMDI-based, Desmodur L-based, and Desmodur N-based composites range from 0.4 to 0.6%, 0.5–0.6%, and 0.4–0.5%, respectively. The equilibrium moisture content of Desmodur L-based composites is slightly higher than those of the others. The equilibrium moisture content of China fir wood is 10% at 55% RH and 20 °C [48]. The equilibrium moisture contents of the composites are lower than 0.6%, which indicates the reduction of hygroscopicity in the woody material. Fig. 4B shows the water absorption of composites. The water absorption also decreases significantly as the NCO/OH ratio increases. The water absorptions of PMDI-based, Desmodur L-based, and

Desmodur N-based composites ranged of 9.6–26.2%, 9.4–15.6%, and 9.7–16.1%, respectively. Using Desmodur L-based and Desmodur N-based resins can improve the water absorption of composites when NCO/OH is set as 1.0 and 1.5. Table 5 shows that the water absorptions of bio-based composites prepared with commercial PU resins ranged from 21 to 70.4% [22,49,50]. The water absorptions of lignocellulosic composites prepared with formaldehyde-based resins at 24 h are 36.4–172.9% [51–53]. Desmodur L-based and Desmodur N-based composites are lower than those found in previous studies. The results demonstrate that using PU resin can help to reduce the water absorptions of wood composites.

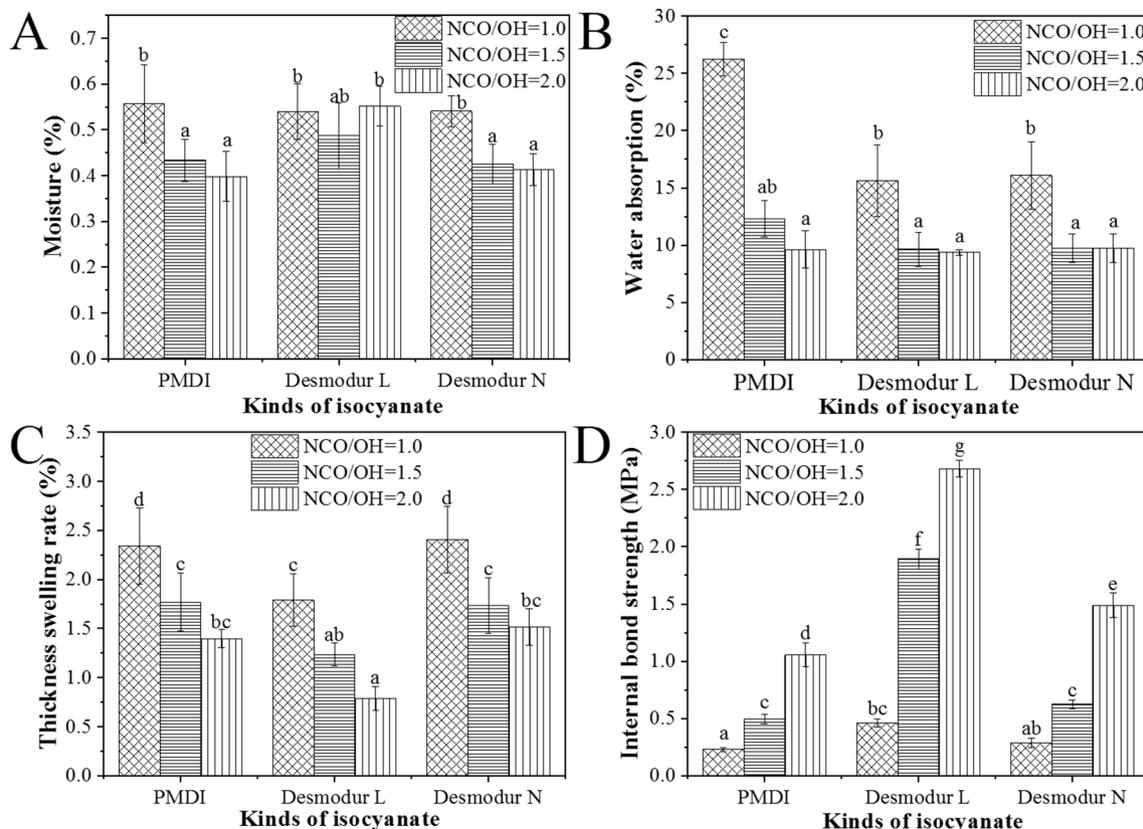


Fig. 4. Moisture (A), water absorption (B), thickness swelling rate (C) and internal bond strength (D) of wood composites.

Table 5
Comparison of properties of bio-based composites.

