

Article

# Utilization of Partially Liquefied Bark for Production of Particleboards

Wen Jiang <sup>1</sup>, Stergios Adamopoulos <sup>1,\*</sup>, Reza Hosseinpourpia <sup>1</sup>, Jure Žigon <sup>2</sup>,  
Marko Petrič <sup>2</sup>, Milan Šernek <sup>2</sup> and Sergej Medved <sup>2,\*</sup>

<sup>1</sup> Department of Forestry and Wood Technology, Linnaeus University, Lückligs Plats 1, 35195 Växjö, Sweden; wen.jiang@lnu.se (W.J.); reza.hosseinpourpia@lnu.se (R.H.)

<sup>2</sup> Department of Wood Science and Technology, Biotechnical Faculty, University of Ljubljana, Rožna Dolina C VIII/34, SI-1000 Ljubljana, Slovenia; jure.zigon@bf.uni-lj.si (J.Ž.); marko.petric@bf.uni-lj.si (M.P.); milan.sernek@bf.uni-lj.si (M.Š.)

\* Correspondence: stergios.adamopoulos@lnu.se (S.A.); sergej.medved@bf.uni-lj.si (S.M.)

Received: 13 July 2020; Accepted: 28 July 2020; Published: 30 July 2020



**Abstract:** Bark as a sawmilling residue can be used for producing value-added chemicals and materials. This study investigated the use of partially liquefied bark (PLB) for producing particleboard with or without synthetic adhesives. Maritime pine (*Pinus pinaster* Ait.) bark was partially liquefied in the presence of ethylene glycol and sulfuric acid. Four types of particleboard panels were prepared with a PLB content of 4.7%, 9.1%, 20%, and 33.3%, respectively. Another five types of particleboard panels were manufactured by using similar amounts of PLB and 10 wt.% of melamine–urea–formaldehyde (MUF) adhesives. Characterization of bark and solid residues of PLB was performed by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and automated vapor sorption (AVS). Mechanical and physical properties of the particleboard were tested according to the European standards EN 310 for determining modulus of elasticity and bending strength, EN 317 for determining thickness swelling after immersion in water, and EN 319 for determining internal bond strength. The results showed that the increase in PLB content improved the mechanical strength for the non-MUF boards, and the MUF-bonded boards with up to 20% of PLB met the requirements for interior uses in dry conditions according to EN 312. The non-MUF boards containing 33.3% of PLB and the MUF-bonded boards showed comparable thickness swelling and water absorption levels compared to the reference board.

**Keywords:** bark; bonding; partial liquefaction; MUF adhesives; water vapor sorption; thickness swelling; wood-based panels

## 1. Introduction

Particleboard is a panel product made from wood particles, originating from low value wooden raw material (e.g., chips and shavings) or other lignocellulosic materials, bonded by synthetic adhesives and pressed at high pressures and temperatures [1,2]. Particleboard is a low-cost panel product with adequate strength for furniture and interior applications and have been widely applied in flooring, wall and ceilings, flat-pack furniture, cabinets, and work surfaces such as speaker boxes, sewing machine tops, etc. [3,4]. Adhesives are an important element in the wood-based panel industry. Particleboard is traditionally produced with wood adhesives such as urea–formaldehyde (UF), melamine–urea–formaldehyde (MUF), and isocyanate-based adhesives. It is estimated that the adhesives used for particleboard production in Europe are split among UF (92%), MUF (7%), and isocyanates (1%) [5]. All these existing commercial adhesives are petroleum-based, and thus not sustainable [6]. At the same time, the concern about formaldehyde emissions from wood-based

panels, especially in indoor applications, is currently the most important driving factor for wood panel manufacturers to move away from using formaldehyde-based synthetic adhesives [7]. Therefore, the development of natural binders and bio-based adhesives for wood panel production is needed. A common problem for bio-based adhesives is their industrialization, which requires stable qualities and quantities of raw materials and final products. Adhesives based on a variety of natural materials such as starch, proteins, lignin and tannin have been proved to be less reactive than their formaldehyde-based counterparts, and this leads to much longer press times and considerably higher production costs. Thus, the particleboard industry has not yet been able to use natural binders in the production and the penetration of such adhesive systems in the market is rather small [8].

Recently, the utilization of bio-based adhesives from liquefied biomass has received considerable attention. Liquefaction is a method that converts wood and other lignocellulosic biomass into liquids for obtaining oils, chemicals, and other value-added materials [9]. Liquefaction of biomass includes two methods: hydrothermal liquefaction (HTL) and moderate acid-catalyzed liquefaction (MACL). HTL is usually carried out in the water or organic solvents at a temperature of 200–400 °C and pressure of 5–20 MPa and MACL takes place at a lower temperature of 120–250 °C under atmospheric pressure with the assistance of acid catalysts [9–13]. The primary products are chosen by the different liquefaction methods and the liquefying conditions. HTL produces bio-oil as main products while MACL mainly produces bio-polyol or phenolated compounds depending on the solvents that are used [9]. Liquefied wood (LW) from MACL with polyhydric alcohols and phenols has been used in different adhesive systems, such as polyurethane, UF, MUF, phenol-formaldehyde, and epoxy systems [14–21]. LW has high reactivity with other adhesives precursors and reactive sites due to a large amount of phenolic and alcoholic hydroxyl groups in their compositions [16].

Kunaver et al. [16] produced particleboard from melamine–formaldehyde (MF) or MUF adhesives with added LW, where spruce was liquefied in glycerol–diethylene glycol mixture as a solvent and *p*-toluenesulfonic acid as a catalyst for 3 h at 180 °C. The results showed that the addition of 50% LW to the MF and MUF adhesives did not influence the mechanical properties of particleboard but significantly reduced the formaldehyde emissions. Čuk et al. [22] bonded particleboard with MF that was partially substituted by LW. Adhesive mixtures containing 20% of LW had the largest improvements in the mechanical properties of the particleboard compared to the reference boards. Substitution of MF by LW of up to 30% resulted in a comparable mechanical strength to board bonded only with MF, while significantly reducing formaldehyde emissions. LW worked as a plasticizer and increased the mobility of the MF resin molecules. However, the thermal stability of MF substituted by LW was reduced because LW prolonged the curing time of the final adhesive, decreased the cross-linking degree, and accelerated the thermal degradation. Janiszewska et al. [23] produced particleboard with a mixture of UF and LW (ratio 4:1) and investigated the influence of different liquefying solvents, e.g., a mixture of solvents from the polyhydroxy alcohol group, including glycerine, ethylene glycol, propylene glycol, diethylene glycol, and dipropylene glycol, on the chemical structure, physical and mechanical properties of the particleboard. For all liquefying solvents, boards exhibited comparable properties to the ones produced without LW.

