Journal of
Composites Science

MDPI

Article

Properties of Plywood Bonded with Formaldehyde-Free Adhesive Based on Poly(vinyl alcohol)–Tannin–Hexamine at Different Formulations and Cold-Pressing Times

Ratih Afrida Lismana Sari [1,2], Muhammad Adly Rahandi Lubis [2,3,*], Rita Kartika Sari [1,*], Lubos Kristak [4,*], Apri Heri Iswanto [5], Efri Mardawati [3,6], Widya Fatriasari [2], Seng Hua Lee [7], Roman Reh [4], Jan Sedliacik [4], Muhammad Iqbal Maulana [2], Lisman Suryanegara [2], Bambang Subiyanto [2] and Sena Maulana [8,9]

[1] Department of Forest Product, Faculty of Forestry and Environment, IPB University, Bogor 16680, Indonesia; raafridalismana1@gmail.com
[2] Research Center for Biomass and Bioproducts, National Research and Innovation Agency, Cibinong 16911, Indonesia; miqbalmaulanaipb@gmail.com (M.I.M.); lism001@brin.go.id (L.S.); bamb004@brin.go.id (B.S.)
[3] Research Collaboration Center for Biomass and Biorefinery between BRIN and Universitas Padjadjaran, Jatinangor 40600, Indonesia; efri.mardawati@unpad.ac.id
[4] Faculty of Wood Sciences and Technology, Technical University in Zvolen, 96001 Zvolen, Slovakia; roman.reh@tuzvo.sk (R.R.); sedliacik@tuzvo.sk (J.S.)
[5] Department of Forest Products Technology, Faculty of Forestry, Universitas Sumatera Utara, Padang Bulan 20355, Indonesia; apri@usu.ac.id
[6] Department of Agro-industrial Technology, Universitas Padjadjaran, Jatinangor 40600, Indonesia
[7] Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM) Cawangan Pahang Kampus Jengka, Bandar Tun Razak 26400, Pahang, Malaysia; leesenghua@hotmail.com
[8] Forestry Engineering Program Study, Institut Teknologi Sumatera (ITERA), South Lampung 35551, Indonesia; sena.maulana@rh.itera.ac.id
[9] Research and Innovation Center for Advanced Materials, Institut Teknologi Sumatera (ITERA), South Lampung 35551, Indonesia
* Correspondence: marl@biomaterial.lipi.go.id (M.A.R.L.); rita_kartikasari@apps.ipb.ac.id (R.K.S.); kristak@tuzvo.sk (L.K.)

check for updates

Citation: Sari, R.A.L.; Lubis, M.A.R.; Sari, R.K.; Kristak, L.; Iswanto, A.H.; Mardawati, E.; Fatriasari, W.; Lee, S.H.; Reh, R.; Sedliacik, J.; et al. Properties of Plywood Bonded with Formaldehyde-Free Adhesive Based on Poly(vinyl alcohol)–Tannin –Hexamine at Different Formulations and Cold-Pressing Times. *J. Compos. Sci.* **2023**, *7*, 113. https://doi.org/10.3390/jcs7030113

Academic Editor: Francesco Tornabene

Received: 3 February 2023
Revised: 17 February 2023
Accepted: 1 March 2023
Published: 10 March 2023

Abstract: The plywood industry's sustainability, performance, and production costs depend on wood adhesives and the hot pressing technique. In this investigation, a cold-setting plywood adhesive based on polyvinyl alcohol (P), tannin (T), and hexamine (H) was produced. The physical and mechanical properties of plywood were examined at different formulations such as tannin concentration (10% and 20%), hexamine content (5%, 10%, and 15%), and cold-pressing time (3, 6, 12, and 24 h). This study showed that high tannin and hexamine content also increased the solids content, but decreased the average viscosity of the adhesive. Markedly, the cohesion strength of PTH-based adhesives increased from 5.57 Pa at 1/s to 1411.6 Pa at 400/s shear rate, regardless of the adhesive formulation. The shear modulus subsequently decreased as a function of the shear rate and increased with a higher tannin and hexamine content. This study revealed that the higher tannin and hexamine content and longer cold-pressing times could produce plywood with the tested adhesive that met the Japanese standard strength requirements. A combination of PTH-based adhesive prepared with formula 2 and 24 h cold-pressing resulted in the highest TSS value of 1.42 MPa, MOR values of 88.7 MPa, MOE values of 14,025.6 MPa, and wood failure of 47.2%. This study showed the possibility of fabricating eco-friendly plywood panels bonded with PTH-based adhesive using the cold-pressing process as an alternative to conventional plywood.

Keywords: adhesion; bio-based adhesives; cold pressing; cohesion; hexamine; PVOH; plywood; tannin

1. Introduction

Wood adhesives are essential to the processing and recombining of the wood unit process used to produce wood-based panel goods. Because the quality of the adhesives impacts the performance of the finished wood product, adhesives play an essential role in the processing of wood [1]. Formaldehyde is the basis for nearly 95% of all wood adhesives used to produce engineered wood composites [2]. The most common kind of resin is UF, which represents about 85% of the total in the world. Melamine comes in second, with 10%, followed by phenolics with 5% [2–4]. Vital benefits of UF adhesives are their low cost, inflammability, quick cure time, and light hue [5]. The bonds are not water resistant, and formaldehyde continues to be emitted by adhesives, which is a disadvantage [6]. Formaldehyde-based UF resins harm human health [7]. In the 1990s, with an emphasis on concerns such as life cycle assessment, the issue of sustainability in manufacturing gained more traction. It has been determined that several techniques help to reduce formaldehyde emissions. The most important ones are the hot pressing parameters, such as the temperature and the amount of time spent pressing, and the addition of formaldehyde scavengers [8,9]. To fabricate plywood sustainably, cold pressing and bio-based adhesive are two main methods.

In recent years, attention has been focused on raising knowledge of environmental conservation and personal health. As a result, natural resins made chiefly from renewable resources have drawn much interest because of the tannin resin's phenolic structure, which allows for its usage as an adhesive and as a partial or total replacement for phenols in adhesives. Research on and applications of the resin have been highly successful in several nations [1]. Tannins are primarily utilized in the tanning of leather, the production of beverages, the pharmaceutical industry, and the treatment of water, adhesives, and natural wood preservatives [10]. Due to its structural resemblance to synthetic phenol, specifically [11], tannin reactions are based on their phenolic character, similar to phenol with formaldehyde. Tannin has been considered a potential replacement for phenol in phenol–formaldehyde resin in the formulation of wood adhesives [12,13].

The main aldehyde utilized in the manufacturing, setting, and curing of tannin resin adhesives is formaldehyde. It is typically employed as a liquid formalin solution or as the polymer paraformaldehyde, which can depolymerize rather quickly in an alkaline environment. Alcohols can be added to the system to limit the formaldehyde reaction with tannin [1]. Such natural extracts were typically coupled with 4,4′-methylene diphenyl diisocyanate (pMDI) [14] or employed as partial components of phenol–formaldehyde resins [15,16] in adhesive formulations for particleboards and fiberboard [13,17,18]. Isocyanates have many benefits when used in adhesive compositions. Isocyanate-based adhesives, however, exhibit severe toxicity [19]. Hexamethylenetetramine, sometimes known as hexamine, is another formaldehyde substitute used to manufacture wood adhesives. Hexamine breaks down into reactive or intermediate fragments, which then interact with the phenolic nuclei of polyflavonoid tannins to produce the cross-linking reaction process between hexamine and tannins [20].

As a wood adhesive for plywood, a bioadhesive based on polyphenol extracts from *Pinus radiata* D. Don bark combined with hexamine as a hardener has been employed. Conditions for preparing the glue were 30% and 40% solid content with 7% hexamine (on extract weight). The findings demonstrate that exterior-grade plywood may be produced from a by-product of the forestry sector without using phenol, formaldehyde, or isocyanates [21]. For many kinds of wood adhesives, lignin and tannin have been combined. If formaldehyde is not employed, lignin can be glyoxalated before being combined with tannin and a hardener (e.g., hexamine). Particleboards bonded with the researched mimosa tannin and glyoxalated wheat straw lignin emit 0.92–1.12 mg/kg of formaldehyde [22]. Various bio-based substances can be combined with tannins to create adhesives. For instance, a plywood adhesive has been created using a mixture of corn starch, mimosa tannin, and hexamine as a hardener. Reducing the high viscosity of starch–tannin adhesives, which restricts their industrial potential, is one topic for improvement and research [23].