Kind of adhesive	Lignocellulosic Material	Density (Kg/m ³)	Equilibrium moisture content (%)	Water absorption at 24 h (%)	Thickness swelling rate (%)	Internal bond strength (MPa)	Reference
PMDI-based PU resin	China fir wood	458.6–468.0	0.4–0.6	9.6–26.2	1.4–2.3	0.22–1.06	In this study
Desmodur L-based PU resin		431.3–444.9	0.5–0.6	9.4–15.6	0.8–1.8	0.46–2.68	
Desmodur N-based PU resin		431.3–472.6	0.4–0.5	9.7–16.1	1.5–2.4	0.28–1.48	
Commercial PU resin	Cement bag	400–600	–	56.8–70.4	8.9–13.1	–	[49]
	Coconut fiber	800–1000	–	21–37	15–20	1.7–2.1	[22]
	Coconut and sugarcane bagasse fibers	529–692	–	40.2–54.6	13.8–23.1	0.2–0.35	[50]
Urea-formaldehyde resin	Stone pine wood and cone	650	12 (20 °C, 65% RH)	36.4–70.4	13.9–19.2	0.29–0.57	[51]
	Wheat straw	700	–	98.34–172.9	16.3–57.7	0.12–0.19	[52]
Melamine-urea-formaldehyde resin	Poplar	750	10	72.3	53.1	0.32	[53]

3.7. Dimensional stability of wood composites

The woody materials attract water molecules through hydrogen bonding because of the presence of hydroxyl groups. This phenomenon causes repeated water absorption and desorption of the fiber cell wall, which leads to a changing dimension [54]. Fig. 4C shows the thickness swelling rate of the composite. The results indicate that the thickness swelling rate of the composite decreases significantly as the NCO/OH ratio increases from 2.0 to 1.5. CNS 2215 establishes a thickness swelling rate of 12–25%. The thickness swelling rates of PMDI-based, Desmodur L-based, and Desmodur N-based composites are in the range of 1.4–2.3%, 0.8–1.8%, and 1.5–2.4%, respectively, which are much lower than the standard requirement. The thickness swelling rate of Desmodur L-based composites is slightly lower than those of the others. The thickness swelling rates of lignocellulosic composites prepared with formaldehyde-based resins at 24 h are 13.9–77.3% (Table 5) [51–53]. Thickness swelling of Desmodur L-based PU composites is decreased more than 494–3206% compared to commercial PU resins [22,49,50]. Notably, the thickness swelling rate of the composite prepared from bio-based PU resin is much lower than those of conventional and commercial PU-based resins. The results demonstrated using bio-based PU resin can effectively improve the dimensional stability of wood composites due to the low water absorption rates.

3.8. Internal bonding strength of wood composites

The internal bond strength of composites has been regarded as an essential adhesive property. The internal bonding strengths of composites are shown in Fig. 4D. The results indicate the internal bonding strength of composites increases significantly as the NCO/OH ratio increases because a high ratio of isocyanate can increase chemical cross-linking [55]. The internal bonding strength of PMDI-based, Desmodur L-based, and Desmodur N-based composites range of 0.22–1.06 MPa, 0.46–2.68 MPa, and 0.28–1.48 MPa, respectively. The materials of the internal bonding strength are as follows: Desmodur L-based composite > Desmodur N-based composite ≈ PMDI-based composites. The ranking is the opposite of that ranking for thermal stability. The results demonstrated the amount of hard segment content affects the mechanical properties [56]. Table 5 shows that the internal bonding strength of bio-based composites in previous studies. The internal bonding strength of lignocellulosic composites prepared with formaldehyde-based resin ranged from 0.12 to 0.57 MPa [51–53]. The internal bonding strength of Desmodur L-based PU composites is increased more than 128–2233% compared to formaldehyde-based and commercial PU resins [22,49,50]. According to CNS 2215, the requirement for internal bonding strength is to reach at least 0.15 MPa. All PU-based composites met the minimum requirement. The results demonstrated that using the Desmodur L-based

PU resin can improve bio-based composites' mechanical and dimensional stability properties.

4. Conclusions

This study used PMDI, Desmodur L, and Desmodur N as isocyanates to manufacture castor oil-based PU resins and their China fir composite. The FTIR results indicate castor oil can react with three kinds of isocyanates directly and completely. The foaming properties and densities of PU resins depend on the structure of isocyanate. The TGA results demonstrated the bio-based PU resin has high thermal stability. The lightweight PU-based composites were prepared with a density of 87.9 to 125.3 kg/m³ using a simple hot-pressing process. The dimensional stability of composites prepared from bio-based PU resin is much better than those of conventional and commercial PU-based resins. The internal bonding strength of Desmodur L-based PU composites is higher than those of commercial PU resins. All PU-based composites can meet the minimum requirement of CNS 2215. The optimal condition was reached with an NCO/OH molar ratio, using Desmodur L to obtain excellent dimensional stability and internal bonding strength. This work developed an eco-friendly approach for bio-based composites and designed a formaldehyde free-based building material for sustainable living and a healthy environment. Based on the observations, bio-based PU resin has a high potential for an environmentally friendly adhesive of composites for industrial application.

CRedit authorship contribution statement

Yi-Hua Chen: Formal analysis, Software, Methodology, Visualization, Validation, Data curation, Writing - original draft. **Cheng-Hao Wu:** Formal analysis, Software, Methodology, Visualization, Validation. **Yi-Chun Chen:** Funding acquisition, Visualization, Project administration, Resources, Writing - review & editing, Conceptualization, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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