Bark, as an industrial residual material, with heterogeneous structure and diverse chemical composition, can be used for the production of a variety of and bio-composites and bio-compounds such as tannin and polyphenols, bio-oil, antioxidants, and bio-based adhesives [24–31]. Particleboard based on larch bark has been reported by Tudor with a much lower formaldehyde emission content than the wood-based panels, which means bark work as formaldehyde scavenger in the particleboard [31]. Limited publications can be found related to the utilization of liquefied bark in wood adhesives and wood-based composites, while, all of them followed a complete liquefaction process. Janiszewska [24] liquefied bark in polyhydric alcohols and *p*-toluenesulfonic acid at 120 °C for 2 h, and then prepared three-layer particleboard by using an adhesive mixture of 80% MUF and 20% liquefied bark (LB) with the addition of 1 M NaOH or 25% ammonium hydroxide for neutralizing the adhesive mixtures. The boards made with MUF-LB adhesives had 10–20% lower modulus of elasticity, 22–29% lower

bending strength, and 25% lower tensile strength in comparison with the ones made with commercial MUF adhesives. It was also determined that replacing of MUF with LB led to a slight reduction in formaldehyde content. Lee and Liu [32] prepared particleboard bonded by LB-based resol adhesives, which was prepared from LB of Taiwan Acacia (*Acacia confusa*) and China fir (*Cunninghamia lanceolata*) with two types of catalysts, i.e., sulfuric acid and hydrochloric acid. The results showed that the resol type adhesives prepared from bark, liquefied with sulfuric acid, had a higher viscosity compared to those made from liquefied bark with hydrochloric acid. Adhesives from liquefied China fir had a higher viscosity than those from liquefied Taiwan acacia with the same acid catalyst. The thermal analysis showed that the adhesives based on hydrochloric acid-catalyzed liquefied wood had a higher maximum temperature, a greater height of exothermic peak, and a larger quantity of exothermic heat at thermosetting than the adhesives based on sulfuric acid-catalyzed liquefied wood. Particleboard made with resol adhesives based on liquefied Taiwan acacia bark catalyzed by sulfuric acid had the best mechanical properties and the lowest thickness swelling among all particleboard panels.

A complete moderate-acid catalyzed liquefaction process of biomass in alcohols or phenols takes approximately 90–120 min under constant stirring and heating [9,12]. The obtained compounds require further purification stage to retrieve liquids for applying in adhesive formulations, which is time- and energy-consuming. Therefore, present work explores a novel approach at the production of partially liquefied bark (PLB) and its further utilization in manufacturing particleboard panels. Changes in the chemical characterization structure, thermal stability, and water vapor sorption behavior of bark due to partial liquefaction process were determined by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), and automated vapor sorption (AVS) apparatus, respectively on the solid residues of PLB. The effect of PLB on the physical, mechanical, and microscopic structure of particleboard made with or without MUF adhesives were then analyzed. It was hypothesized that bark was partially solvolyzed after liquefaction generating PLB, which is a chemical-activated particle that can be incorporated for better compatibility with wood particles, and can thus enhance the physical and mechanical properties of the particleboard.

## 2. Materials and Methods

### 2.1. Materials

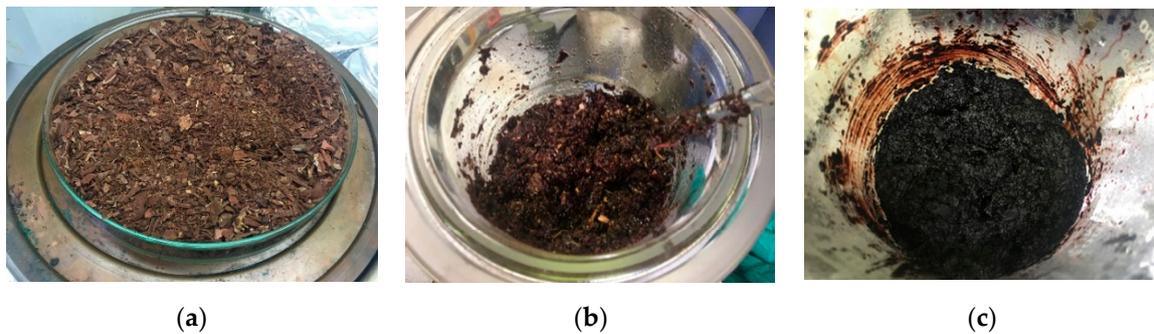
Bark of maritime pine (*Pinus pinaster* Ait.) was used for liquefaction. Bark was purchased from BVB Substrates (De Lier, The Netherlands), and then milled by a Condux mill CSK 360/N1 (Hanau, Germany) to particles. Chemicals used for liquefaction were ethylene glycol (EG) (Honeywell, Charlotte, NC, USA) as a solvent and 96% sulfuric acid (SA) (KEMIKA d.d., Zagreb, Croatia) as a catalyst. 1,4-dioxane, purchased from Honeywell GmbH (Seelze, Germany) was used for purification after liquefaction. Fresh wood particles from spruce (*Picea* spp.) were collected from a local sawmill in Ljubljana, Slovenia. Melamine–urea–formaldehyde (MUF) adhesives H97 was provided by Melamine Kočevje d.d. (Kočevje, Slovenia). Ammonium sulfate with 20% solid content was used as an adhesive hardener at a content of 3% in the adhesive formulations.

### 2.2. Partial Liquefaction Process

Oven-dried bark particles (103 °C for 24 h) together with the solvent and catalyst were added into a three-neck glass reactor submerged in an oil bath equipped with a mechanical stirrer and a water condenser. A weight ratio of 3:1 was used for solvent and bark. The catalyst concentration was 3% (*w/w*) based on the solvent mass. The liquefaction process was initiated at 180 °C with constant stirring under ambient atmosphere. After 30 min, the liquefaction was stopped by removing the reactor from the oil bath and transferring the liquefied bark to a clean beaker for cooling down to room temperature.

Figure 1 shows the bark, bark mixed with solvent and catalyst before liquefaction, and PLB after liquefaction. PLB (Figure 1c) used for the production of particleboard is a wet material with a high solid content (un-liquefied bark), unreacted EG and SA, and liquefaction liquid intermediates. PLB had a

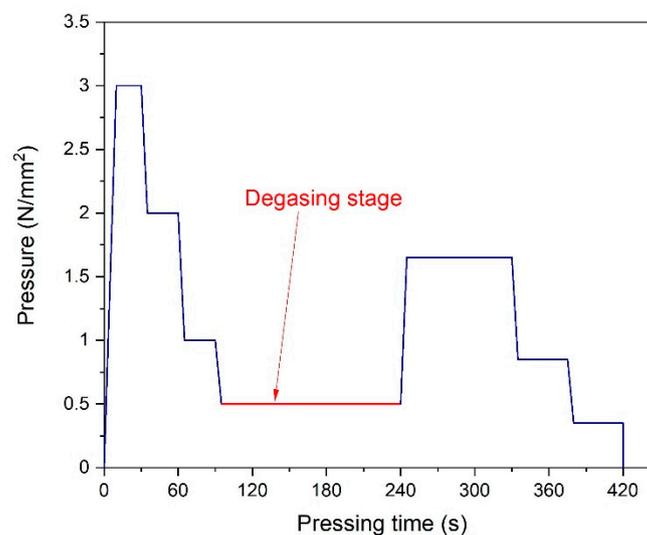
solid content of 41% (oven-dry mass of solids divided by total PLB mass). For further characterization, PLB was oven-dried at 103 °C for 24 h as the solvent-containing solid residue of PLB. Purified PLB as a solvent-free solid residue of PLB was prepared by first dissolving wet PLB in a mixture solvent of 1,4-dioxane and water at a mass ratio of 4:1. Then the wet PLB and solvent mixture was centrifuged at 1000 rpm for 10 min by removing the residual solvents and the intermediate chemicals. The obtained solids as purified PLB were dried in the oven at 103 °C for 24 h. Bark, oven-dried PLB, and purified PLB were milled to powders with a size of 2 mm for subsequent analysis.



**Figure 1.** Bark (a), mixture of bark with the solvent and catalyst (b), and partially liquefied bark (c).

### 2.3. Particleboard Production

Single-layer particleboard panels were manufactured with a target thickness of 8 mm by following standard procedures that simulate industrial production in the laboratory. Wet PLB was mixed with dry wood particles (less than 4% moisture content) at different loading levels of 4.7%, 9.1%, 20%, and 33.3%, and then the corresponding panels were labelled as I, II, III, and IV. It should be mentioned that the PLB content was measured based on the total mass of the mixture of PLB and wood particles. Five panels were manufactured by adding 10 wt.% of MUF adhesives and PLB at a loading level of 0, 4.7%, 9.1%, 20%, and 33.3% to dry wood particles, and these panels were labelled as V, VI, VII, VIII, and IX. For MUF, 3% (*w/w* of dry adhesives) of hardener was used. The mats were then manually formed into frame dimensions of 500 × 500 mm<sup>2</sup>. The hot-pressing temperature was set as 190 °C. The pressing speed was set to 52 s·mm<sup>-1</sup> (pressing time including closing and opening was 420 s). Such a long-pressing time was needed due to high mat moisture content due to the usage of wet PLB, hence there is a degassing stage in the middle of the pressing schedule (Figure 2). The final density and thickness of the particleboard are shown in Table 1.