Cold-setting adhesive is becoming increasingly necessary for on-site bonding, as engineered wood products evolve quickly. Resorcinol–formaldehyde (RF), phenol–resorcinol–formaldehyde (PRF), melamine–urea–formaldehyde (MUF), and polyurethanes (PU) resins are among the most widely used cold-set adhesives [24,25]. As formaldehyde-based adhesives, RF, PRF, and MUF frequently contain residual amounts of the carcinogenic formaldehyde released during the manufacture of panels [26–28]. PU resins are adhesives with an isocyanate base, and isocyanates are incredibly hazardous. Good ventilation and quality personal protection equipment are ordinarily necessary for applying PU resins [29]. However, PU resins emit hazardous gases such as hydrogen cyanide. It would be great for making formaldehyde-free and non-isocyanate cold-setting wood adhesives. Because of its exceptional performance, such as strong adhesion, good thermal and chemical stability, and low curing temperature requirements, PU resins adhesive is widely utilized in the wood-based composites sector. Plywood bonded with PU resins demonstrated dry tensile shear strength (TSS) in the 1.2–2.5 MPa range [30–32], which is higher than the minimum requirement of 0.7 MPa [33].

Numerous environmentally friendly adhesives have been studied, including tannin and hexamethylenetetramine (hexamine). These studies demonstrated that tannins have a strong capacity for self-condensation, which can significantly enhance the mechanical properties of plywood and particleboard as well as the bonding strength of the materials [34]. More hydroxyl groups are encouraged in the system using poly(vinyl alcohol) (PVOH), which improves the bond between tannin and hexamine. PVOH, a highly polar and water-soluble polymer, has been successfully combined with natural polymeric substances such as cellulose, chitosan, and tannin in polymer blends. It was shown that, in these systems, the hydroxyl groups of the individual polymers formed intermolecular hydrogen bonds, which were responsible for the excellent material performance.

The dry TSS values for PVOH-based adhesives ranged between 0.1 and 1.2 MPa [31,35,36]. PVOH-based adhesives utilize hydrogen bonding with wood, which has a lower bonding strength than covalent bonds. Thus, the development of bio-based cold-setting adhesives is necessary. As indicated previously, tannin units are covalently and ionically linked to mixed hexamine. In order to strengthen the bond between tannin and hexamine, PVOH is typically utilized to promote extra hydroxy (OH) groups in the system. The highly polar and water-soluble polymer PVOH has been successfully mixed with natural polymeric components such as cellulose, starch, chitosan, and lignin [36]. Good material performance was related to the development of intermolecular hydrogen bonding among the hydroxyl groups of the various polymers. Thus, PVOH–tannin–hexamine is anticipated to offer a cold-setting wood adhesive alternative.

This study aims to develop an alternative cold-setting wood adhesive for plywood based on PVOH, tannin, and hexamine, as well as to examine the influence of various adhesive formulations and cold-pressing times on the characteristics of plywood. Functional group analysis was carried out with Fourier transform infrared spectroscopy (FTIR), flow behavior was examined with a rotational rheometer, and bonding strength was determined with a universal testing machine (UTM).

2. Materials and Methods

2.1. Materials

Tanjung Enim Lestari Pulp and Paper, Palembang, Indonesia, provided acacia bark (Acacia mangium) as the source of tannin. PT. Bratachem, Bogor, Indonesia, supplied technical grade PVOH (22.000 g/mole), hexamine, and calcium carbonate ($CaCO_3$). Meranti (*Shorea leprosula* Miq.) wood veneers with 300 mm × 300 mm × 2 mm were purchased at a local market in Cibinong, Indonesia, to manufacture three-layer plywood samples. Anugerah Raya Kencana Company, Banten, Indonesia, supplied PU resins (MDI:Polyol 1.2:1.0, solids content 96.52%, viscosity 2056.5 mPa.s, and gelation time 187.5 min) as a control adhesive.

2.2. Preparation of Tannin Extract

The extraction of tannin from *A. mangium* bark followed a modified published method [37]. The bark of *A. mangium* was first pulverized using a hammermill with a 40–60-mesh screen;

then, tannin was extracted using the maceration technique. The tannin was removed using hot water. A glass container was filled with 100 g of acacia bark powder and one thousand milliliters of distilled water (w/v 1:10). The combination was heated at 80 ± 2 °C for three hours, then cooled for twenty-four hours. The resultant extract was extracted from the powder using a filter. A viscous extract was produced by evaporating the filtrate in a rotary evaporator (Buchi, Germany) at a temperature and pressure of 60 ± 2 °C and 22 mBar. This calculation was utilized to calculate the tannin yield.

$$\%\ Yield\ of\ Tannin = \frac{weight\ of\ extract\ tannnin\ (\text{g})}{weight\ of\ dried\ oven\ bark\ (\text{g})} \times 100\%$$

2.3. Characterization of Tannin Extract

2.3.1. Solids Content

To characterize the solids content of tannin, the Petri dish was put in an oven at 103 ± 2 °C for approximately four hours, followed by thirty minutes in a desiccator. After determining the mass of the empty Petri dishes, about 1 g of tannin was added, and then the plates were heated for three hours at 103 ± 2 °C. After thirty minutes in a desiccator, the sample was weighed to ascertain its constant weight. The tannin's solids content was determined using the following equation.

$$Solids\ content\ of\ Tannin(\%) = \frac{B - (C - A)}{B} \times 100\%$$

Description:
A = weight of empty Petri dishes (g);
B = weight of tannin sample (g);
C = weight of the oven-dried sample and the Petri dishes (g).

2.3.2. FTIR Spectroscopy Analysis

The functional groups of extracted tannin were investigated utilizing FTIR spectroscopy (SpectrumTwo, PerkinElmer, Waltham, MA, USA) and the Universal Attenuated Total Reflectance (UATR) technique. At wavenumber 4000–400 cm^{-1}, the experiment was conducted with a resolution of 4 cm^{-1} and 25 ± 2 °C. Each spectrum was normalized using the Spectrum program's min–max normalization feature (Ver. 10.5.3, Perkin Elmer, Waltham, MA, USA).

2.4. Preparation of PVOH–Tannin–Hexamine-Based Adhesive

The 15% w/v PVOH solution was made by dissolving PVOH beads in distilled water at 80 ± 2 °C [38,39], and the 15% w/v hexamine solution was made by dissolving the hexamine powder in distilled water at 25 ± 2 °C. The adhesive was formulated at 25 ± 2 °C with a stirring speed of 300 rpm. Figure 1 displays the images of PVOH–tannin–hexamine (PTH)-based adhesive at different hexamine and tannin contents. The PTH-based adhesives were prepared following two formulations presented in Table 1.

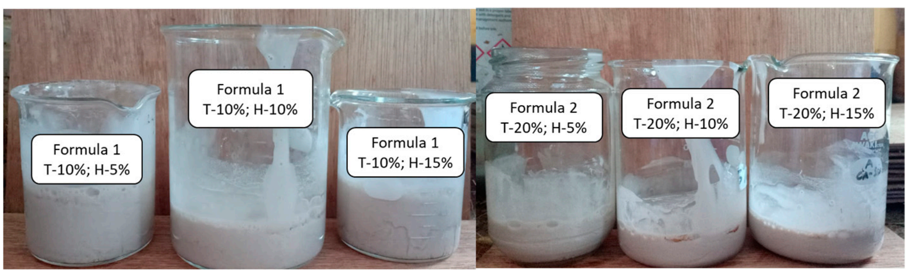

Figure 1. The PTH-based adhesive at different hexamine and tannin contents.

Table 1. Formulation of PVOH–tannin–hexamine (PTH)-based adhesive at different hexamine and tannin contents.

Formula 1					
Composition	**Content (g)**	**Composition**	**Content (g)**	**Composition**	**Content (g)**
P	60.00	P	60.00	P-15%	60.00
T-10% *	0.95	T-10%	0.95	T-10%	0.95
H-5% **	3.05	H-10%	6.10	H-15%	9.14
$CaCO_3$ 15% ***	9.60	$CaCO_3$ 15%	10.06	$CaCO_3$ 15%	10.51
Formula 2					
Composition	**Content (g)**	**Composition**	**Content (g)**	**Composition**	**Content (g)**
P	60.00	P	60.00	P	60.00
T-20%	1.91	T-20%	1.91	T-20%	1.91
H-5%	3.10	H-10%	6.19	H-15%	9.29
$CaCO_3$ 15%	9.75	$CaCO_3$ 15%	10.21	$CaCO_3$ 15%	10.68

* Hexamine was added based on the solids content of PVOH. ** Tannin was added based on the solids content of PVOH. *** $CaCO_3$ was added based on the total adhesive (PVOH–tannin–hexamine).

2.5. Characterization of PVOH–Tannin–Hexamine-Based Adhesive

2.5.1. Solids Content

By drying the samples in an oven at 103 ± 2 °C for 3 h and separating the dry samples from the wet samples, the non-volatile solids content of various formulations of PTH-based glue was measured. The PTH-based adhesives' viscosity was determined using a rotating rheometer (Rheolab QC, Anton Paar, Graz, Austria). The average viscosity of the PTH-based adhesives was determined at 25 ± 2 °C, with a spindle number of 27 and a constant speed of 100 rpm. At 25 ± 2 °C, the PTH-based adhesive gelation time was measured using a gel time meter (Techne GT-6, Coleparmer, Vernon Hills, IL, USA). Each measurement was repeated thrice.

2.5.2. Flow Behavior Analysis

The flow behavior of PTH-based adhesives at various tannin and hexamine concentrations was studied using a rotational rheometer (RheolabQC, Anton Paar, Graz, Austria). The adhesive's cohesion strength, dynamic viscosity, and shear modulus were assessed at a temperature of 25 ± 2 °C and a dynamic shear rate of 1–400/s.

2.5.3. FTIR Spectroscopy

An FTIR spectrometer (Spectrum Two, Perkin Elmer, Waltham, MA, USA) combined with UATR was used to investigate the functional groups of a PTH-based glue at varied tannin concentrations ranging from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and 16 scans per sample. A min–max normalization was conducted using Pyris Software (Ver. 10.5.3, Perkin Elmer, Waltham, MA, USA) to normalize the adhesive spectrum.

2.6. Fabrication of Plywood Bonded with PVOH–Tannin–Hexamine-Based Adhesive

PTH-based adhesives were used to glue Meranti veneers to plywood samples of various formulations. As a filler, roughly 15% $CaCO_3$ was added depending on the adhesive's solids composition. Using the double spread method of 180 g/m^2 glue spread, 75 samples of three-layer plywood with a target size of 300 mm × 300 mm × 6 mm were produced by spreading the glue mixture on the veneer surface (Table 2). The plywood was pressed at 27 ± 2 °C for 3, 6, 12, and 24 h at a target pressure of 1.0 MPa. Before the plywood was characterized, each sample was conditioned for two weeks at 20 °C. As a control, plywood bonded with PU resins was produced with a glue spread of 180 g/m^2 using the double spread method and cold-pressed at 27 ± 2 °C for 3 h at a target pressure of 1.0 MPa.

Table 2. Fabrication of plywood bonded with PTH-based adhesive at different adhesive formulations and cold-pressing times.

Adhesive Formulation	Cold-Pressing Time (h)				Number of Plywood
	3	6	12	24	
Control *	3	-	-	-	3
Formula 1 **	9	9	9	9	36
Formula 2 ***	9	9	9	9	36

* Control was PU resins. ** Detailed formulation is presented in Table 1. *** Detailed formulation is presented in Table 1.

2.7. Characterization of Plywood Bonded with PVOH–Tannin–Hexamine-Based Adhesive

The plywood's qualities were examined following Japanese Agriculture Standard (JAS) No. 233:2003 [33]. Average density, moisture content (MC), and delamination measurements were performed on 75 mm × 75 mm × 6 mm samples. The plywood's density was calculated by comparing the mass and volume of samples, and the MC was calculated by dividing the original and final mass after drying at 103 ± 2 °C for 24 h and reaching a constant weight. Meanwhile, the delamination test followed the Type II plywood for general use [33]. Plywood samples were soaked in hot water for 2 h before drying at 60 ± 3 °C for 3 h. The delamination percentage was calculated by dividing the total length of delaminated lines by the total length of glue lines. The length of the non-delaminated region of the sample on the same bonding layer must be at least 2/3 of the length of each side (>50 mm).

Plywood samples were measured for tensile shear strength (TSS), modulus of rupture (MOR), modulus of elasticity (MOE), and wood failure following JAS No. 233:2003 [33]. TSS values of six plywood specimens with dimensions of 80 mm × 25 mm × 6 mm were measured with a universal testing machine (UTM AGX Series, Shimadzu, Kyoto, Japan) at a crosshead speed of 2 mm/min and a load cell of 10 kN. Following the analysis, wood failure analysis was performed on the TSS samples. Three MOR and MOE values of three plywood specimens with dimensions of 200 mm × 50 mm × 6 mm were measured with a universal testing machine (UTM AGX Series, Shimadzu, Kyoto, Japan) at a crosshead speed of 10 mm/min and a load cell of 10 kN.

3. Results and Discussion

3.1. Properties of PVOH–Tannin–Hexamine-Based Adhesives

The viscous tannin had a solids content of 94.5%, a yield of 11.7%, and a moisture content of 5.0%. The viscous tannin was then utilized to produce wood adhesives based on PVOH–tannin–hexamine (PTH). Prior to blending, the functional groups of PVOH, tannin, and hexamine were analyzed using FTIR spectroscopy; the results are depicted in Figure 2. At 3375 cm^{-1}, both PVOH and tannin contained a distinct hydroxyl group (–OH). At 1640 cm^{-1}, intermolecular hydrogen bonding of PVOH was detected. At wavenumbers 3400 cm^{-1} and 1450 cm^{-1}, the –OH functional group is essential for bonding with the amine ($-NH_2$) functional group of hexamine. Several vibrations of methylene and amine were observed at wavenumbers of 2965 cm^{-1}, 2875 cm^{-1}, 1450 cm^{-1}, 1370 cm^{-1}, 1230 cm^{-1}, 995 cm^{-1}, 810 cm^{-1}, and 675 cm^{-1}. The methylene and methyl groups of tannin were detected at 2940 cm^{-1} and 2850 cm^{-1}, respectively. At 1610 cm^{-1} and 1010 cm^{-1}, aromatic C=C stretching and ether linkages were observed in tannin.

The properties of PTH-based adhesives in different formulations are summarized in Table 3. As the amount of tannin and hexamine increased, the average viscosity of the PTH-based adhesives decreased. In this study, the adhesive base, PVOH 15% w/v, exhibited an average viscosity of approximately 2000 mPa.s. Adding tannin increased the average viscosity to 5404.06 mPa.s for 10% tannin concentration and 4749.97 mPa.s for 20%. Hexamine reduced the viscosity of the PTH-based adhesive to 3673.38 mPa.s at 15% hexamine concentration. This could be attributed to the slow decomposition rate of hexamine, particularly because at basic conditions the decomposition of hexamine becomes difficult, slowing the crosslinking process with tannin [40]. Therefore, no increment in viscosity was observed, but instead a decrease in viscosity was recorded at the time of testing. PU resins, on the other hand, had a high solids content and viscosity of 96.52% and 2056.51 mPa.s, respectively. The gel time meter could not detect the gelation time of different PTH-based adhesive formulations, indicating that the gelation process of the adhesive exceeded the instrument's maximum of 999 min, or approximately 17 h. Comparatively, the gel time of PU resins was 187.50 min, or nearly 3 h.