**Figure 2.** Pressing diagram.

**Table 1.** Density and thickness of the manufactured particleboard.

| Panel | Description         | Density (kg/m <sup>3</sup> ) | Thickness (mm) |
|-------|---------------------|------------------------------|----------------|
| I     | 4.7% PLB            | 399 ± 19                     | 7.98 ± 0.21    |
| II    | 9.1% PLB            | 397 ± 65                     | 8.05 ± 0.54    |
| III   | 20.0% PLB           | 554 ± 18                     | 8.32 ± 0.27    |
| IV    | 33.3% PLB           | 540 ± 74                     | 8.18 ± 0.21    |
| V *   | 10.0% MUF           | 755 ± 17                     | 7.63 ± 0.09    |
| VI    | 10% MUF + 4.7% PLB  | 662 ± 23                     | 7.70 ± 0.05    |
| VII   | 10% MUF + 9.1% PLB  | 734 ± 22                     | 7.60 ± 0.15    |
| VIII  | 10% MUF + 20.0% PLB | 686 ± 62                     | 7.79 ± 0.11    |
| IX    | 10% MUF + 33.3% PLB | 632 ± 16                     | 8.03 ± 0.12    |

\* as a reference board made from melamine–urea–formaldehyde (MUF) adhesives and wood particles.

## 2.4. Characterizations

### 2.4.1. Fourier Transform Infrared (FTIR) Spectroscopy

The chemical structure of bark, oven-dried PLB, and purified PLB powders was analyzed with a Fourier Transform Infrared Spectrometer (Alpha FTIR spectrometer, Bruker, Karlsruhe, Germany) with a versatile high throughput ZnSe ATR crystal. The FTIR analysis was conducted in a wavelength region from 4000 to 800 cm<sup>-1</sup> at room temperature, accumulating 64 scans with a resolution of 4 cm<sup>-1</sup>.

### 2.4.2. Thermogravimetric Analysis (TGA)

The thermal stability of bark, oven-dried PLB, and purified PLB powders were analyzed using a NETZSCH STA 409PC instrument (Netzsch, Selb, Germany). Approximately 5 mg of dried samples (24 h at 105 °C) were heated from 30 to 800 °C at a rate of 10 °C/min under a flowing nitrogen atmosphere.

### 2.4.3. Automated Vapor Sorption (AVS)

The water vapor sorption behavior of bark, oven-dried PLB, and purified PLB powders was determined using an automated vapor sorption (AVS) apparatus (Q5000 SA, TA Instruments, New Castle, DE, USA) as reported previously [33,34]. Approximately 5 mg of grounded samples, passed through a 10-mesh sieve, were exposed to the relative humidity (RH) from 0 to 90% in step sequences of 15% and then continued to reach 95% at a constant temperature of 25 °C. The instrument maintained a constant target RH until the mass change in the sample (dm/dt) was less than 0.01% per min over a 10 min period. The equilibrium moisture content (EMC) for each sample was assessed based on their equilibrium weight at each given RH step throughout the adsorption run.

### 2.4.4. Mechanical Properties of Particleboard

The bending test for measuring the modulus of elasticity (MOE) and modulus of rupture (MOR) of the particleboard panels manufactured with PLB was performed according to EN 310:1993 [35] by using a universal testing machine (Zwick/Roell Z005, Zwick/Roell GmbH, Ulm, Germany). Six samples per board measuring 210 × 25 mm<sup>2</sup> were tested using a span of 160 mm and a cross-head speed of 7 mm min<sup>-1</sup> (time to break was between 45 and 75 s). MOE was determined between 10 and 40% maximum load.

Six samples measuring 210 × 25 mm<sup>2</sup> (width × length) were cut from each panel and tested for their tensile strength parallel to the surface by using a universal testing machine (Zwick/Roell Z005, Ulm, Germany).

The internal bond (IB) strength test was conducted following EN 319:1993 [36]. Six samples per particleboard measuring 50 × 50 mm<sup>2</sup> were bonded with hot-melt glue and the test perpendicular to their surfaces were performed using a universal testing machine (Instron 4466, Darmstadt, Germany). A loading speed of 0.75 mm·min<sup>-1</sup> was used for testing (time to break was between 50 and 70 s).

#### 2.4.5. Thickness Swelling and Water Absorption of Particleboard

Samples measuring  $50 \times 50 \text{ mm}^2$  were cut from the particleboard and immersed in water at  $20 \pm 2 \text{ }^\circ\text{C}$  for 2 h and 24 h. Thickness swelling (TS) was evaluated by the difference between the final and initial thickness, and water absorption (WA) was evaluated by the weight difference. Four samples per panel were used for the determinations according to EN 317:1993 [37].

#### 2.4.6. Scanning Electron Microscopy (SEM)

The formed bonds between wood particles, PLB and MUF adhesives were studied on the cross-section of the particleboard with a scanning electron microscope (SEM, FEI Quanta 250, FEI, Hillsboro, OR, USA), equipped with the energy dispersive X-ray spectrometer (EDX, AMETEK Inc., Berwyn, PA, USA). Before observations, the surfaces of the selected area of samples were evened by cutting on a Leica SM2010R microtome (Leica, Wetzlar, Germany). The SEM micrographs were taken with large field detector (LFD) at 100 $\times$ , 500 $\times$  and 1000 $\times$  magnifications in a low vacuum (50 Pa), at a voltage of 5.0 kV, a spot size of 3.0, and a beam transition time of 45  $\mu\text{s}$ .

### 2.5. Statistical Analysis

The SPSS version 25.0 statistical software package (IBM Corp., Armonk, NY, USA) was used for the statistical analysis. One-way ANOVA was performed on the mechanical and water-related results for the analysis of variance at a 95% confidence interval ( $p < 0.05$ ). The statistical differences between mean values were assessed by using the Tukey's honestly significant difference (HSD) test.