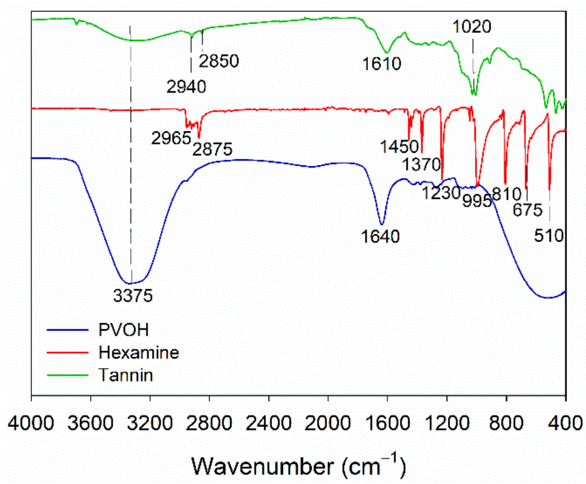

Figure 2. FTIR spectra of PVOH, tannin, hexamine.

Table 3. Basic properties of PVOH–lignin–hexamine (PTH)-based adhesive.

Formulation	Solids Content (%)	Average Viscosity (mPa·s)	Gelation Time (min)
Control *	96.52 ± 0.25	2056.51 ± 50.31	187.50 ± 2.0
Formula 1			
PTH-15-10-5	23.92 ± 1.99	5404.06 ± 208.28	Nd **
PTH-15-10-10	23.95 ± 0.98	4251.71 ± 248.19	Nd
PTH-15-10-15	24.86 ± 0.97	3821.52 ± 177.71	Nd
Formula 2			
PTH-15-20-5	24.68 ± 0.75	4749.97 ± 185.00	Nd
PTH-15-20-10	24.88 ± 0.19	3824.12 ± 137.48	Nd
PTH-15-20-15	24.94 ± 0.29	3673.38 ± 105.86	Nd

* Control was PU resins. ** Not detected by the gel time meter at 25 °C (max 999 min).

Utilizing a rotational rheometer, the flow behavior of different PTH-based adhesive formulations was determined (Figure 3). The cohesion strength of PTH-based adhesives increased from 5.57 Pa at 1/s to 1411.6 Pa at 400/s shear rate, regardless of the adhesive formulation. The higher tannin concentration increased the cohesion strength of PTH-based adhesives, whereas a higher hexamine concentration slightly decreased the cohesion strength. Formulas 1 and 2 yielded PTH-based adhesives with initial viscosities of approximately 5560 mPa.s and 4920 mPa.s, respectively. The dynamic viscosity decreased as the shear rate increased. The viscosity of PTH-based adhesives increased in proportion to their tannin and hexamine content. This could be attributed to the slow decomposition rate of hexamine. Hexamine is a monoprotic base, and therefore it has to be decomposed first to ensure the reaction can be started. Particularly at basic condition, the decomposition of hexamine becomes difficult, slowing the crosslinking process with tannin [40]. Therefore, no increment in viscosity was observed, but instead a decrease in viscosity was recorded at the time of testing. The reduction in viscosity was mainly due to the dilution effect of the addition of liquid hexamine into the viscous tannin solution. It is expected that, after some specific time, when the reactive substances start to form, the reaction between hexamine and tannin would be very rapid [40]. Similar trends were observed for the shear modulus of the adhesive. Formulas 1 and 2 yielded adhesives with an initial shear modulus of approximately 1.49 Pa and 1.30 Pa, respectively. The shear modulus subsequently decreased as a function of the shear rate. PTH-based adhesives with a higher tannin and hexamine content exhibited a greater shear modulus. Higher shear modulus indicates a higher stiffness of materials, showing that PTH-based adhesives prepared using Formula 1 were stiffer than those using Formula 2.

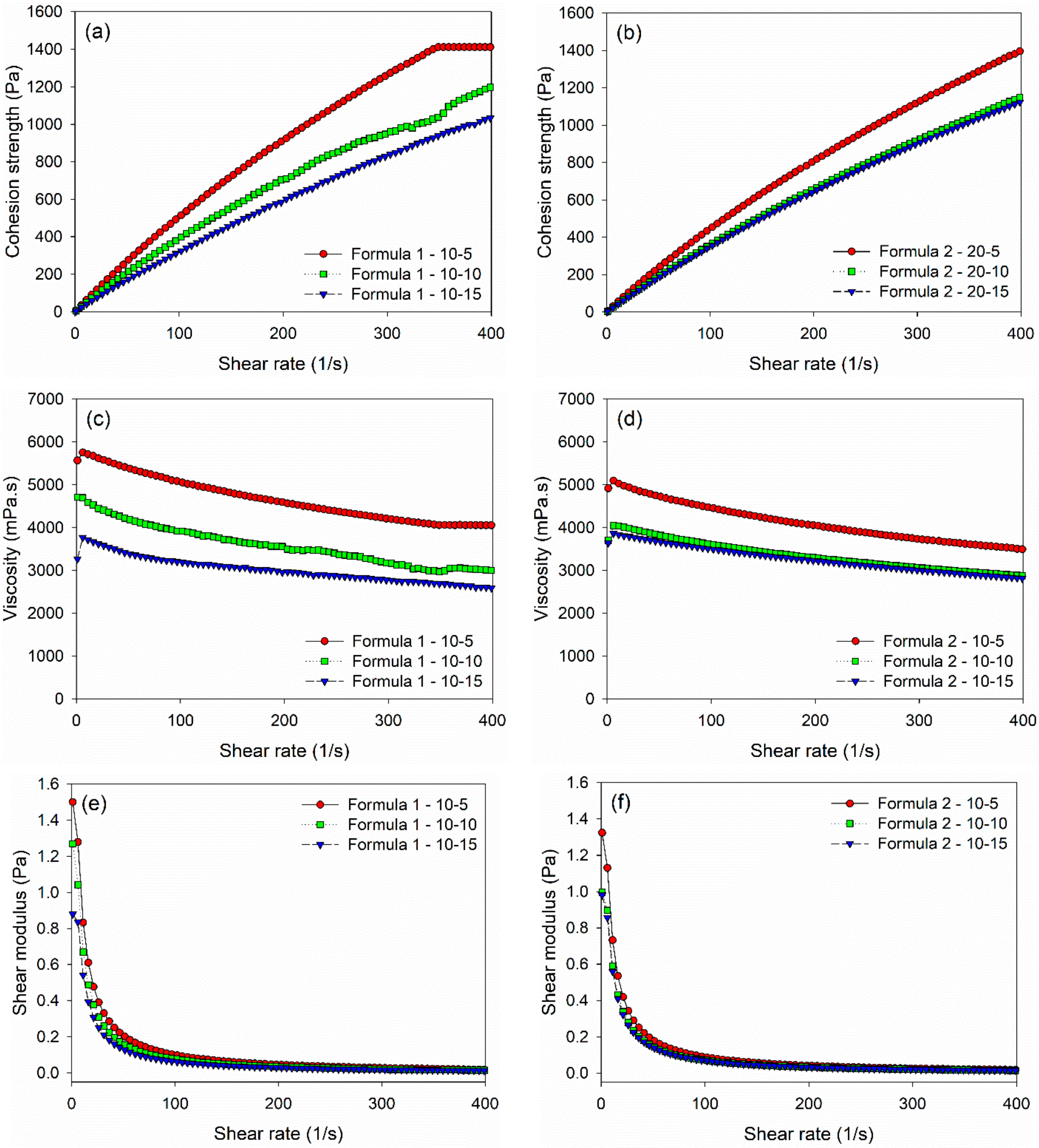

Figure 3. Flow behavior analysis of PVOH–tannin–hexamine-based adhesives. (**a**) Cohesion strength of Formula 1, (**b**) cohesion strength of Formula 2, (**c**) dynamic viscosity of Formula 1, (**d**) dynamic viscosity of Formula 2, (**e**) shear modulus of Formula 1, (**f**) shear modulus of Formula 2.

FTIR spectroscopy enabled the evaluation of the influence of different formulations of PTH-based adhesives on the adhesives' functional groups (Figure 4). The adhesives displayed the characteristic free OH group peak at 3375 cm^{-1} and the intermolecular hydrogen bonding peak at 1640 cm^{-1} due to the use of PVOH in their synthesis. After adding them to the mixture, the C=O and C-O stretch of tannin were found at wavenumbers 1710 cm^{-1} and 1110 cm^{-1}, respectively. The remaining functional groups in the PTH-based adhesive belonged to the methylene vibrations of hexamine at 1450 cm^{-1}, 1370 cm^{-1}, 1230 cm^{-1}, and 995 cm^{-1}. After curing the glue at 105 $\pm$ 3 °C for 3 h, the functional groups of PTH-based adhesives changed significantly. At 3300 cm^{-1}, a secondary amine signal came from the PVOH–tannin and hexamine reaction. It is known that hexamine may form covalent bonds with the –OH of tannin [31]. In the PVOH–tannin blends, the –OH group concentration was much greater than that of tannin alone. Therefore, the mixtures might increase the adhesive's cohesion and adhesion strength. After curing, the vibration of hexamine's methylene linkages was measured at wavenumbers 2940 cm^{-1} and 2880 cm^{-1}. The C=O group of aldehyde was observed at 1740 cm^{-1} due to the breakdown of hexamine at high temperatures. At wavenumbers 1450 cm^{-1}, 1370 cm^{-1}, 1230 cm^{-1}, 810 cm^{-1}, 675 cm^{-1}, and 510 cm^{-1}, several vibrations of methylene of hexamine were identified.

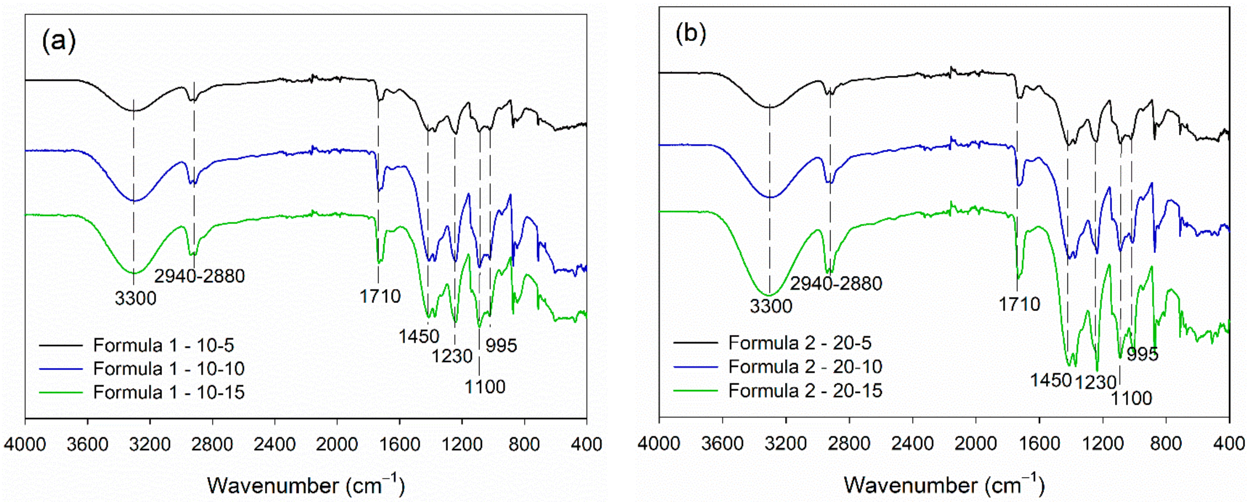

Figure 4. FTIR spectra of PVOH–tannin–hexamine-based adhesives. (**a**) Formula 1, (**b**) Formula 2.

3.2. Plywood Properties

JAS No. 233:2003 [33] examined plywood's physical performance bonded with PTH-based adhesives at various formulations and cold-pressing periods. Figure 5 depicts the average density of plywood for various formulas and cold-pressing durations, with values between 0.35 and 0.48 g/cm^3. The average density of plywood-bonded standard PU resins was 0.42 g/cm^3. The results revealed that varying the concentrations of tannin and hexamine and the pressing time varied the average density of plywood. In addition, as shown in Figure 5, an increase in tannin and hexamine content increased the MC of plywood, whereas an increase in pressing time lowered MC values. The MC of control plywood was lower than that of PTH-based adhesive-bound plywood, which was 5.3%. The JAS No. 233:2003 standard provides a maximum MC value of 14.0% for all MC levels. However, the MC values remained higher than those of commercial plywood bonded with UF resins and manufactured at higher temperatures [7]. With a delamination value of 100%, plywood's wet bonding strength to PTH-based adhesives was insufficient. In contrast, there was no delamination in the control plywood, suggesting that PU resins had superior wet bonding strength. The delamination of plywood bonded with a PTH-based adhesive did not meet the JAS No. 233 minimum criteria of a non-delaminated section of at least 50 mm or less than 33.3%. This is mainly due to the hydrogen bonding in PTH-based adhesive being susceptible to hydrolysis. This represents a severe drawback for the industrial applications of the tested PTH-based adhesives compared to the PU wood adhesives. The chemical modification of veneers is a viable approach to increase the dimensional stability of plywood in order to reduce its delamination and deformation [31]. Delamination is a necessary property of plywood, mainly when it is intended for outdoor usage, i.e., exposure to cyclic fluctuations in MC. These alterations result in mechanical tensions in the glue joint due to the disparities in the shrinking and swelling of neighboring veneer layers caused by the varying MC.

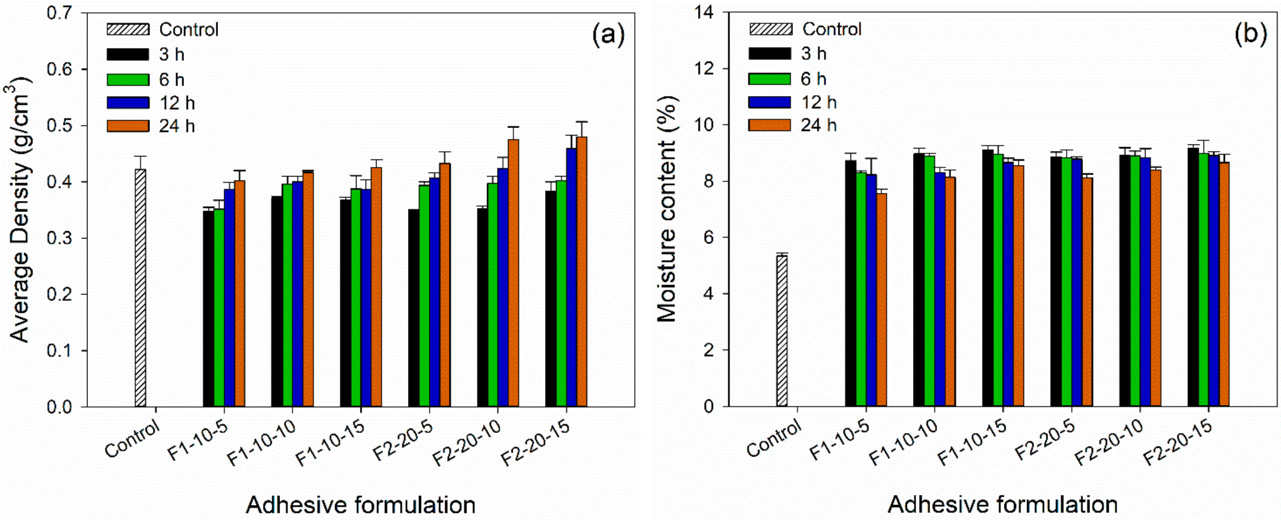

Figure 5. Physical properties of plywood bonded with PVOH–tannin–hexamine-based adhesives. (**a**) Average density, (**b**) moisture content.