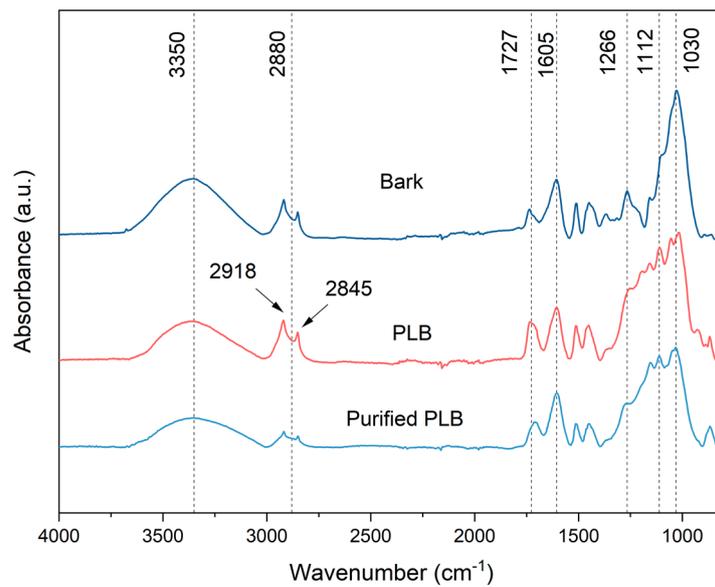
## 3. Results and Discussion

### 3.1. Characterization of Bark and Solid Residues of PLB

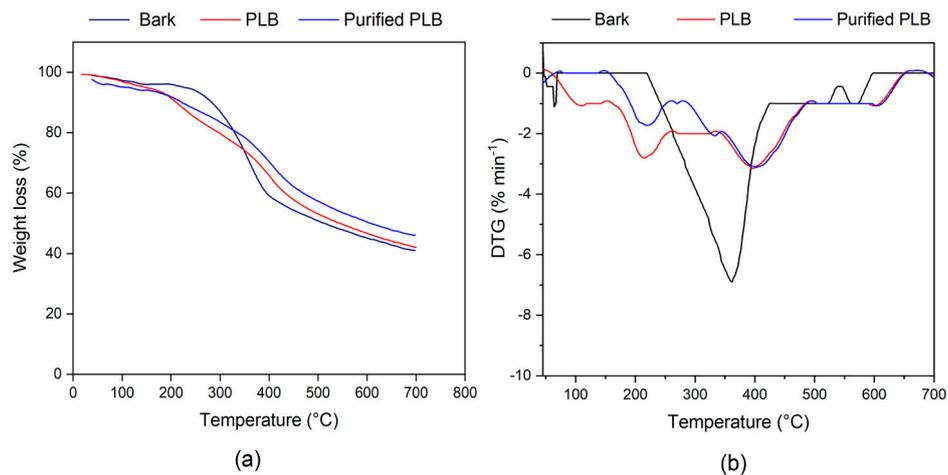
FTIR spectroscopy analysis detected the chemical structure of bark and solid residues of PLB (oven-dried PLB and purified PLB) (Figure 3). Raw bark showed a strong absorption peak at  $3350 \text{ cm}^{-1}$ , which corresponds to -OH stretch vibration in cellulose, lignin, and hemicelluloses. Bark and oven-dried PLB illustrated two distinct peaks at  $2918$  and  $2845 \text{ cm}^{-1}$ , which are assigned to -CH stretch vibration in aromatic methoxyl groups and aliphatic methyl and methylene groups [38,39]. The spectra for oven-dried PLB appears similar to that of purified PLB. A slight decrease in the -OH and -CH bonds were observed in oven-dried PLB and purified PLB compared to bark. This might be related to the degradation and dehydration of bark, and the formation of alcohol-soluble intermediates [12,40–42]. A peak representing the C-O linkage of alcohol or ether that are typical polyol products from the complete liquefaction was found at around  $1112 \text{ cm}^{-1}$  in oven-dried PLB and purified PLB (Figure 3). This peak verified the production of polyols through the partial liquefaction [43]. The absorption band at  $1030 \text{ cm}^{-1}$  corresponding to -CO stretching for both PLB and purified PLB was weakened due to the cleavage of  $\beta$ -O-4 bonds of lignin [42]. The broad band between  $1266$  and  $1030 \text{ cm}^{-1}$  in the spectrum for oven-dried PLB and purified PLB indicates -CO stretching in primary alcohol, secondary alcohol, ethers, and esters. The changes in the absorbance of -CO groups in bark and PLB confirmed that the liquefaction has occurred with the formation of the above intermediates. The intensive vibration at  $1727$  and  $1605 \text{ cm}^{-1}$  in bark, oven-dried PLB and purified PLB correspond to -C=O in hemicelluloses and lignin, and to -C=C- stretching in lignin, which indicates the high content of lignin remained in the bark structure after partial liquefaction.

Thermal degradation behavior of bark, PLB, and purified PLB was examined by TGA (Figure 4a) and derivative thermogravimetric (DTG, Figure 4b) analyses of the samples after drying in the oven at  $105 \text{ }^\circ\text{C}$  for 24 h. There were apparent differences in the thermal degradation pattern of bark after partial liquefaction and purification compared to raw bark. Figure 4a shows the weight loss of the three tested samples up to a maximum of 40–60% of their initial weight. It was previously reported by Yang et al. (2007) that cellulose pyrolysis occurs in a higher temperature range than lignin and hemicelluloses, and lignin is the most difficult polymer to decompose with a solid residue of 45.7 wt.% [44]. As shown

in Figure 4b and Table 2, decomposition of bark ( $T_{onset}$ ) initiated at 219 °C and reached a maximum mass loss ( $T_{max1}$ ) at 361 °C, thus representing typical pyrolysis of lignocellulosic material [45,46]. The respective  $T_{onset}$  of PLB and purified PLB were, respectively, 152 and 148 °C and were both lower than that of bark. The decomposition of PLB and purified PLB started earlier than bark, which might be attributed to a large number of hemicelluloses and amorphous part of cellulose that decomposed in the liquefaction due to the effect of the acid catalyst [42]. The decomposition of the intermediate products such as alcohols and esters in the PLB and purified PLB caused a shifted second maximum degradation temperature  $T_{max2}$ . As shown in Table 2, the  $T_{onset}$ ,  $T_{max1}$ , and  $T_{max2}$  of PLB and purified PLB were very close to each other but considerably lower than bark, which can be related to the lower content of volatiles in PLB and purified PLB [47].



**Figure 3.** Fourier transform infrared (FTIR) spectrum of raw bark, oven-dried partially liquefied bark (PLB), and purified PLB.

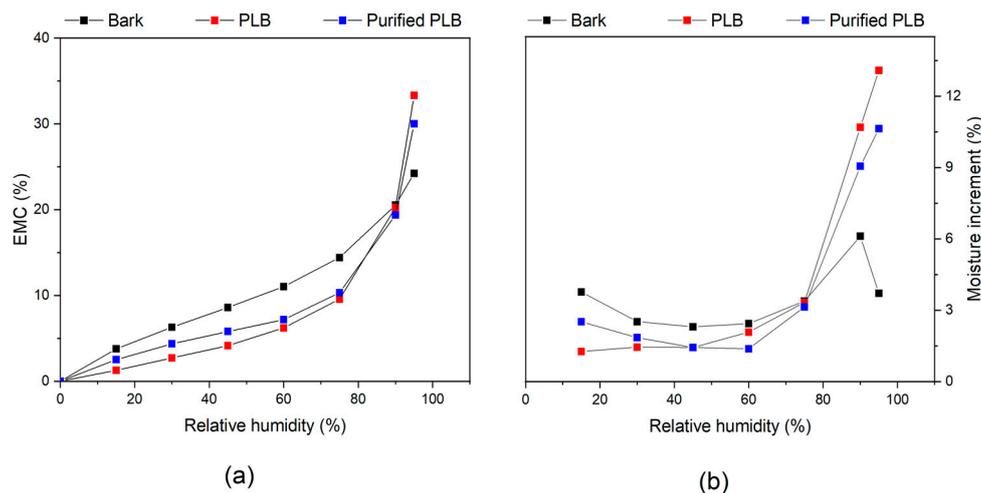


**Figure 4.** Mass loss (a) and first derivative (DTG) (b) of bark, PLB, and purified PLB.

**Table 2.** Thermal degradation properties of bark, PLB, and purified PLB.

| Material     | T <sub>onset</sub> (°C) | T <sub>max1</sub> (°C) | T <sub>max2</sub> (°C) | T <sub>offset</sub> (°C) |
|--------------|-------------------------|------------------------|------------------------|--------------------------|
| Bark         | 219                     | 361                    | –                      | 428                      |
| PLB          | 152                     | 215                    | 397                    | 495                      |
| Purified PLB | 148                     | 218                    | 403                    | 495                      |