Figure 6 illustrates the bending strength of plywood bonded with various PTH-based adhesive formulations and prepared at various pressing times. The MOR and MOE values of plywood were improved by increasing its tannin and hexamine content and pressing it for an extended time. MOR values varied between 40.7 MPa and 88.7 MPa, whereas MOE values varied between 6411.1 MPa and 14,025.6 MPa. After twenty-four hours of cold pressing, plywood's MOR and MOE values bonded with Formula 2 were approximately 88.7 MPa and 14,055.6 MPa, respectively. After 3 h of cold pressing, roughly 40.7 MPa and 6411.1 MPa were reported for plywood bonded with Formula 1. After three hours of cold pressing, plywood bonded with PU resins had better MOR and MOE values of 46.3 MPa and 43,505.5 MPa, respectively. This study showed that PTH-based adhesives could produce plywood with high bending properties comparable to commercial PU-bonded plywood.

Figure 7 depicts the dry tensile shear strength (TSS) and wood failure of plywood bonded using PTH-based adhesives. TSS values varied from 0.54 MPa to 1.42 MPa, and wood failure values ranged from 1.27% to 47.2%. The TSS values of plywood rose when the tannin and hexamine contents and pressing periods were increased. The plywood bonded with Formula 1 after 3 h of cold pressing yielded the lowest TSS value of 0.54 MPa, whereas the plywood bonded with Formula 2 after 24 h of cold pressing yielded the highest TSS value of 1.42 MPa. Consequently, the wood failure followed the same trend as the TSS values. The plywood bonded with Formula 1 after 3 h of cold pressing yielded the lowest wood failure value of 1.27%, whereas plywood bonded with Formula 2 after 24 h of cold pressing yielded the most outstanding wood failure value of 47.2%. Due to the short cold pressing time and poor cohesive strength, the PTH-based adhesives could not maintain bonding integrity. Regardless of the adhesive formulations, PTH-based adhesive could produce plywood with an acceptable TSS value of $\geq$0.7 MPa after cold-pressing for 12 h, while none of the formulation could meet the minimum requirement of 50% wood failure. By contrast, the TSS value and wood failure rate of the control plywood were around 1.2 MPa and 86%, respectively, demonstrating that the PU resins exhibited superior cohesive strength to sustain bonding integrity after only 3 h of cold pressing. The result of wood failure showed that higher tannin and hexamine content, and longer pressing time, enhanced the adhesion strength and increased the wood failure. Plywood prepared with PTH-based adhesives showed this type of cohesive failure (Figure 8). The PTH-based adhesives could not hold the bonding integrity in this type due to the short cold pressing time and low cohesive strength. By contrast, the control plywood had a wood failure of around 86%, indicating the PU resins had superior cohesive strength to maintain the bonding integrity with only 3 h of cold pressing. This result followed the previous work, which revealed that the PVOH–lignin–hexamine-based adhesive could not hold the bonding integrity owing to the short cold pressing time and low cohesive strength [31].

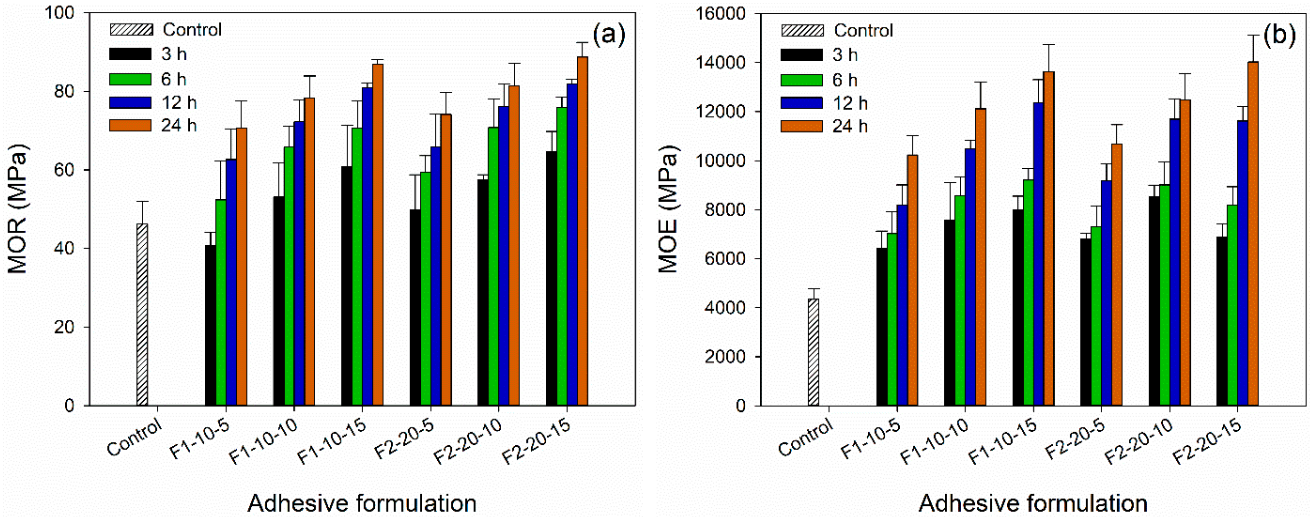

Figure 6. Mechanical properties of plywood bonded with PVOH–tannin–hexamine-based adhesives. (**a**) MOR, (**b**) MOE.

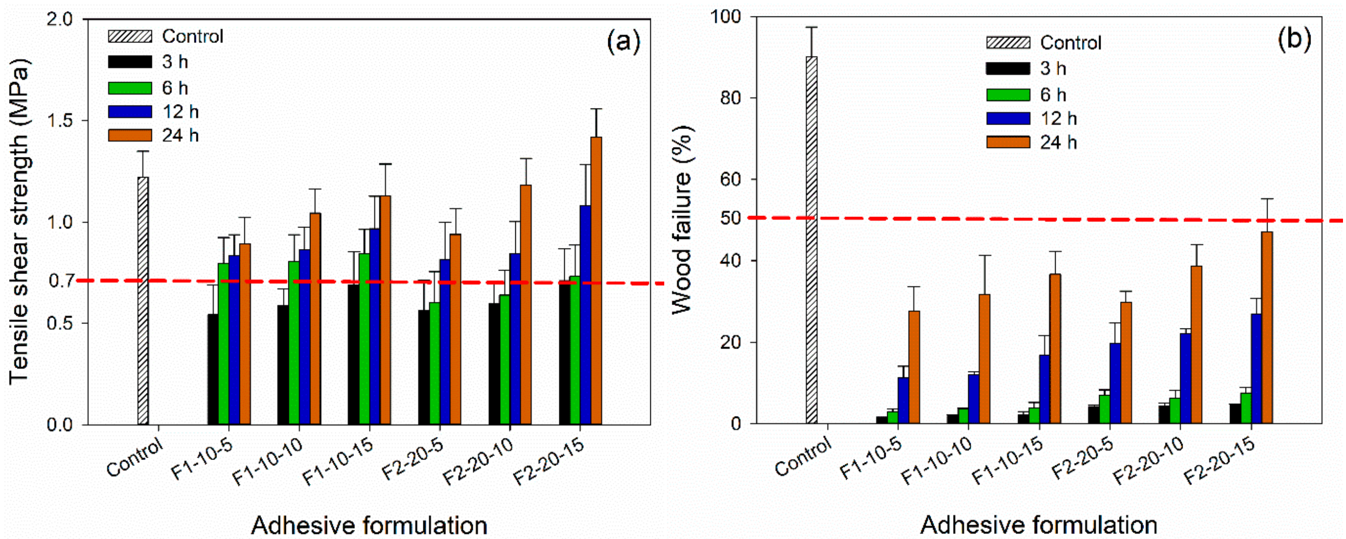

Figure 7. The bonding strength of plywood bonded with PVOH–tannin–hexamine-based adhesives. (**a**) Tensile shear strength, (**b**) wood failure.