The water vapor sorption isotherms of bark, PLB and purified PLB are presented in Figure 5a. PLB and purified PLB showed considerably lower EMC than bark in the RH range of 0% to 75%. A strong upward bend was observed in the EMC of PLB and purified PLB from 75% to 95% and surpassed bark at 95% RH. PLB showed an EMC of 33% at 95% RH, while the EMC values of purified PLB and bark at this RH level were 30% and 24%, respectively. Moisture increment (MI) of bark was found to vary little over the entire RH range (Figure 5b), as it was slightly decreased from 15% to 45% RH, then gradually increased from 45% to 90% RH, and then decreased from 90% to 95% RH. PLB and purified PLB, however, showed a different MI trend. The MI of PLB gradually increased with increasing the RH from 15% to 75% and then sharply increased from 75% to 95%. MI was decreased in purified PLB at the RH range of 15% to 60% but then increased greatly after 60% RH. PLB and purified PLB illustrated a more hydrophilic behavior than bark at the higher RH range over 75%. This can be related to more accessible hygroscopic hydroxyl sites after partial liquefaction from the degradation of cellulose due to alcohol hydrolysis catalyzed by strong acids [48,49]. It was reported previously that liquefaction of lignocellulosic materials in polyhydric alcohols initially hydrolyzes the glucoside linkage of the cellulose to produce glucoside monomers, which further decomposed to levulinic acid esters [41,50]. During the liquefaction process, the polymeric structure of lignin was degraded, and the obtained lignin monomers reacted with ethylene glycol to form a condensed lignin-based polymeric material with predominant aromatic hydroxyl groups, which can enhance the hydrophilicity of PLB [51]. The higher moisture sorption of PLB as compared to purified PLB can be attributed to the remaining ethylene glycol that provided extra hydroxyl groups in the PLB. Some part of these hydroxyl groups may have also been removed in purified PLB by the solvent during the purification step.

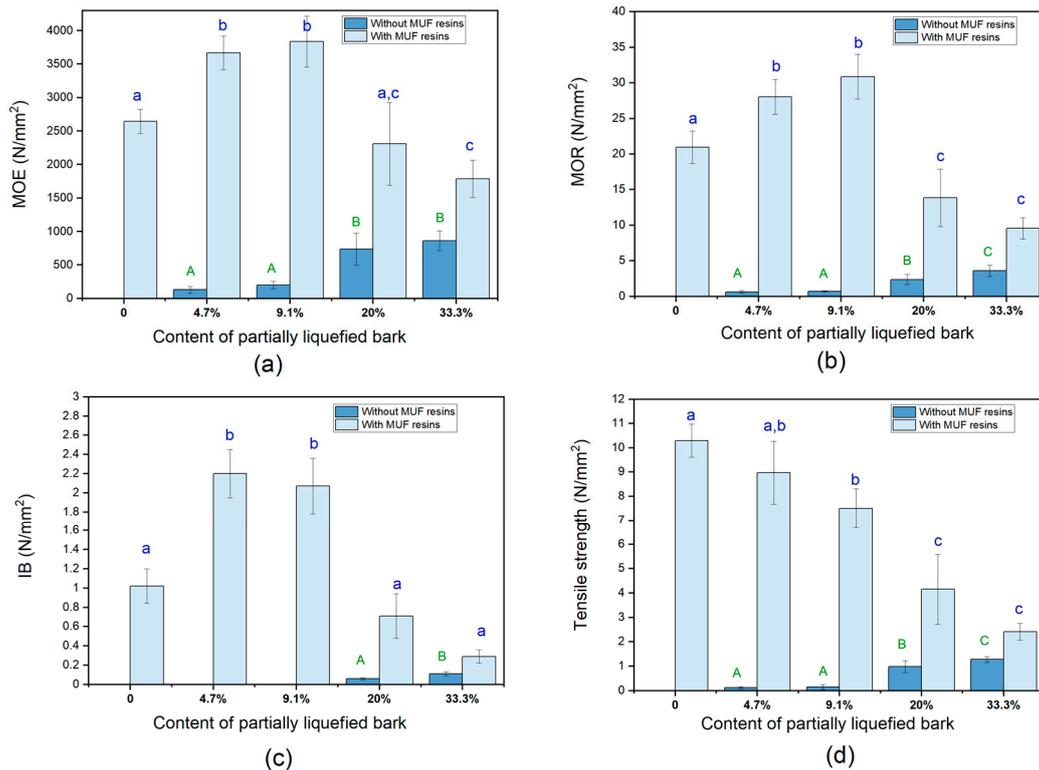


**Figure 5.** (a) Equilibrium moisture content (EMC) of bark, PLB and purified PLB samples exposed to increasing water vapor from relative humidity (RH) of 0 to 95%; (b) moisture increment during adsorption of bark, PLB, and purified PLB samples.

### 3.2. Performance of the Particleboard Containing PLB

The mechanical properties (i.e., MOE, MOR, IB, and tensile strength) of the particleboard panels containing PLB in the presence of MUF or not are presented in Figure 6. The non-MUF bonded boards

containing 4.7% and 9.1% PLB (boards I and II) did not show any cohesion, and, thus, easily decomposed during cutting as illustrated in Figure 7. The MOR, MOE, and tensile strength values of the non-MUF boards were improved by increasing the PLB content. The particleboard containing wood particles and the highest amount of PLB (board IV) exhibited the highest values. A significant increment in the MOE, MOR and tensile strength of the non-MUF boards occurred when the PLB content increased from 9.1% to 20%. At least 20% of PLB was required for the non-MUF panels to be able to perform the IB test. It should be noted that the mechanical property values of all the non-MUF boards (I, II, III, and IV) were very low and did not meet the requirement of particleboard for interior uses in dry conditions according to EN 312:2010.



**Figure 6.** Average MOE (a), MOR (b), IB (c), and tensile strength (d) of particleboard containing partially liquefied bark, with or without MUF adhesives. Values labelled with the same letter (small for MUF boards, and capital for non-MUF boards) are not statistically different from each other (ANOVA, Tukey’s HSD test,  $p < 0.05$ ). Error bars represent standard deviations.

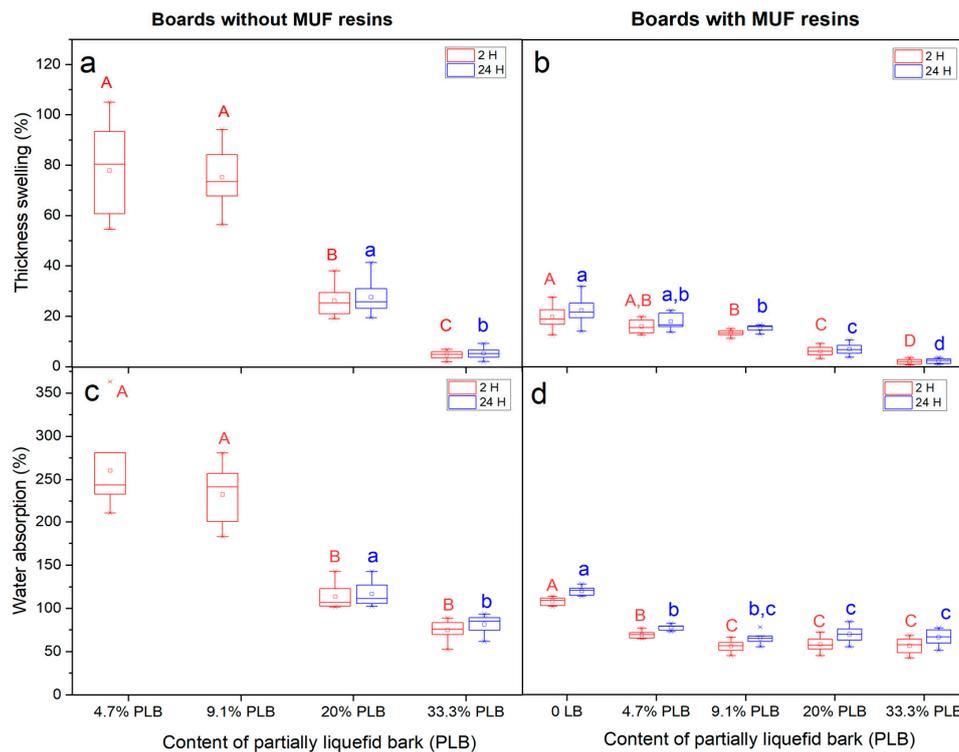


**Figure 7.** Particleboard samples containing 4.7%, 9.1%, 20%, and 33.3% (I–IV in order) partially liquefied bark without using MUF adhesives.