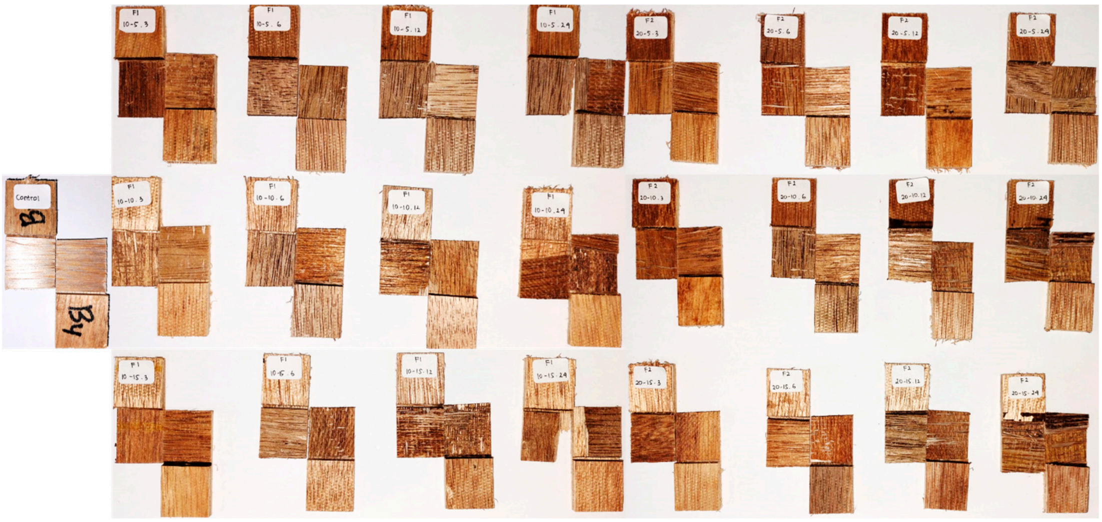

Figure 8. The wood failure images of plywood bonded with PVOH–tannin–hexamine-based adhesives.

4. Conclusions

Cold-setting plywood adhesives were produced based on PVOH–tannin–hexamine (PTH) adhesives. The effects of adhesive formulation (varying amounts of tannin and hexamine) and cold-pressing duration (3, 6, 12, and 24 h) on the plywood's physical and mechanical characteristics were studied. This investigation demonstrated that the high tannin and hexamine concentration increased the adhesive's solids content but lowered its average viscosity. Regardless of the adhesive formulation, the cohesion strength of PTH-based adhesives rose significantly from 5.57 Pa at 1/s to 1411.6 Pa at 400/s shear rate. A more significant percentage of tannin boosted the cohesion strength of PTH-based adhesives, while a higher concentration of hexamine lowered the cohesion strength marginally.

Consequently, the shear modulus dropped as a function of the shear rate. PTH-based adhesives with a higher concentration of tannin and hexamine had a more robust shear modulus. This investigation indicated that by increasing the tannin and hexamine content and the cold-pressing period, it is possible to create plywood with the tested glue that meets the Japanese standard for strength. The most excellent TSS value of 1.42 MPa, MOR values of 88.7 MPa, MOE values of 14,025.6 MPa, and wood failure of 47.2% was achieved by combining a PTH-based adhesive according to Formula 2 with 24 h cold pressing. This study demonstrated the feasibility of cold-pressing environmentally friendly plywood panels bonded using PTH-based glue as an alternative to standard plywood.

Author Contributions: Conceptualization, R.A.L.S., M.A.R.L. and R.K.S.; methodology, R.A.L.S., M.A.R.L. and R.K.S.; formal analysis, R.A.L.S., M.I.M. and W.F.; investigation, R.A.L.S., L.K. and A.H.I.; resources, M.A.R.L., W.F. and L.S.; data curation, R.A.L.S., R.K.S. and E.M.; writing—original draft preparation, R.A.L.S., M.A.R.L., R.K.S. and L.K.; writing—review and editing, L.K., S.H.L., J.S., R.R. and B.S.; visualization, R.A.L.S., S.H.L., M.I.M. and S.M.; supervision, M.A.R.L. and R.K.S.; project administration, M.A.R.L., R.K.S. and L.K.; funding acquisition, M.A.R.L. and L.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Japan-Asean Science and Technology Innovation Platform (JASTIP) 2022, grant number B-5815/III.5.6/HK.01.00/4/2022, titled "Development of High-Performance Bio-Based Adhesives for Wood Composites".

Data Availability Statement: Not applicable.

Acknowledgments: This study was supported by Japan-Asean Science and Technology Innovation Platform (JASTIP) 2022, grant number B-5815/III.5.6/HK.01.00/4/2022, titled "Development of High Performance Bio-Based Adhesives for Wood Composites". This work was also supported by the Slovak Research and Development Agency under the contracts APVV-19-0269 and No. SK-CZ-RD-21-0100.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zhou, X.; Du, G. Applications of Tannin Resin Adhesives in the Wood Industry. In *Tannins: Structural Properties, Biological Properties and Current Knowledge*; Books on Demand: Norderstedt, Germany, 2020; pp. 97–103. [CrossRef]
2. Kumar, R.N.; Pizzi, A. Environmental Aspects of Adhesives—Emission of Formaldehyde. *Adhes. Wood Lignocellul. Mater.* **2019**, *1*, 293–315. [CrossRef]
3. Park, B.; Kim, J. Dynamic mechanical analysis of urea-formaldehyde resin adhesives with different formaldehyde-to-urea molar ratios. *J. Appl. Phys.* **2008**, *108*, 2045–2051. [CrossRef]
4. Costa, N.A.; Pereira, J.; Ferra, J.; Cruz, P.; Martins, J.; Magalhães, F.D.; Mendes, A.; Carvalho, L.H. Scavengers for achieving zero formaldehyde emission of wood-based panels. *Wood Sci. Technol.* **2013**, *47*, 1261–1272. [CrossRef]
5. Kim, S. Environment-friendly adhesives for surface bonding of wood-based flooring using natural tannin to reduce formaldehyde and TVOC emission. *Bioresour. Technol.* **2009**, *100*, 744–748. [CrossRef] [PubMed]
6. Frihart, C.R. Wood adhesion and adhesives. In *Handbook of Wood Chemistry and Wood Composites*; CRC Press: Boca Raton, FL, USA, 2012; pp. 255–320. [CrossRef]
7. Kristak, L.; Antov, P.; Bekhta, P.; Lubis, M.A.R.; Iswanto, A.H.; Reh, R.; Sedliacik, J.; Savov, V.; Taghiyari, H.R.; Papadopoulos, A.N.; et al. Recent progress in ultra-low formaldehyde emitting adhesive systems and formaldehyde scavengers in wood-based panels: A review. *Wood Mater. Sci. Eng.* **2022**, 1–20. [CrossRef]
8. Petinarakis, J.H.; Kavvouras, P.K. Technological factors affecting the emission of formaldehyde from particleboards. *Wood Res.* **2006**, *51*, 31–40.
9. Auriga, R.; Gumowska, A.; Szymanowski, K.; Wronka, A.; Robles, E.; Ocipka, P.; Kowaluk, G. Performance properties of plywood composites reinforced with carbon fibers. *Compos. Struct.* **2020**, *248*, 112533. [CrossRef]
10. Shirmohammadli, Y.; Efhamisisi, D.; Pizzi, A. Tannins as a sustainable raw material for green chemistry: A review. *Ind. Crops Prod.* **2018**, *126*, 316–332. [CrossRef]
11. Ping, L.; Brosse, N.; Chrusciel, L.; Navarrete, P.; Pizzi, A. Extraction of condensed tannins from grape pomace for use as wood adhesives. *Ind. Crops Prod.* **2011**, *33*, 253–257. [CrossRef]
12. Zhao, Z.; Umemura, K. Investigation of a new natural particleboard adhesive composed of tannin and sucrose. *J. Wood Sci.* **2014**, *60*, 269–277. [CrossRef]
13. Ghahri, S.; Pizzi, A. Improving soy-based adhesives for wood particleboard by tannins addition. *Wood Sci. Technol.* **2018**, *52*, 261–279. [CrossRef]
14. Valenzuela, J.; Von Leyser, E.; Pizzi, A.; Westermeyer, C.; Gorrini, B. Industrial production of pine tannin-bonded particleboard and MDF. *Eur. J. Wood Wood Prod.* **2012**, *70*, 735–740. [CrossRef]
15. Li, C.; Wang, W.; Mu, Y.; Zhang, J.; Zhang, S.; Li, J.; Zhang, W. Structural Properties and Copolycondensation Mechanism of Valonea Tannin-Modified Phenol-formaldehyde Resin. *J. Polym. Environ.* **2018**, *26*, 1297–1309. [CrossRef]
16. Feng, S.; Yuan, Z.; Leitch, M.; Shui, H.; Xu, C.C. Effects of bark extraction before liquefaction and liquid oil fractionation after liquefaction on bark-based phenol formaldehyde resoles. *Ind. Crops Prod.* **2016**, *84*, 330–336. [CrossRef]
17. Zhang, J.; Liang, J.; Du, G.; Zhou, X.; Wang, H.; Lei, H. Development and characterization of a bayberry tannin-based adhesive for particleboard. *BioResources* **2017**, *12*, 6082–6093. [CrossRef]
18. Fitzken Da Vinci M. Niro, J.; Kyriazopoulos, M.; Bianchi, S.; Mayer, I.; Eusebio, D.A.; Arboleda, J.R.; Lanuzo, M.M.; Pichelin, F. Development of medium- and low-density fibreboards made of coconut husk and bound with tannin-based adhesives. *Int. Wood Prod. J.* **2016**, *7*, 208–214. [CrossRef]
19. Carré, C.; Zoccheddu, H.; Delalande, S.; Pichon, P.; Avérous, L. Synthesis and characterization of advanced biobased thermoplastic nonisocyanate polyurethanes, with controlled aromatic-aliphatic architectures. *Eur. Polym. J.* **2016**, *84*, 759–769. [CrossRef]
20. Mosiewicki, M.; Aranguren, M.I.; Borrajo, J. Thermal and mechanical properties of woodflour/tannin adhesive composites. *J. Appl. Polym. Sci.* **2004**, *91*, 3074–3082. [CrossRef]
21. Santos, J.; Delgado, N.; Fuentes, J.; Fuentealba, C.; Vega-Lara, J.; García, D.E. Exterior grade plywood adhesives based on pine bark polyphenols and hexamine. *Ind. Crops Prod.* **2018**, *122*, 340–348. [CrossRef]
22. Navarrete, P.; Pizzi, A.; Tapin-Lingua, S.; Benjelloun-Mlayah, B.; Pasch, H.; Rode, K.; Delmotte, L.; Rigolet, S. Low formaldehyde emitting biobased wood adhesives manufactured from mixtures of tannin and glyoxylated lignin. *J. Adhes. Sci. Technol.* **2012**, *26*, 1667–1684. [CrossRef]
23. Moubarik, A.; Allal, A.; Pizzi, A.; Charrier, F.; Charrier, B. Characterization of a formaldehyde-free cornstarch-tannin wood adhesive for interior plywood. *Eur. J. Wood Wood Prod.* **2010**, *68*, 427–433. [CrossRef]
24. Karacabeyli, E.; Gagnon, S. *Canadian Cross Laminated Timber Handbook: 2019 Edition*; FPInnovations: Pointe-Claire, QC, Canada, 2019; ISBN 978-0-86488-590-6.
25. Sikora, K.S.; McPolin, D.O.; Harte, A.M. Shear strength and durability testing of adhesive bonds in cross-laminated timber. *J. Adhes.* **2016**, *92*, 758–777. [CrossRef]
26. Gumowska, A.; Kowaluk, G.; Labidi, J.; Robles, E. Barrier properties of cellulose nanofiber film as an external layer of particleboard. *Clean Technol. Environ. Policy* **2019**, *21*, 2073–2079. [CrossRef]
27. Meyer, B.; Andrews, B.A.K.; Reinhardt, R.M. Formaldehyde release from Wood Products. *Anal. Chem.* **1986**, *58*, 1364. [CrossRef]

28. Banks, W.B. *Formaldehyde Release from Wood Products*; Meyer, B., Kottes Andrews, B.A., Reinhardt, R.M., Eds.; ACS Symposium Series No. 316; American Chemical Society: Washington, DC, USA, 1986.
29. Aristri, M.A.; Lubis, M.A.R.; Iswanto, A.H.; Fatriasari, W.; Sari, R.K.; Antov, P.; Gajtanska, M.; Papadopoulos, A.N.; Pizzi, A. Bio-Based Polyurethane Resins Derived from Tannin: Source, Synthesis, Characterisation, and Application. *Forests* **2021**, *12*, 1516. [CrossRef]
30. Chen, X.; Pizzi, A.; Fredon, E.; Gerardin, C.; Zhou, X.; Zhang, B.; Du, G. Low curing temperature tannin-based non-isocyanate polyurethane (NIPU) wood adhesives: Preparation and properties evaluation. *Int. J. Adhes. Adhes.* **2022**, *112*, 103001. [CrossRef]
31. Lubis, M.A.R.; Labib, A.; Sudarmanto; Akbar, F.; Nuryawan, A.; Antov, P.; Kristak, L.; Papadopoulos, A.N.; Pizzi, A. Influence of Lignin Content and Pressing Time on Plywood Properties Bonded with Cold-Setting Adhesive Based on Poly (Vinyl Alcohol), Lignin, and Hexamine. *Polymers* **2022**, *14*, 2111. [CrossRef]
32. Arias, A.; González-García, S.; Feijoo, G.; Moreira, M.T. Tannin-based bio-adhesives for the wood panel industry as sustainable alternatives to petrochemical resins. *J. Ind. Ecol.* **2022**, *26*, 627–642. [CrossRef]
33. *Japanese Agricultural Standard (JAS) for Plywood Japanese Agricultural Standard for Plywood*; Japan Plywood Inspection Corporation: Tokyo, Japan, 2003.
34. Pizzi, A. Recent developments in eco-efficient bio-based adhesives for wood bonding: Opportunities and issues. *J. Adhes. Sci. Technol.* **2006**, *20*, 829–846. [CrossRef]
35. Sridach, W.; Jonjankiat, S.; Wittaya, T. Effect of citric acid, PVOH, and starch ratio on the properties of cross-linked poly(vinyl alcohol)/starch adhesives. *J. Adhes. Sci. Technol.* **2013**, *27*, 1727–1738. [CrossRef]
36. Aladejana, J.T.; Wu, Z.; Li, D.; Guelifack, K.; Wei, W.; Wang, X.A.; Xie, Y. Facile Approach for Glutaraldehyde Cross-Linking of PVA/Aluminophosphate Adhesives for Wood-Based Panels. *ACS Sustain. Chem. Eng.* **2019**, *7*, 18524–18533. [CrossRef]
37. Aristri, M.A.; Lubis, M.A.R.; Laksana, R.P.B.; Sari, R.K.; Iswanto, A.H.; Kristak, L.; Antov, P.; Pizzi, A. Thermal and mechanical performance of ramie fibers modified with polyurethane resins derived from acacia mangium bark tannin. *J. Mater. Res. Technol.* **2022**, *18*, 2413–2427. [CrossRef]
38. Lubis, M.A.R.; Sari, F.P.; Laksana, R.P.B.; Fatriasari, W.; Hermiati, E. Ambient curable natural rubber latex adhesive cross-linked with polymeric isocyanate for bonding wood. *Polym. Bull.* **2022**, *79*, 6745–6757. [CrossRef]
39. Lubis, M.A.R.; Falah, F.; Harini, D.; Sudarmanto; Kharisma, A.; Tjahyono, B.; Fatriasari, W.; Subiyanto, B.; Suryanegara, L.; Iswanto, A.H. Enhancing the performance of natural rubber latex with polymeric isocyanate as cold-pressing and formaldehyde free adhesive for plywood. *J. Adhes.* **2023**, *99*, 58–73. [CrossRef]
40. Pichelin, F.; Nakatani, M.; Pizzi, A.; Wieland, S.; Despres, A.; Rigolet, S. Structural beams from thick wood panels bonded industrially with formaldehyde-free tannin adhesives. *For. Prod. J.* **2006**, *56*, 31–36.