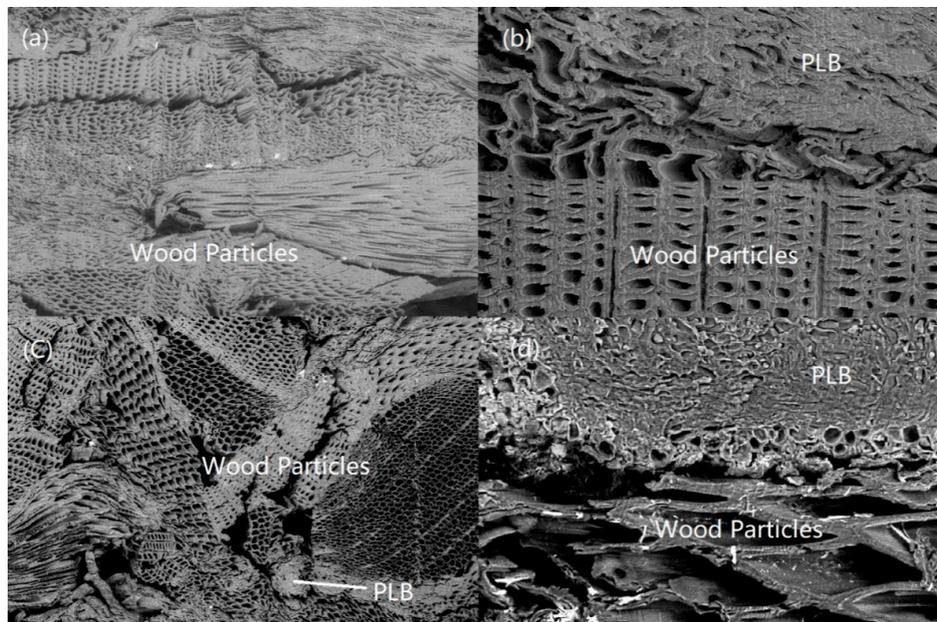
The mechanical properties of the particleboard were apparently changed by the synergistic effect of MUF adhesives and PLB. The MOE, MOR, and IB strength of the boards bonded with MUF adhesives increased by adding 4.7% and 9.1% PLB (boards VI and VII), and they were significantly higher than the reference one, board V. However, the differences between MOE, MOR, and IB values of the boards with 4.7% and 9.1% of PLB, i.e., boards VI and VII, were not statistically significant. Further, increasing the PLB content to 20% and 33.3% drastically decreases the MOE, MOR, and IB strength of the boards. This might be attributed to the decreasing proportion of the wood particles in the board content, which led to a decrease in the density (as shown in Table 1). The higher PLB amount may have also increased the inhomogeneity of the boards, and thus disturbed the equal distribution of the applied stresses during the mechanical tests. The results of mechanical properties showed that up to 20% of PLB can be used in the particleboard content to produce boards that meet the minimum requirements for interior use in dry conditions according to EN 312:2010, in terms of MOR, MOE, and IB values that are, respectively, 13, 1800, and 0.40 N/mm<sup>2</sup>. The tensile strength parallel to surface was negatively affected by increasing the PLB content in the MUF-bonded boards. When over 20% PLB was applied, the tensile strength of the boards (VIII, IX) was lower than half of the strength of the reference (V). As a conclusion, 9.1% of PLB loading should be allowed for producing particleboard with good overall mechanical properties.

Thickness swelling (TS) and water absorption (WA) of the particleboard after 2 and 24 h immersion in water are shown in Figure 8. The boards I and II exhibited remarkably high TS and WA after 2 h immersion in water, and they were decomposed after 24 h. This can be related to the very low internal bond strength between wood particles and PLB. Low interaction of PLB and wood particles may also be an additional reason, which caused poor interfaces. The increase of the PLB level in the non-MUF panels from 4.7% to 33.3% decreased the TS and WA suggesting that the PLB protected the wood particles against water. Similar trends were observed in TS of the boards made with MUF adhesives. This might be attributed to the increasing amount of compact PLB particles in the particleboard mat, which resulted in a reduction of liquid water penetration into the board. The lowest TS value obtained in the MUF-bonded boards containing the highest amount of PLB (33.3%), which was 3.15% after 2 h and 4.04% after 24 h immersion in water. According to EN 312:2010, the maximum thickness swelling within 24 h of particleboard for non-load bearing applications in humid conditions is 17%. Therefore, the boards produced of the highest amount of PLB (33.3%) without MUF adhesives (panel IV) as well as the panels manufactured with MUF adhesives and 9.1, 20, and 33.3% PLB (panels VII, VIII, and IX) fulfilled the standard requirement. The WA values of the particleboard manufactured with MUF adhesives and 4.7–33.3% PLB (VI, VII, VIII, and IX) were statistically lower than the reference (board V). The current result from TS and WA test indicated that PLB acted as an excellent water-resistant reagent in the particleboard.

The overall results from the mechanical and water-related tests confirmed the hypothesis of this study that PLB particles provided an activated surface that can enhance its compatibility with wood particles. The SEM micrographs provided a visual explanation of the mechanical properties and TS changes due to the incorporation of different PLB levels in the particleboard. In detail, the SEM micrographs displayed that PLB caused a compact region with good interaction with wood particles (Figure 9). The compact PLB provided a less porous structure than wood particles and resulted in a reduction of water penetration in the particleboard. The PLB itself showed a homogeneous compact structure that can facilitate the transfer of stresses from the surface layers through the board [22]. An equal distribution of applied stresses at the PLB-wood particles interfaces could be achieved at a PLB level of 9.1% in the particleboard. Moreover, PLB has an advantage of modifying the surfaces of wood particles with the presence of unreacted solvent, acid and intermediates from partial liquefaction. Pressing of particleboard took place under the same temperature of 180 °C as partial liquefaction helps to transfer the liquid phases of PLB, containing remaining polyhydric alcohol and strong acids, to the wood surface for creating chemical bonding and self-adhesion ability. It can be seen from Figure 9b–d that cell walls of wood near the interface between PLB and wood particles are densified that can be caused by the chemical-active components of PLB.



**Figure 8.** Results of thickness swelling and water absorption of particleboard without (a,c) and with MUF (b,d) after 2 and 24 h of testing. Values labelled in the same colored letter (small blue for 24 h, and capital red for 2 h) are not statistically different from each other (ANOVA, Tukey’s HSD test,  $p < 0.05$ ).



**Figure 9.** Scanning Electron Microscopy (SEM) micrographs showing the interaction of partially liquefied bark (PLB) and wood particles in the particleboard: (a) reference; (b) with 20% PLB and no MUF; (c) with 9.1% PLB and 10% MUF; and (d) with 20% PLB and 10% MUF.

#### 4. Conclusions

Bark as an abundant and easily accessible industrial waste has not been economically and significantly used. The current paper provides a new method for developing bio-based panels from

pine bark with the partial liquefaction technique. In this study, pine bark was partially liquefied and then used to produce single-layer particleboard. Four particleboard panels were produced (I–IV) with wood particles and different load levels of PLB (4.7%, 9.1%, 20%, and 33.3%), and five boards (V–IV) were manufactured with wood particles, 10% MUF adhesives and different load levels of PLB (0, 4.7%, 9.1%, 20%, and 33.3%).

Characterization of bark and solid residues of PLB (oven-dried PLB and purified PLB) revealed that the cleavage of the glucoside linkage of cellulose and the  $\beta$ -O-4 bonds of lignin occurred during the partial liquefaction for forming intermediates. PLB and purified PLB decomposed faster than bark during the thermogravimetric analysis because the bark was degraded in the partial liquefaction. PLB and purified PLB were more hydrophilic than bark at higher RHs, meaning that PLB has more hydroxyl groups accessible to water. Excessive hydroxyl groups can be attributed to the bonding between particles and PLB.

Production of particleboard by replacing wood particles with PLB was possible with or without adding MUF adhesives. However, the boards made without MUF adhesives exhibited inferior mechanical properties as compared to the ones with MUF. The mechanical properties and thickness swelling of the non-MUF boards were considerably improved by increasing the content of PLB from 9.1% to 20%. The best mechanical properties were obtained in the particleboard with MUF adhesives and a PLB content of 9.1%. However, up to 20% of PLB content can be used for manufacturing particleboard for meeting the standard requirements. The boards manufactured with 4.7% and 9.1% PLB (I and II) without MUF adhesives showed very poor water resistance, while further addition of PLB at 20% and 33.3% in boards III and IV significantly enhanced the hydrophobicity of the boards. The boards bonded with MUF and different load levels of PLB from 4.7% to 33.3% exhibited significantly lower TS and WA values than the reference board V. The above results indicated that PLB acted as a good water-resistant substance in the particleboard.

**Author Contributions:** Conceptualization, W.J., S.A., M.P., M.Š., and S.M.; methodology, S.M. and R.H.; software, W.J.; validation, W.J. and S.M.; formal analysis, W.J.; investigation, W.J., R.H., and J.Ž.; resources, M.P. and M.Š.; data curation, W.J.; writing—original draft preparation, W.J.; writing—review and editing, S.A., R.H., and J.Ž.; visualization, W.J.; supervision, S.A. and S.M.; project administration, S.A.; funding acquisition, S.A. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Formas project 942-2016-2 (2017-21) titled “Utilization of renewable biomass and waste materials for production of environmental-friendly, bio-based composites”.

**Acknowledgments:** The authors would like to thank Ove Eklund from Ikea Industry AB, Hultsfred, Sweden for his technical support in testing internal bond strength.

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

## References

1. Nemli, G.; Demirel, S.; Gümüşkaya, E.; Aslan, M.; Acar, C. Feasibility of incorporating waste grass clippings (*lolium perenne* L.) in particleboard composites. *Waste Manag.* **2009**, *29*, 1129–1131. [[CrossRef](#)] [[PubMed](#)]
2. Rowell, R.M. *Handbook of Wood Chemistry and Wood Composites*; CRC Press: Boca Raton, FL, USA, 2013; Volume 2.
3. Jones, D.; Brischke, C. *Performance of Bio-Based Building Materials*; Woodhead Publishing: Cambridge, UK, 2017.
4. Wang, D.; Sun, X.S. Low density particleboard from wheat straw and corn pith. *Ind. Crop. Prod.* **2002**, *15*, 43–50. [[CrossRef](#)]
5. Sandberg, D. Additives in wood products—Today and future development. In *Environmental Impacts of Traditional and Innovative Forest-Based Bioproducts*; Kutnar, A., Muthu, S.S., Eds.; Springer: Singapore, 2016; pp. 105–172.
6. Ferdosian, F.; Pan, Z.; Gao, G.; Zhao, B. Bio-based adhesives and evaluation for wood composites application. *Polymers* **2017**, *9*, 70. [[CrossRef](#)] [[PubMed](#)]
7. Hemmilä, V.; Adamopoulos, S.; Karlsson, O.; Kumar, A. Development of sustainable bio-adhesives for engineered wood panels—A review. *RSC Adv.* **2017**, *7*, 38604–38630. [[CrossRef](#)]

8. Solt, P.; Konnerth, J.; Gindl-Altmutter, W.; Kantner, W.; Moser, J.; Mitter, R.; van Herwijnen, H.W.G. Technological performance of formaldehyde-free adhesive alternatives for particleboard industry. *Int. J. Adhes. Adhes.* **2019**, *94*, 99–131. [[CrossRef](#)]
9. Jiang, W.; Kumar, A.; Adamopoulos, S. Liquefaction of lignocellulosic materials and its applications in wood adhesives—A review. *Ind. Crop. Prod.* **2018**, *124*, 325–342. [[CrossRef](#)]
10. Huang, H.-J.; Yuan, X.-Z.; Wu, G.-Q. Liquefaction of biomass for bio-oil products. In *Waste Biomass Management—A Holistic Approach*; Singh, L., Kalia, V.C., Eds.; Springer International Publishing: Cham, Switzerland, 2017; pp. 231–250.
11. Dimitriadis, A.; Bezergianni, S. Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review. *Renew. Sustain. Energy Rev.* **2017**, *68*, 113–125. [[CrossRef](#)]
12. Hu, S.; Luo, X.; Li, Y. Polyols and polyurethanes from the liquefaction of lignocellulosic biomass. *ChemSusChem* **2014**, *7*, 66–72. [[CrossRef](#)]
13. Chen, H. *Lignocellulose Biorefinery Engineering: PRINCIPLES and Applications*; Woodhead Publishing: Cambridge, UK, 2015.
14. Kishi, H.; Akamatsu, Y.; Noguchi, M.; Fujita, A.; Matsuda, S.; Nishida, H. Synthesis of epoxy resins from alcohol-liquefied wood and the mechanical properties of the cured resins. *J. Appl. Polym. Sci.* **2011**, *120*, 745–751. [[CrossRef](#)]
15. Kobayashi, M.; Hatano, Y.; Tomita, B. Viscoelastic properties of liquefied wood/epoxy resin and its bond strength. *Holzforchung* **2001**, *55*, 667. [[CrossRef](#)]
16. Kunaver, M.; Medved, S.; Čuk, N.; Jasiukaitytė, E.; Poljanšek, I.; Strnad, T. Application of liquefied wood as a new particle board adhesive system. *Bioresour. Technol.* **2010**, *101*, 1361–1368. [[CrossRef](#)] [[PubMed](#)]
17. Tohmura, S.-I.; Li, G.-Y.; Qin, T.-F. Preparation and characterization of wood polyalcohol-based isocyanate adhesives. *J. Appl. Polym. Sci.* **2005**, *98*, 791–795. [[CrossRef](#)]
18. Lee, W.-J.; Lin, M.-S. Preparation and application of polyurethane adhesives made from polyhydric alcohol liquefied taiwan acacia and china fir. *J. Appl. Polym. Sci.* **2008**, *109*, 23–31. [[CrossRef](#)]
19. Poljanšek, I.; Likozar, B.; Čuk, N.; Kunaver, M. Curing kinetics study of melamine–urea–formaldehyde resin/liquefied wood. *Wood Sci. Technol.* **2013**, *47*, 395–409. [[CrossRef](#)]
20. dos Santos, R.G.; Carvalho, R.; Silva, E.R.; Bordado, J.C.; Cardoso, A.C.; do Rosário Costa, M.; Mateus, M.M. Natural polymeric water-based adhesive from cork liquefaction. *Ind. Crop. Prod.* **2016**, *84*, 314–319. [[CrossRef](#)]
21. Pan, H. Synthesis of polymers from organic solvent liquefied biomass: A review. *Renew. Sustain. Energy Rev.* **2011**, *15*, 3454–3463. [[CrossRef](#)]
22. Čuk, N.; Kunaver, M.; Poljanšek, I.; Ugovšek, A.; Šernek, M.; Medved, S. Properties of liquefied wood modified melamine-formaldehyde (mf) resin adhesive and its application for bonding particleboards. *J. Adhes. Sci. Technol.* **2015**, *29*, 1553–1562. [[CrossRef](#)]
23. Janiszewska, D.; Frąckowiak, I.; Bielejewska, N. Application of selected agents for wood liquefaction and some properties of particleboards produced with the use of liquefied wood. *Drew. Pr. Naukowe Doniesienia Komun.* **2016**, *59*, 223–230.
24. Janiszewska, D. Bark liquefaction for use in three-layer particleboard bonding. *Drew. Pr. Naukowe Doniesienia Komun.* **2018**, *61*, 119–127.
25. González-García, S.; Lacoste, C.; Aicher, T.; Feijoo, G.; Lijó, L.; Moreira, M.T. Environmental sustainability of bark valorisation into biofoam and syngas. *J. Clean. Prod.* **2016**, *125*, 33–43. [[CrossRef](#)]
26. Lazar, L.; Talmaciu, A.I.; Volf, I.; Popa, V.I. Kinetic modeling of the ultrasound-assisted extraction of polyphenols from picea abies bark. *Ultrason. Sonochem.* **2016**, *32*, 191–197. [[CrossRef](#)]
27. Zhao, Y.; Yan, N.; Feng, M.W. Bark extractives-based phenol–formaldehyde resins from beetle-infested lodgepole pine. *J. Adhes. Sci. Technol.* **2013**, *27*, 2112–2126. [[CrossRef](#)]
28. D’Souza, J.; Yan, N. Producing bark-based polyols through liquefaction: Effect of liquefaction temperature. *ACS Sustain. Chem. Eng.* **2013**, *1*, 534–540. [[CrossRef](#)]
29. Feng, S.; Cheng, S.; Yuan, Z.; Leitch, M.; Xu, C. Valorization of bark for chemicals and materials: A review. *Renew. Sustain. Energy Rev.* **2013**, *26*, 560–578. [[CrossRef](#)]
30. Sillero, L.; Prado, R.; Labidi, J. Optimization of different extraction methods to obtaining bioactive compounds from larix decidua bark. *Chem. Eng. Trans.* **2018**, *70*, 1369–1374.

31. Tudor, E.M.; Barbu, M.C.; Petutschnigg, A.; Réh, R.; Krišťák, L. Analysis of larch-bark capacity for formaldehyde removal in wood adhesives. *Int. J. Environ. Res. Public Health* **2020**, *17*, 764. [[CrossRef](#)] [[PubMed](#)]
32. Lee, W.-J.; Liu, C.-T. Preparation of liquefied bark-based resol resin and its application to particle board. *J. Appl. Polym. Sci.* **2003**, *87*, 1837–1841. [[CrossRef](#)]
33. Hosseinpourpia, R.; Echart, A.S.; Adamopoulos, S.; Gabilondo, N.; Eceiza, A. Modification of pea starch and dextrin polymers with isocyanate functional groups. *Polymers* **2018**, *10*, 939. [[CrossRef](#)]
34. Hosseinpourpia, R.; Adamopoulos, S.; Parsland, C. Utilization of different tall oils for improving the water resistance of cellulosic fibers. *J. Appl. Polym. Sci.* **2019**, *136*, 47303. [[CrossRef](#)]
35. British Standards Institution. *310: 1993 Wood-Based Panels: Determination of Modulus of Elasticity in Bending and of Bending Strength*; BSI: London, UK, 1993.
36. British Standards Institution. *Particleboards and Fibreboards: Determination of Tensile Strength Perpendicular to the Plane of the Board*; BSI: London, UK, 1993.
37. CEN. *317 Particleboards and Fibreboards—Determination of Swelling in Thickness after Immersion in Water*; CEN: Brussels, Belgium, 1993.
38. Ding, R.; Wu, H.; Thunga, M.; Bowler, N.; Kessler, M.R. Processing and characterization of low-cost electrospun carbon fibers from organosolv lignin/polyacrylonitrile blends. *Carbon* **2016**, *100*, 126–136. [[CrossRef](#)]
39. Chupin, L.; Motillon, C.; Charrier-El Bouhtoury, F.; Pizzi, A.; Charrier, B. Characterisation of maritime pine (*pinus pinaster*) bark tannins extracted under different conditions by spectroscopic methods, ftir and hplc. *Ind. Crop. Prod.* **2013**, *49*, 897–903. [[CrossRef](#)]
40. Dussan, K.; Girisuta, B.; Lopes, M.; Leahy, J.J.; Hayes, M.H.B. Conversion of hemicellulose sugars catalyzed by formic acid: Kinetics of the dehydration of d-xylose, l-arabinose, and d-glucose. *ChemSusChem* **2015**, *8*, 1411–1428. [[CrossRef](#)]
41. Yamada, T.; Ono, H. Characterization of the products resulting from ethylene glycol liquefaction of cellulose. *J. Wood Sci.* **2001**, *47*, 458–464. [[CrossRef](#)]
42. Zou, X.; Qin, T.; Huang, L.; Zhang, X.; Yang, Z.; Wang, Y. Mechanisms and main regularities of biomass liquefaction with alcoholic solvents. *Energy Fuels* **2009**, *23*, 5213–5218. [[CrossRef](#)]
43. Zhao, Y.; Yan, N.; Feng, M. Polyurethane foams derived from liquefied mountain pine beetle-infested barks. *J. Appl. Polym. Sci.* **2012**, *123*, 2849–2858. [[CrossRef](#)]
44. Yang, H.; Yan, R.; Chen, H.; Lee, D.H.; Zheng, C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* **2007**, *86*, 1781–1788. [[CrossRef](#)]
45. Pinto, O.; Romero, R.; Carrier, M.; Appelt, J.; Segura, C. Fast pyrolysis of tannins from pine bark as a renewable source of catechols. *J. Anal. Appl. Pyrolysis* **2018**, *136*, 69–76. [[CrossRef](#)]
46. Arteaga-Pérez, L.E.; Segura, C.; Bustamante-García, V.; Gómez Cápiro, O.; Jiménez, R. Torrefaction of wood and bark from eucalyptus globulus and eucalyptus nitens: Focus on volatile evolution vs feasible temperatures. *Energy* **2015**, *93*, 1731–1741. [[CrossRef](#)]
47. Neiva, D.M.; Araújo, S.; Gominho, J.; Carneiro, A.d.C.; Pereira, H. An integrated characterization of picea abies industrial bark regarding chemical composition, thermal properties and polar extracts activity. *PLoS ONE* **2018**, *13*, e0208270. [[CrossRef](#)]
48. Väisänen, S.; Pönni, R.; Hämäläinen, A.; Vuorinen, T. Quantification of accessible hydroxyl groups in cellulosic pulps by dynamic vapor sorption with deuterium exchange. *Cellulose* **2018**, *25*, 6923–6934. [[CrossRef](#)]
49. Huntley, C.J.; Crews, K.D.; Abdalla, M.A.; Russell, A.E.; Curry, M.L. Influence of strong acid hydrolysis processing on the thermal stability and crystallinity of cellulose isolated from wheat straw. *Int. J. Chem. Eng.* **2015**, *2015*, 658163. [[CrossRef](#)]
50. Kobayashi, M.; Asano, T.; Kajiyama, M.; Tomita, B. Analysis on residue formation during wood liquefaction with polyhydric alcohol. *J. Wood Sci.* **2004**, *50*, 407–414. [[CrossRef](#)]
51. Jasiukaitytė-Grojzdek, E.; Kunaver, M.; Crestini, C. Lignin structural changes during liquefaction in acidified ethylene glycol. *J. Wood Chem. Technol.* **2012**, *32*, 342–360. [[CrossRef](#)]

